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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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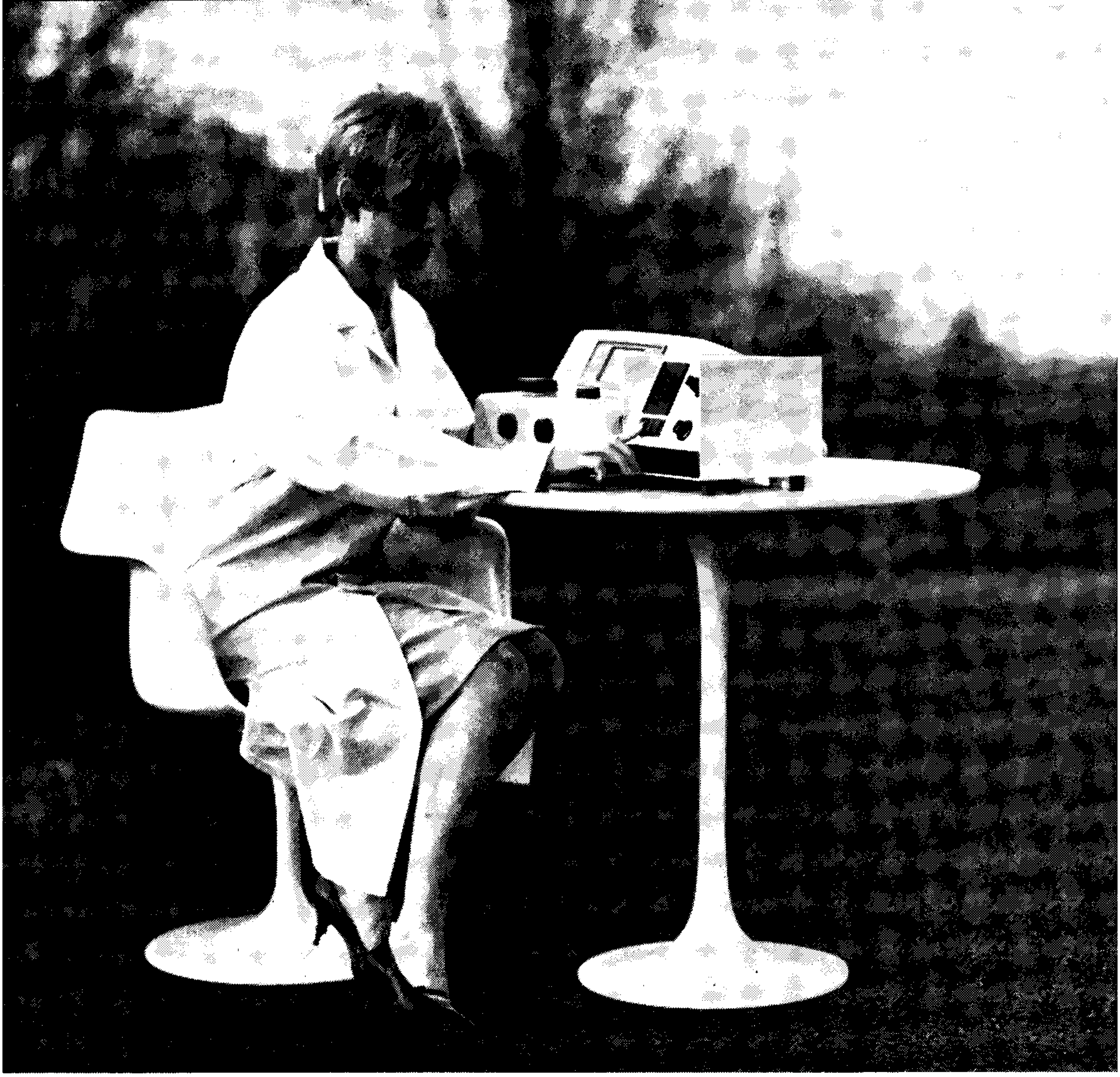

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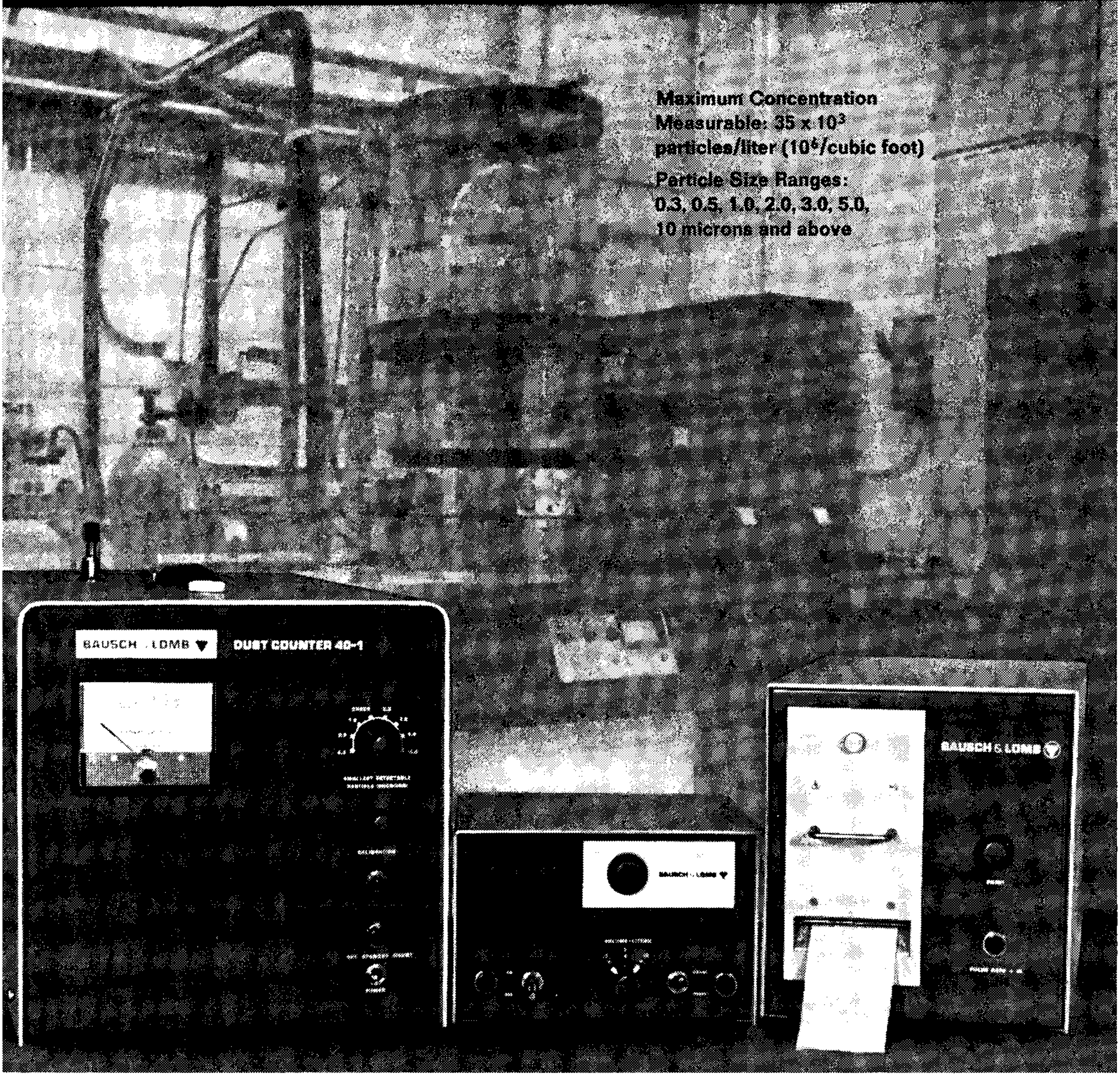
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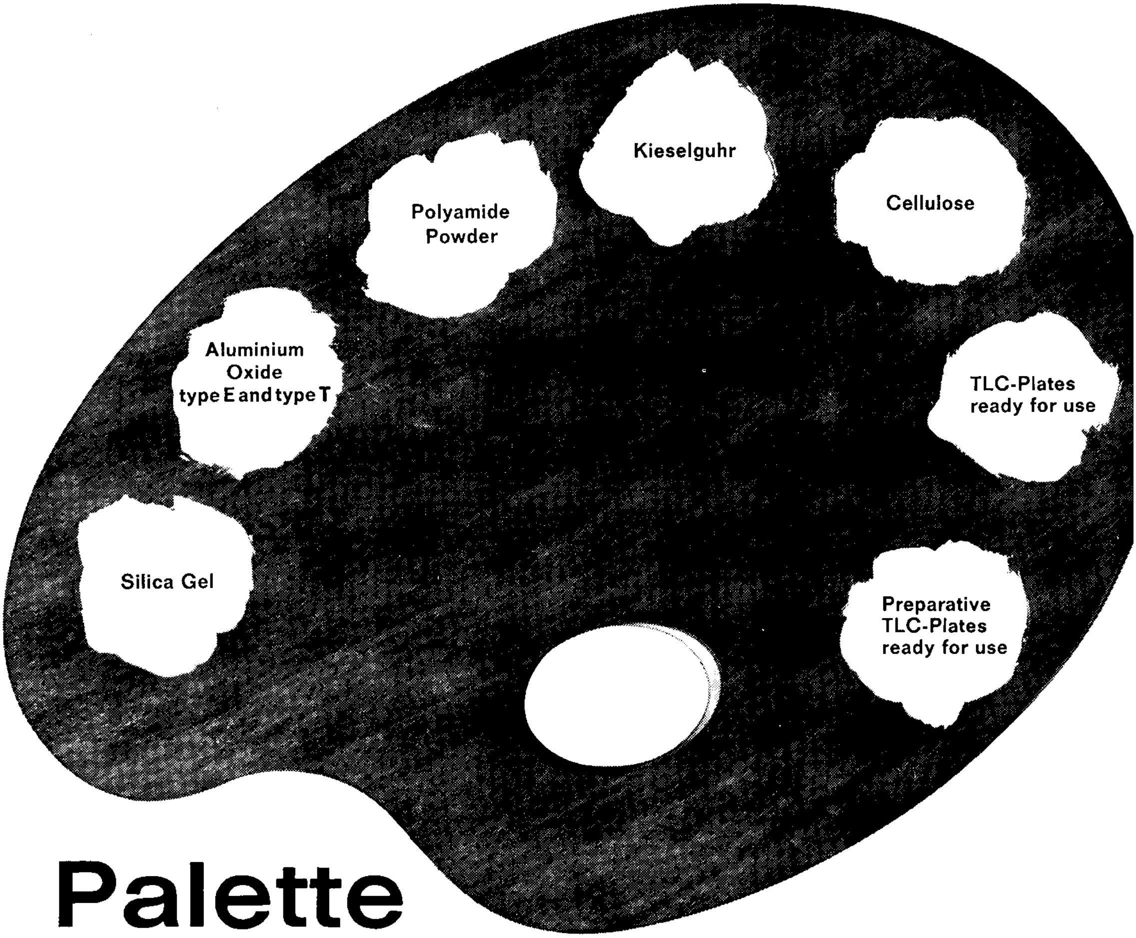
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 43, No. 2, November 1968

DETERMINATION OF IRON AND NICKEL IN WATER AND BRINE BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROSCOPY

A rapid, reliable and sensitive atomic absorption method for the determination of traces of iron and nickel in concentrated brine and in water has been developed. A simple, single extraction procedure is effective for iron in water at concentrations of 0.4–200 p.p.b. and in 25% (w/w) sodium chloride solutions at concentrations between 0.8 p.p.b. and 200 p.p.b. A similar procedure has been developed for nickel concentrations in the range 2–200 p.p.b. in water and 4–200 p.p.b. in brine. Extraction for 15 min with MIBK from a system buffered at pH 7 yields optimum results. The complexing agents are 0.2% solutions of 8-hydroxyquinoline and dimethylglyoxime for iron and nickel, respectively.

J. L. Jones and R. D. Eddy,
Anal. Chim. Acta, 43 (1968) 165–171

THE DETERMINATION OF GOLD, PLATINUM, PALLADIUM AND RHODIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY WITH AN ULTRASONIC NEBULIZER AND A MULTI-ELEMENT HIGH-INTENSITY HOLLOW-CATHODE LAMP WITH SELECTIVE MODULATION

The use of a multi-element high-intensity hollow-cathode lamp with selective modulation and a 2-MHz ultrasonic nebulizer for the determination of Au, Pt, Pd and Rh by atomic absorption spectroscopy is described. The sensitivities for the various elements in aqueous and organic media were studied. Only some organic solutions could be nebulized satisfactorily; a solution containing 95% acetone proved to be the best. For aqueous solutions, the detection limits (concn. giving 0.004 O.D.) were as follows: Au, 0.03 p.p.m.; Pd, 0.02 p.p.m.; Pt, 0.3 p.p.m.; and Rh, 0.09 p.p.m. For a 95% acetone solution the detection limits were: Au, 0.009 p.p.m.; Pd, 0.012 p.p.m.; Pt, 0.20 p.p.m. and Rh, 0.06 p.p.m. The coefficients of variation for aqueous and organic media were satisfactory.

H. C. van Rensburg and P. B. Zeeman,
Anal. Chim. Acta, 43 (1968) 173–182

AN OXYGEN STANDARD FOR THE DETERMINATION OF OXYGEN IN STEEL BY 14-MeV NEUTRON ACTIVATION ANALYSIS

A relative method for the determination of oxygen in steel via the ^{16}O(n,p)^{16}N reaction by means of 14-MeV neutrons is described. A standard is irradiated immediately behind the sample disks and the induced activities are counted simultaneously with two separate but identical detector systems. The standard mixture (*ca.* 5 g of graphite plus iron oxide containing 80.00 mg of oxygen per g) is compressed into a steel capsule of the same external dimensions as the samples (26 mm diameter, 9 mm thick). Dimensional tolerances, choice and purity control of the oxygen compound and preparation of the standard mixture are discussed. Fast neutron shielding, absorption of fast neutrons, self-absorption of the ^{16}N γ-rays and the average neutron flux in sample and standards are considered and a total correction factor is established. Flux inhomogeneities and differences in counting geometry and discriminator setting can be determined by irradiation and counting of two identical standards. The accuracy of this method was checked by comparison of the results with those of the reducing fusion method; satisfactory agreement was observed, although the activation results tended to be slightly higher. The mean long-term standard deviation for analysis of a given sample over a period of 6 months was found to be ± 3%.

R. Gijbels, A. Speecke and J. Hoste,
Anal. Chim. Acta, 43 (1968) 183–198

THE DETERMINATION OF SILICON IN STEEL BY 14-MeV NEUTRON ACTIVATION ANALYSIS

A fast (2–5 min) non-destructive determination of silicon in steel by 14-MeV neutron activation is described. The 1.78-MeV ^{28}Al activity, induced by the reaction ^{28}Si(n,p)^{28}Al, is counted on a NaI(Tl) detector. An oxygen flux monitor is used to normalise to the same neutron flux.

Two methods are described to correct for the ^{56}Mn activity (2.58 h), induced into the iron matrix via ^{56}Fe(n,p)^{56}Mn. Nuclear interferences of phosphorus and aluminium have been examined. Special attention has been paid to stainless steels. A sensitivity of 0.02 to 0.05% of silicon is obtained. The precision is 2 to 3% for steels containing above 1% silicon, and 7% for 0.1% of silicon.

R. Van Grieken, R. Gijbels, A. Speecke and J. Hoste,
Anal. Chim. Acta, 43 (1968) 199–209

THE PREPARATION OF PRECISELY DEFINED LITHIUM ISOTOPE MIXTURES

The need for accurate (< 0.06%) isotopic blends of ^{6}Li and ^{7}Li is explained and their preparation is discussed. It is shown that lithium must be determined at an accuracy level better than 0.035%. Four methods — acid–base titration with hydrochloric acid or benzoic acid, and weighing as sulphate or carbonate — were tested and improved for the precise and accurate analysis of lithium hydroxide solutions. The results of these four methods for a 0.1 *M* solution agreed whitin $\pm$ 0.02%. The preparation of pure isotopically enriched lithium hydroxide solutions, with specially purified cation- and anion-exchangers, is described. The prepared products contain as little as 100 μg of other metals and 50 μg of alkaline-earth metals per gram of lithium, and are sufficiently free of anions to permit accurate chemical assay of lithium. No changes in the isotopic compositions of 99% ^{6}Li or 99.99% ^{7}Li were detected during the treatment.

J. Pauwels, K. F. Lauer, Y. Le Duigou, P. J. De Bièvre and G. H. Debus,
Anal. Chim. Acta, 43 (1968) 211–220

THE DETERMINATION OF LOW LEVELS OF POLONIUM-210 IN ENVIRONMENTAL MATERIALS

A method is presented for the determination of polonium-210 at very low levels in the presence of many different ions. Essentially quantitative recoveries were obtained in 60 min by deposition on to a silver plate in a special holder from 50 ml solution at 85–90° with sodium citrate present.

W. W. FLYNN,
Anal. Chim. Acta, 43 (1968) 221–227

OPTICAL NITROGEN-15 ANALYSIS OF SMALL NITROGEN SAMPLES WITH A MIXTURE OF HELIUM AND XENON TO SUSTAIN THE DISCHARGE IN AN ELECTRODELESS TUBE

A spectrographic technique has been developed for the determination of the nitrogen-15 abundance, with a mixture of rare gases, helium and xenon, to sustain the nitrogen discharge. The average natural abundance obtained with 0.2-μg samples of nitrogen was 0.370 ± 0.005 at-%. Preliminary work indicates that this method is applicable directly to plant and liquid samples.

J. A. GOLEB AND V. MIDDELBOE,
Anal. Chim. Acta, 43 (1968) 229–234

NEW AMPLIFICATION METHODS IN TITRIMETRIC ANALYSIS

(in German)

A new type of amplification reaction is described. The mass of a substance to be determined, or its equivalent, is increased by successive stoichiometric processes, the reaction sequence being repeated as often as required. All reactions are carried out on a chromatography tube on a suitable substrate. The accumulated amplified reaction product is finally dissolved from the column and titrated. The method is illustrated for three systems. Phosphate, hexacyanoferrate(II), chromate, zinc, iron and silver can be amplifed directly or indirectly. The amplification technique can be automated. A series of results (with amplification factors up to 153) shows the utility of the method.

H. WEISZ UND M. GÖNNER,
Anal. Chim. Acta, 43 (1968) 235–244

DETERMINATION OF TRACES OF FLUORINE OR SULFUR BY X-RAY ANALYSIS

New X-ray methods have been developed for the determination of as little as 1 μg of fluorine or as little as 0.1 μg of sulfur. Fluorine as fluoride is precipitated as lanthanum fluoride in 75% ethanol–water mixture and determined by measuring the amount of lanthanum present in the precipitate. Sulfur as sulfate is precipitated as barium sulfate from a barium sulfate saturated 50% ethanol–buffer mixture, using selenate as a coprecipitant, and determined by measuring the amount of sulfur present. Sulfur as sulfide is precipitated as cadmium sulfide and determined by measuring the amount of sulfur or cadmium in the precipitate.

C. L. LUKE,
Anal. Chim. Acta, 42 (1968) 245–251

A FLUORIMETRIC KINETIC METHOD FOR THE DETERMINATION OF ORGANOPHOSPHORUS AND ORGANOCARBONYL COMPOUNDS

A direct reaction rate method is proposed for the rapid, sensitive determination of organophosphorus and organocarbonyl compounds, based on a fluorimetric SCHOENEMANN reaction. From 0.02 to 100 μg/ml of benzoyl chloride, benzoyl bromide, phthalic anhydride, diisopropyl phosphorofluoridate, parathion, methyl parathion, diethyl chlorophosphate and dimethyl chlorothiophosphate can be determined with an accuracy and precision of about 1.5%.

G. G. GUILBAULT AND G. J. LUBRANO,
Anal. Chim. Acta, 43 (1968) 253–261

THE DETERMINATION OF TRACES OF ANTIMONY, TIN AND ARSENIC IN CADMIUM BY PULSE POLAROGRAPHY

Traces of antimony, tin and arsenic in cadmium products were determined by pulse polarography. Arsenic was distilled, while antimony and tin were precipitated as hydroxides with manganese dioxide as carrier; some lead was coprecipitated with tin, hence these elements were further separated by distillation. In all cases quantitative recoveries were obtained. Antimony(III) was determined in a hydrochloric acid–sodium hypophosphite mixture, tin(IV) in a hydrochloric–hydrobromic acid mixture and arsenic(III) in sulphuric acid as supporting electrolytes; for arsenic(III), methylene blue had to be added. A sample weight of 10 g and an end volume of 10 ml allowed the determination down to about 0.004 p.p.m. antimony, 0.006 p.p.m. tin and 0.003 p.p.m. arsenic in cadmium. Several synthetic samples and commercially available cadmium products were analysed.

E. TEMMERMAN AND F. VERBEEK,
Anal. Chim. Acta, 43 (1968) 263–272

POLAROGRAPHIC DETERMINATION OF ACIDS BY MEANS OF THE REDUCTION WAVE OF QUINONES IN METHYL CELLOSOLVE SOLUTION

Methyl-*p*-benzoquinone (MQ) gives a single polarographic wave in methyl cellosolve media containing perchlorate as suppporting electrolyte, but a prewave corresponding to the reaction $Q + 2\ HA + 2\ e \rightleftarrows H_2Q + 2\ A^-$, is found when an acid is added. The height of the prewave is proportional to the concentration of added acid. Traces (*ca.* 0.2%) of free perchloric acid can be determined in crude lithium perchlorate.

The half-wave potential of the prewave depends on the pK_a value of the acid; if the dissociation constants of acids differ sufficiently, two prewaves are found and each acid species can be determined simultaneously. This method was applied to the MQ–$HClO_4$–CH_3COOH, MQ–CCl_3COOH–CH_3COOH and MQ–$CHCl_2COOH$–CH_3COOH systems.

K. TAKAMURA AND Y. HAYAKAWA,
Anal. Chim. Acta, 43 (1968) 273–279

VOLTAMMETRIC BEHAVIOR OF NEPTUNIUM(VI) IN GLUTAMIC ACID MEDIA AT THE ROTATING GLASSY CARBON ELECTRODE

The voltammetry of neptunium(VI) glutamate was investigated over the pH range 3.8–10.0. A reversible, one-electron wave was obtained for glutamate concentrations above 0.1 *M* in the pH range 3.8–6.1, or above 0.3 *M* in the pH range 6.1 –10.0. At pH 3.8–6.1, the half-wave potential was independent of pH, but at pH 6.1–10.0, it was a function of pH. The metal–ligand ratio was found to be 1 : 2 by conductometric titration. The limiting current was proportional to the concentration of the neptunium(VI) from $7.83 \cdot 10^{-5}$ to $1.96 \cdot 10^{-3}$ *M*. The diffusion coefficient was $0.35 \cdot 10^{-5}$ cm^2 sec^{-1} at pH 4.5 and $0.30 \cdot 10^{-5}$ cm^2 sec^{-1} at pH 9.4.

C. E. Plock,
Anal. Chim. Acta, 43 (1968) 281–287

VOLTAMMETRIC STUDIES WITH SILICONE RUBBER-BASED GRAPHITE ELECTRODES

The behaviour of a new type of graphite electrode prepared by mixing spectral graphite with silicone rubber before cold vulcanisation, is described. Electrodes can be prepared as plates or rods. The residual current is reproducibly small or negligible in the potential range −0.3 V to +0.7 V. The height of the peak current is proportional to the concentration for a wide range of substances. The reproducibility of *i–E* curves at the same electrode surface is excellent. The electrode requires no preliminary treatment and the surface can be easily cleaned or renewed. The temperature coefficient measured for hexacyanoferrate(II) was 1.1%/°C.

E. Pungor and É. Szepesváry,
Anal. Chim. Acta, 43 (1968) 289–296

SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) WITH 2-THENOYLTRIFLUOROACETONE AND THE SYNERGETIC EFFECT OF PYRIDINE

Pyridine has a synergetic effect on the extraction of iron(II) with TTA. The spectrophotometric determination of iron (7–100 μg) based on this reaction is rapid, highly reproducible and reasonably selective. The optimal pH range is wide and the sensitivity is 0.012 μg/cm^2 at 580 mm. The method can be applied to the analysis of natural waters.

H. Akaiwa, H. Kawamoto and M. Hara,
Anal. Chim. Acta, 43 (1968) 297–302

THE EXTRACTION OF THORIUM FROM NITRIC ACID SOLUTIONS BY LONG-CHAIN ALIPHATIC AMINES

The partition of thorium between nitric acid solutions and solutions of long-chain aliphatic amines in benzene is described. The organic phase was examined by infrared spectroscopy. Tertiary amines are more efficient extractants for thorium than are secondary amines; the efficiency is enhanced when the alkyl chain is branched and is strongly influenced by the organic solvent used as diluent.

T. Sato,
Anal. Chim. Acta, 43 (1968) 303–310

REGULARITIES IN THE DISTRIBUTION OF TTA AND ITS SCANDIUM CHELATE INTO A SERIES OF ESTER SOLVENTS

The distribution ratios of TTA and its scandium chelate between aqueous perchlorate solutions ($\mu = 0.1$) and 15 ester solvents including ethyl acetate were determined at 25°. A good correlation was found between the distribution coefficients of TTA and the "solubility parameter" of the ester solvents. The relationship between the distribution coefficients of the scandium chelate (P_M) and those of TTA (P_{HA}) was shown to be, $\log P_M = n \log P_{HA} + \text{const.}$ The distribution of this chelate into another ester can thus be predicted.

N. Suzuki, K. Akiba and T. Kanno,
Anal. Chim. Acta, 43 (1968) 311–320

YTTRIUM 8-HYDROXYQUINOLINATES

The preparation of two yttrium 8-hydroxyquinolinates, one by conventional means and the other by precipitation from homogeneous solution, was investigated. Analytical data indicated that the complex prepared conventionally corresponds to $Y(C_9H_6NO)_3$, and the complex prepared by precipitation from homogeneous solution corresponds to $Y(C_9H_6NO)_3 \cdot C_9H_7NO$. Thermogravimetric analyses, infrared, ultraviolet–visible and diffuse reflectance spectroscopic studies were carried out on both compounds. They were shown to be very similar structurally.

T. J. Cardwell and R. J. Magee,
Anal. Chim. Acta, 43 (1968) 321–327

A DIRECT AMPEROMETRIC METHOD FOR CONTINUOUS DETERMINATION OF LOW CONCENTRATIONS OF IODINE IN AQUEOUS SOLUTIONS

(Short Communication)

A. F. M. Barton and G. A. Wright,
Anal. Chim. Acta, 43 (1968) 328–331

THE VOLATILITIES OF SOME LEAD β-DIKETONATES

(Short Communication)

G. Schweitzer, B. Pullen, and Y.-H. Fang,
Anal. Chim. Acta, 43 (1968) 332–334

SPECTROPHOTOMETRIC TITRATION OF ALIPHATIC AMINES WITH CINNAMIC ANHYDRIDE

(Short Communication)

K. A. Connors and W.-H. Hong,
Anal. Chim. Acta, 43 (1968) 334–337

SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH 2,4-DIHYDROXYACETOPHENONE

(Short Communication)

M. H. Gandhi and M. N. Desai,
Anal. Chim. Acta, 43 (1968) 338–340

THE SUCCESSIVE TITRATION OF CALCIUM AND MAGNESIUM WITH EDTA IN ETHANOLIC SOLUTION

(Short Communication; in German)

T. A. Kiss, F. F. Gaál, T. M. Surányi and I. J. Zsigrai,
Anal. Chim. Acta, 43 (1968) 340–342

IRON(III) COMPLEX INTERFERENCE IN THE IODOMETRIC DETERMINATION OF HYDROGEN PEROXIDE

(Short Communication)

S. B. Brown, P. Jones and A. Suggett,
Anal. Chim. Acta, 43 (1968) 343–346

COMPLEXIMETRIC TITRATION OF PHOSPHATE WITH LANTHANUM AS PRECIPITANT

(Short Communication)

J. Yofè and B. R. Rappart,
Anal. Chim. Acta, 43 (1968) 346–347

USE OF A PYROLYTIC BORON NITRIDE THIMBLE IN DETERMINING OXYGEN BY THE INERT GAS FUSION METHOD

(Short Communication)

E. J. Beck and W. E. Chambers,
Anal. Chim. Acta, 43 (1968) 348–351

THE DETERMINATION OF MICRO-CONCENTRATION GRADIENTS ON THE SURFACES OF SOLID SAMPLES BY MEANS OF THE LASER-MICROPROBE

(Short Communication)

M. S. W. Webb and J. C. Cotterill,
Anal. Chim. Acta, 43 (1968) 351-353

CALCEIN BLUE AS A FLUORESCENT ADSORPTION INDICATOR IN THE DIRECT TITRATION OF SILVER IONS

(Short Communication)

A. M. Escarrilla,
Anal. Chim. Acta, 43 (1968) 353–356

INORGANIC ELECTRONIC SPECTROSCOPY

by A. B. P. LEVER, Associate Professor of Chemistry,
York University, Toronto, Canada

*The first monograph in the series PHYSICAL INORGANIC CHEMISTRY,
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Electronic spectroscopy has become, in recent years, a commonplace tool in inorganic research and development although few books dealing with the topic have appeared. Those books dealing with spectroscopy in general devote but a few pages to a discussion of the electronic spectra of inorganic compounds.

The aim of this book is (a) to provide the reader with a basic understanding of the methods and procedures involved in a study of the electronic spectra of inorganic compounds, (b) to discuss the information which may be derived from such study, with particular emphasis on stereochemistry and chemical bonding, and (c) to provide a reference text.

A beginning is made at a level which can be understood by an average student with a first degree, the first third of the book dealing with atomic theory, symmetry and group theory. In progressing further with the material presented, the reader can proceed from the construction of qualitative energy level diagrams and the assignment of transitions observed in the spectra of cubic molecules, to quantitative diagrams and the spectra of non-cubic molecules.

Having mastered this material the reader is shown how to derive useful information concerning stereochemistry and chemical bonding and even, qualitatively, such properties as effective nuclear charge and mean *d*-orbital radii. The spectra of the more common transition metal ions in their many oxidation states and stereochemistries are discussed in Chapter 9, which is a mine of information for the practising inorganic spectroscopist.

The book is unique in being the only reference work available which will bring the new graduate up to the level where he can read and usefully digest the original research papers in inorganic spectroscopy. Much of the material has not appeared in book form before and some of it has not appeared in print at all.

Contents: Preface. 1. Atomic structure. 2. Molecular symmetry. 3. Group theory. 4. Crystal field diagrams. 5. Term diagrams. 6. Selection rules, band intensities and dichroism. 7. Some theoretical aspects of electronic spectra. 8. Charge transfer spectra. 9. Crystal field spectra. Appendices. Indexes.

xii + 420 pages, 66 tables, 130 illus., 465 lit. refs., 1968, Dfl. 90.00, £11.10.0.

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Photoluminescence of Solutions

With Applications to Photochemistry and Analytical Chemistry

by C. A. Parker, Royal Naval Scientific Service, Head of Chemistry Division of the Admiralty Materials Laboratory, Holton Heath, Poole, Dorset, England

6 × 9″, xvi + 544 pages, 53 tables, 188 illus., 443 lit. refs., 1968, Dfl. 85.00, £11.10.0.

Contents: 1. Basic principles and definitions. 2. Kinetics of photoluminescence. 3. Apparatus and experimental methods. 4. Special topics and applications. 5. Application to analytical chemistry. Indexes.

Comprehensive Analytical Chemistry

edited by C. L. Wilson, Professor of Inorganic and Analytical Chemistry, University of Belfast (Northern Ireland)
and D. W. Wilson, Head of the Chemistry Department, Sir John Cass College, London (England)

VOLUME IIB: Physical Separation Methods

6 × 9″, xvi + 445 pages, 30 tables, 116 illus., 897 lit.refs., 1968, Dfl. 70.00, £8.10.0.

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The next chapter, on ion exchangers, is notable for the account it gives of analytical applications, while distillation (theory and technique) is the last topic to be treated in the present volume.

Contents: I. *Liquid Chromatography in Columns.* 1. Introduction. 2. Theory. 3. Apparatus and operation. II. *Gas Chromatography.* 1. Introduction and general principles. 2. Theoretical aspects. 3. Apparatus. 4. The partitioning phases. 5. Absorbents and gas-solid chromatography. 6. Gas-liquid chromatography. 7. Analytical methods. 8. Applications. III. *Ion Exchangers.* 1. Foreword. 2. Introduction. 3. The constitution of ion exchangers. 4. The mechanism of ion exchange. 5. Technique. 6. Analytical applications. Appendix 1: Ion-exchanger data. Appendix 2: Methods of testing ion exchangers. Appendix 3: Bibliography. IV. *Distillation.* 1. Introduction. 2. Theoretical background. 3. Experimental techniques.

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 × 9″, xii + 493 pages, 23 tables, 156 illus., 950 lit. refs., 1968, Dfl. 80.00, £9.15.0.

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.

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DETERMINATION OF IRON AND NICKEL IN WATER AND BRINE BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROSCOPY*

JERRY L. JONES AND RAYMOND D. EDDY**
Department of Chemistry, Texas A &M University, College Station, Texas (U.S.A.)

(Received May 31st, 1968)

Lower limits of detection for atomic absorption spectroscopy with direct aspiration of aqueous samples are commonly in the range 0.05–1.0 p.p.m.[1]. These have been reported for iron and nickel as 0.05 p.p.m. by BARRAS[2]. The purpose of the present study was a systematic attempt to lower considerably the limits of detection for these two metals in water and brines by using the advantages offered by solvent extraction.

ALLEN[3] was one of the first to apply solvent extraction to analysis by atomic absorption. He extracted zinc from water solutions at pH values between 2.5 and 5.0 with ammonium pyrollidine dithiocarbamate (APDC) in methyl isobutyl ketone (MIBK), and obtained a lower limit of detection of 0.006 p.p.m. SPRAGUE AND SLAVIN[4] demonstrated that cadmium, cobalt, iron, manganese and nickel could be extracted from potassium chloride brine with APDC and MIBK. MANSELL[5] also investigated these same reagents in the extraction of manganese from water. DE-LAUGHTER[6] used diphenylthiocarbazone and dithiol in the extractions of chromium and molybdenum, respectively, into MIBK. MULFORD[7] has briefly reviewed the principle of solvent extraction as it applies to atomic absorption analysis.

Even though several metals have been analyzed by atomic absorption spectroscopy in combination with selected complexing agents and organic solvents, an examination of the existing literature indicates that in many cases thorough studies to determine the pH, solvent, extraction time, and optimal complexing agent were not performed. Only a systematic approach is likely to result in the greatest possible sensitivity.

EYPERIMENTAL

Instrumentation

Analyses were performed with a Model 82-360 Jarrell-Ash atomic absorption spectrometer, a HETCO total consumption burner, and a Leeds–Northrup recorder equipped with optional 10 × scale expansion. Commercial hydrogen and dry, filtered air were used for supply gases.

Chemicals

Primary-standard or reagent-grade chemicals were used wherever possible. All solutions were prepared with distilled, deionized water. Solutions of iron and

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nickel containing 20 p.p.m. were prepared from the pure metals and these were further diluted to prepare standards.

Extraction procedures

The extractions used to survey the effectiveness of various complexing agents at selected pH values were generally accomplished with 10-ml portions of a buffered standard which contained 0.1 p.p.m. nickel or iron. These were prepared by dilution of 5 ml of the more concentrated solutions (20 p.p.m.) with 500 ml of a solution containing 80 g of potassium sodium tartrate per liter and sufficient additional buffer solution of the desired pH to give 1 l. The buffer solutions were of pH 1, 3, 5, 7, 9, or 11 for the exploratory work. An aliquot of 100 ml of the 0.1-p.p.m., buffered, standard metal solution was then pipetted into a 125-ml pear-shaped separatory funnel and 5 ml of a 0.2% (weight/volume) solution of the complexing agent in the appropriate solvent was added. The mixture was shaken for 5 min on a mechanical shaker and the organic layer was retained for analysis. A 2-ml aliquot was burned for the analysis.

Calibration curves

After the selection of the optimum solvent, pH, and complexing agent, the preparation of the working curves was accomplished by the same procedure except that 15-min extraction times were used and the sample consisted of 100 ml of a water or brine solution containing the metal ion. To this was then added 10 ml of a buffered tartrate solution (76 g of $NaH_2PO_4 \cdot H_2O$, 110 g of $Na_2C_4H_4O_6 \cdot 2H_2O$, and 40 g of 50% sodium hydroxide dissolved in water and diluted to 1 l). Then 5 ml of the 0.2% solution of complexing agent in methyl isobutyl ketone (MIBK) was added. Dimethylglyoxime and 8-hydroxyquinoline (oxine) were used for nickel and iron, respectively. The aqueous phase pH was approximately 7.2. Extraction and analysis on 2 ml of the organic phase were then carried out as before. Multiple dilutions were necessary in some cases to obtain the desired concentration.

The brine was prepared by dissolving 1400 g of sodium chloride in enough water to give 5.5 l of a 25% solution. This was purified from iron contamination before use by 4-h extractions with four successive 250-ml portions of 0.2% oxine in MIBK after the addition of a small amount of sodium tartrate to the brine solution which was buffered at pH 7. The fourth and final organic layer gave an absorbance of 0.015 on the atomic absorption spectrometer; MIBK saturated with water gave an absorbance of 0.013. Solvent remaining dissolved in the brine was removed by bubbling dry air through it for 24 h.

Nickel was removed from the sodium chloride brine by passing the slightly alkaline solution through a column of Dowex A-1 chelating resin. The column was prepared by passing dilute hydrochloric acid, water, and 10% sodium hydroxide through the resin in that order. The column was rinsed with water until the effluent was nearly neutral before the addition of the brine. The brine was virtually nickel-free after a single pass through a 100-ml buret filled with the resin.

Gas pressures at the burner of 5 p.s.i. for hydrogen and 10 p.s.i. for air yielded maximum sensitivity. Burner height was not critical. Current settings for the iron and nickel hollow cathode tubes were 10 mA and 8 mA, respectively. The line at 2483 Å was used for iron while nickel analyses were accomplished by means of the line at 2320 Å.

Times required for complete aspiration of a 2.00-ml sample were noted in every case and if deviation became greater than 5% of an established reference time, the burner was disassembled and cleaned before proceeding. After each sample was burned, a 2-ml portion of the pure solvent was burned to clean the sample tube and tip of the burner.

When metal concentrations were very low (0–10 p.p.b.) the 10-fold expansion scale of the recorder was used and pen excursions were measured in arbitrary units of chart divisions.

DETERMINATION OF IRON

A number of solvents were considered but most were readily eliminated. Amyl alcohol and tributyl phosphate exhibited very long aspiration times because of their high viscosity. 2,4-Pentanedione exhibited high absorptivity at both analytical wavelengths. The solubility of ethyl acetate in water was believed to be higher than desirable. Petroleum ether would not dissolve most of the complexing agents. Methylene chloride offered no advantage over chloroform. Chloroform performed as expected and gave lower absorbances than could be obtained using 3-heptanone, amyl acetate or MIBK. The solvent which gave highest sensitivity was methyl isobutyl ketone.

With MIBK as the solvent, 0.1-p.p.m. solutions of iron were extracted with eleven different complexing agents under identical conditions at pH values of 1, 3, 5, 7, 9, and 11. Solutions of 0.2% concentration were prepared with oxine, cupferron, sodium diethyldithiocarbamate, 1-nitroso-2-naphthol, ammonium pyrollidine dithiocarbamate, thenoyltrifluoroacetone, anthranilic acid, 1,10-phenanthroline, diphenylcarbohydrazide, and dimethylglyoxime. A 0.2% solution of diphenylthiocarbazone could not be prepared because of low solubility and a filtered, saturated solution was used.

Three of the complexing agents used with iron gave significant absorption after corrections for iron impurities in the buffers and the tartrate solutions. These were oxine, cupferron, and sodium diethyldithiocarbamate.

Increasing their concentrations from 0.2% to 1% gave no significant differences in absorbance.

Oxine gave the highest absorbance values for iron over the broadest pH range. Cupferron was most efficient at low pH values. The absorbances obtained with the three complexing agents, corrected for blanks, are shown in Table I.

Three other solvents, amyl acetate, 3-heptanone, and chloroform, were used at

TABLE I

INFLUENCE OF pH ON CORRECTED ABSORBANCES FOR THE EXTRACTION OF 0.1 p.p.m. IRON WITH MIBK AND SELECTED COMPLEXING AGENTS

pH	*8-Hydroxyquinoline*	*Sodium diethyldithiocarbamate*	*Cupferron*
1	0.008	0.008	0.112
3	0.009	0.009	0.160
5	0.185	0.073	0.200
7	0.195	0.170	0.017
9	0.190	0.010	0.016
11	0.164	0.008	0.016

TABEL II

COMPARISON OF CORRECTED ABSORBANCES OF 0.1 p.p.m. IRON WITH DIFFERENT SOLVENTS AND SELECTED COMPLEXING AGENTS

Solvent	*8-Hydroxy-quinoline*		*Cupferron*		*Sodium diethyl dithiocarbamate*	
	pH 5	*pH 7*	*pH 5*	*pH 7*	*pH 5*	*pH 7*
MIBK	0.185	0.195	0.200	0.017	0.073	0.170
Chloroform	0.054	0.056	—	—	0.015	0.002
Amyl acetate	0.095	0.100	0.100	—	—	0.085
3-Heptanone	0.140	0.135	0.160	—	—	0.040

pH 5 and pH 7 with the three reagents that gave the largest response in MIBK. Chloroform gave no absorbances greater than 0.060 and was omitted from further consideration. Comparison of these three solvents with MIBK (Table II) showed that MIBK is the best solvent of those examined.

Extraction was not improved after 5 min and was nearly complete after 2 min. Extraction of 0.1 p.p.m. iron at pH 7 with MIBK, oxine, and buffered sodium potassium tartrate, gave absorbances of 0.312, 0.360, 0.365, 0.357, and 0.369 after 2, 5, 10, 15, and 20 min, respectively. A second 10-min extraction yielded an absorbance of 0.009.

Previous experiments have shown that the iron-oxine complex is more efficiently extracted in the presence of tartrate[8]. It was found that potassium tartrate gave some solubility problems occasionally and contained very significant amounts of iron as an impurity. Substitution of sodium tartrate during the course of the investigation improved on both situations since it was more soluble and contained half as much iron. The amount of tartrate necessary to give maximum extraction of iron was determined empirically.

Working curves for iron

Working curves were prepared for the determination of iron in water in an

TABEL III

ABSORBANCE DATA FOR EXTRACTIONS OF IRON AND NICKEL AT pH 7 FROM WATER WITH MIBK SOLUTIONS

Concentration p.p.b.	*Iron*[a]		*Nickel*[b]	
	Absorbance	*Chart divisions*	*Absorbance*	*Chart divisions*
200	0.496	—	0.330	—
100	0.250	—	0.193	—
50	0.115	—	0.088	—
25	0.044	—	0.046	—
10.0	0.023	—	0.024	37
8.0	—	46	—	—
5.0	—	36	—	21
2.5	—	22	—	11
1.0	—	9	—	5
0.5	—	4	—	2

[a] Extractant was 0.2% oxine in MIBK.
[b] Extractant was 0.2% dimethylglyoxime in MIBK.

TABEL IV

ABSORBANCE DATA FOR EXTRACTIONS OF IRON AND NICKEL AT pH 7 FROM NaCl BRINE WITH MIBK SOLUTIONS

Concentration	*Iron*[a]		*Nickel*[b]	
p.p.b.	*Absorbance*	*Chart divisions*	*Absorbance*	*Chart divisions*
200	0.203	—	0.130	—
100	0.103	—	0.080	—
50	0.046	—	0.035	—
25	0.022	—	0.020	—
10.0	0.008	24	0.010	16
5.0	—	16	—	12
2.5	—	11	—	6
1.0	—	6	—	3
0.5	—	3	—	2

[a] Extractant was 0.2% oxine in MIBK.
[b] Extractant was 0.2% dimethylglyoxime in MIBK.

aqueous 25% solution of sodium chloride. The extractions were performed as outlined in the above experimental section. Tables III and IV show the results obtained for the range up to 200 p.p.b. iron in water and brine. All absorbances have been corrected for any absorbance resulting from the buffer-tartrate solutions. The results obtained with concentrations up to 10 p.p.b. of iron were recorded with a ten-fold scale expansion and arbitrary units of chart division. A peak height of 50 divisions represents 50% full scale on a 9-in chart.

DETERMINATION OF NICKEL

Four complexing agents were evaluated for the nickel determination. The extraction time and solvent used were the same as for the iron study. The use of oxine, cupferron, and sodium diethyldithiocarbamate gave only minimal absorption of the organic extract. Dimethylglyoxime gave very good results at pH values of 7, 9, and 11 but essentially no response at lower pH values.

In the preliminary study, solutions containing 0.1 p.p.m. of nickel in water were extracted for 5 min with 0.2% dimethylglyoxime in MIBK. Absorbance values of 0.165, 0.190, and 0.180 were obtained at pH values of 7, 9, and 11, respectively. Since these values are of the same order of magnitude as those obtained for iron, dimethylglyoxime was chosen as a satisfactory complexing agent.

The working curves for the determination of nickel were prepared in the same manner as those for iron. Tables III and IV show the results for nickel up to 200 p.p.b. in water and in brine. Arbitrary units of chart divisions were used with solutions containing up to 10 p.p.b. of nickel and were obtained using the ten-fold scale expansion of the recorder.

DISCUSSION

Two different procedures were used to remove the iron and nickel from the brine and tartrate solutions needed in the preparation of the working curves. The extraction technique was used to remove the iron and was satisfacory but very time-consuming. The ion-exchange method used to remove nickel was much easier and will probably remove iron as well as a number of other metal ions at the same time[9]. Because of its simplicity and effectiveness, an ion-exchange technique is recommended for purification of reagents whenever possible.

At low concentrations nickel formed a yellow solution when complexed with dimethylglyoxime in MIBK. According to ATACK[10], this is the yellow monomolecular nickel compound $NI(II)C_4H_6N_2O_2$. Others have observed this[11]. As the nickel content was raised, conversion to the more stable red compound $Ni(II)(HC_4H_6N_2O_2)_2$ took place on standing. At nickel concentrations above about 400 p.p.b., the red precipitate forms almost immediately. The precipitate is relatively insoluble in MIBK. This may account, in part, for the slight curvature of the nickel working curve.

The precision of the results obtained with such low concentrations is very dependent upon the signal-to-noise ratio at the recorder input. When scale expansion was not used the base line was virtually noise-free but fluctuations rose to 0.5–1% of full scale when a sample was being burned. When the 10 ×-expansion was used, the noise level was about ±2% of full scale. When this information is applied to the slopes (sensitivities) shown by the working curves, it is conservatively estimated that the lower limits of detection for iron in water, iron in brine, nickel in water, and nickel in brine are 0.2 ± 0.1 p.p.b., 0.4 ± 0.2 p.p.b., 1.0 ± 0.5 p.p.b. and 2.0 ± 1.0 p.p.b., respectively. In each case, the lower limit of detection was chosen such that the precision was 50% of the amount present.

It should be noted that in both cases, absorptions are less when the metal is extracted from brine. This effect may be chemical and result from the lowered activity of the metal ion in the salt solutions or it may be simply attributed to a solubility effect. In all cases the recovery of the organic phase was nearly complete when brines were extracted whereas the solubility loss in water solutions was about 50% of the original 5.0-ml sample of MIBK. If quantitative extraction is assumed in both cases, this volume difference could result in a dilution of the extracted metal complex. Since a 2-ml aliquot was chosen for aspiration in any case, the net absorbances probably reflect this dilution. One possible solution would be to aspirate the entire organic phase, regardless of the recovered volume, and then to integrate the area under the peaks. To simplify the procedure this was not done in the present study. A standard aliquot size was chosen from both the water and the brine extractions. In the case of 3-heptanone the recovery of the organic phase was practically the same for both the brine and the water systems although absorbances were consistently lower.

The authors wish to express their gratitude to the Dow Chemical Company for providing a sample of Dowex A-1 chelating resin.

SUMMARY

A rapid, reliable and sensitive atomic absorption method for the determination of traces of iron and nickel in concentrated brine and in water has been developed. A simple, single extraction procedure is effective for iron in water at concentrations of 0.4–200 p.p.b. and in 25% (w/w) sodium chloride solutions at concentrations between 0.8 p.p.b. and 200 p.p.b. A similar procedure has been developed for nickel concentrations in the range 2–200 p.p.b. in water and 4–200 p.p.b. in brine. Extraction for

15 min with MIBK from a system buffered at pH 7 yields optimum results. The complexing agents are 0.2% solutions of 8-hydroxyquinoline and dimethylglyoxime for iron and nickel, respectively.

RÉSUMÉ

Une méthode par adsorption atomique sensible et rapide est proposée pour le dosage de traces de fer et de nickel dans des saumures concentrées et dans l'eau. Une simple extraction convient pour le dosage du fer dans l'eau, à des concentrations de 0.4 à 200 p.p.b. et dans des solutions de chlorure de sodium à 25% à des concentrations allant de 0.8 à 200 p.p.b. Un procédé similaire est proposé pour des concentrations en nickel de 2 à 200 p.p.b. dans l'eau et 4 à 200 p.p.b. dans la saumure. Les meilleurs résultats sont obtenus par extraction de 15 minutes, à l'aide de MIBK, en milieu tampon pH 7. Les agents complexants sont des solutions d'hydroxy-8-quinoléine et de diméthylglyoxime à 0.2%, respectivement pour le fer et le nickel.

ZUSAMMENFASSUNG

Es wurde eine schnelle, verlässliche und empfindliche Methode zur Bestimmung von Spuren Eisen und Nickel in konzentrierten Solen und im Wasser mit Hilfe der Atomabsorptionsanalyse entwickelt. Mit einem einfachen, einstufigen Extraktionsverfahren lässt sich Eisen wirksam in Wasser in Konzentrationen von 0.4 bis 200 p.p.b. und in 25-gew.%igen Natriumchloridlösungen bei Konzentrationen zwischen 0.8 und 200 p.p.b. bestimmen. Ein ähnliches Verfahren wurde für Nickel entwickelt für Konzentrationen von 2 bis 200 p.p.b. in Wasser und 4 bis 200 p.p.b. in Solen. Eine 15 minütige Extraktion mit MIBK aus einem gepufferten System bei pH 7 führt zu optimalen Ergebnissen. Die Komplexbildner waren 0.2%ige Lösungen von 8-Hydroxychinolin für Eisen und Dimethylglyoxim für Nickel.

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THE DETERMINATION OF GOLD, PLATINUM, PALLADIUM AND RHODIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY WITH AN ULTRASONIC NEBULIZER AND A MULTI-ELEMENT HIGH-INTENSITY HOLLOW-CATHODE LAMP WITH SELECTIVE MODULATION

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Atomic absorption spectrophotometry, originated by WALSH[1], has been used with great success in a variety of problems. Improvements in the sensitivity of the method can be obtained by improving the atomization process of the sample, and by using a light source which emits resonance lines with narrow line-widths, *e.g.*, the high-intensity hollow-cathode lamp of SULLIVAN AND WALSH[2].

The usual method of atomization of the sample is by means of a pneumatic nebulizer into a flame. The efficiency of nebulization for atomic absorption work can be improved by using a process which gives a higher degree of dispersion and concentration of the aerosol, *e.g.* ultrasonic nebulization. The use of this type of nebulizer for flame photometry and atomic absorption spectrophotometry has been reported by various workers[3-6], who used focussing ultrasonic nebulizers in which dispersion was effected from the sample surface. KIRSTEN AND BERTILSSON[7], on the other hand, used a type of ultrasonic nebulizer in which the sample is sprayed on the vibrating surface. In this paper, details are given of a practical form of a focussing ultrasonic nebulizer and single and multi-element high-intensity hollow-cathode lamps.

EXPERIMENTAL

High-intensity hollow-cathode lamps

The high-intensity hollow-cathode lamps (Fig. 1) were made as described by SULLIVAN AND WALSH[2]. The conventional cathode (1) was made of stainless steel 15 mm long and 10 mm in diameter; it was lined on the inside, with strips of the element, or elements, of which the spectrum was required. These strips were folded double across the opening of the cathode to extend tube life, because the discharge tended to burn away the edges. The booster discharge was excited in two side-tubes as shown, and was conducted from the oxide-coated cathodes (4) *via* the quartz tubes (3) to the entrance holes (2) of the conventional hollow cathode. This discharge was run from a power supply which could give a stabilized current up to 500 mA at 25–30 V. The intensity of the conventional lamps was boosted by a factor of about 40.

Use was also made of selective modulation, and for this purpose a conventional cylindrical hollow-cathode lamp (5) was built in the same glass envelope. The same element or elements which were excited in the primary hollow-cathode lamp, were also generated here in order to facilitate selective modulation. For this purpose, a power source giving stabilized square waves was used.

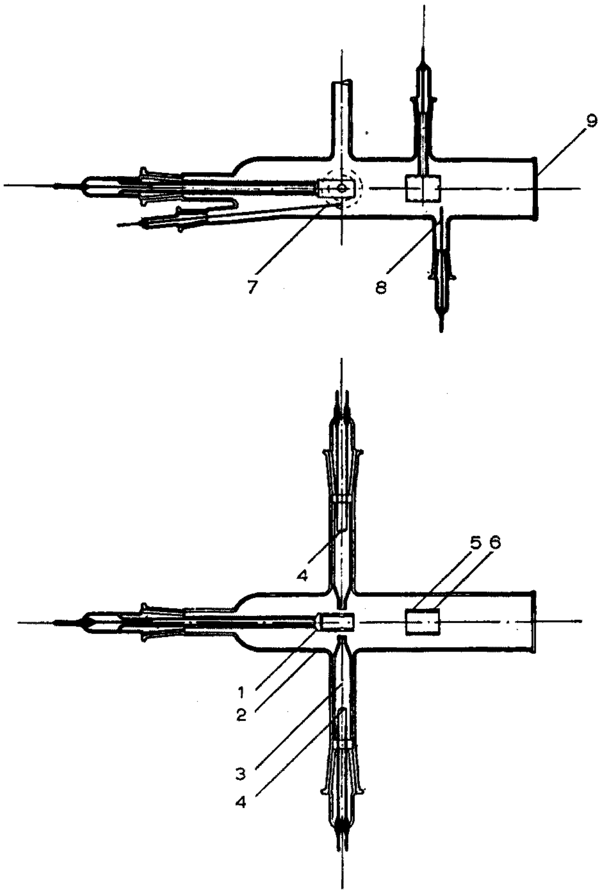

Fig. 1. Hollow-cathode lamp for high intensity and selective modulation.

Mono- and multi-element high-intensity lamps were built for gold, platinum, palladium and rhodium. Neon was used as carrier gas. No great differences were observed in the characteristics of the two types of lamps. However, multi-element lamps would be time-saving when used with a multi-channel direct reading spectrometer.

Spectrophotometer and burner system

A Zeiss PMQ II spectrophotometer was used as monochromator and detector. The burner was laboratory-made and was 12 cm long with 55 parallel slits each 0.5 mm wide and 17 mm long.

The ultrasonic nebulizer

The nebulizer used (Fig. 2) was designed and built in this laboratory. The quartz crystal (9) (Steeg and Reuter) had a diameter of 40 mm and a thickness of 1.4 mm, and was ground spherical with a "focal length" of *ca.* 50 mm.

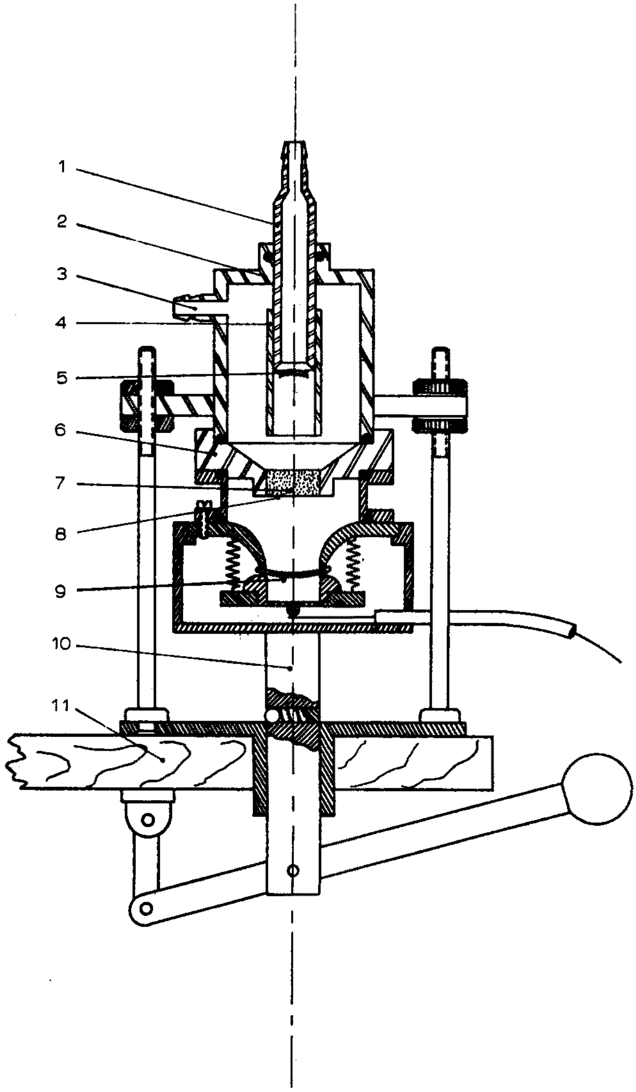

Fig. 2. Ultrasonic nebulizer with Perspex spray-chamber and sample holder.

The power input to the high-frequency oscillator could be varied between 0 and 80 W. The conversion factor from the input power of the oscillator to the output power of the crystal can be assumed to be *ca.* 20%, hence the output power of the crystal could be varied between 0 and 16 W. The oscillation frequency was 2 MHz.

The surface of each solution must be brought into the focal plane to be nebulized and for this purpose the solutions (7) were placed in a demountable container (6) which had a fixed position relative to the framework (11). The bottom (8) of this container was a polyethylene membrane with a thickness of 10 μ. Water was used as a coupling liquid between the crystal and the solution.

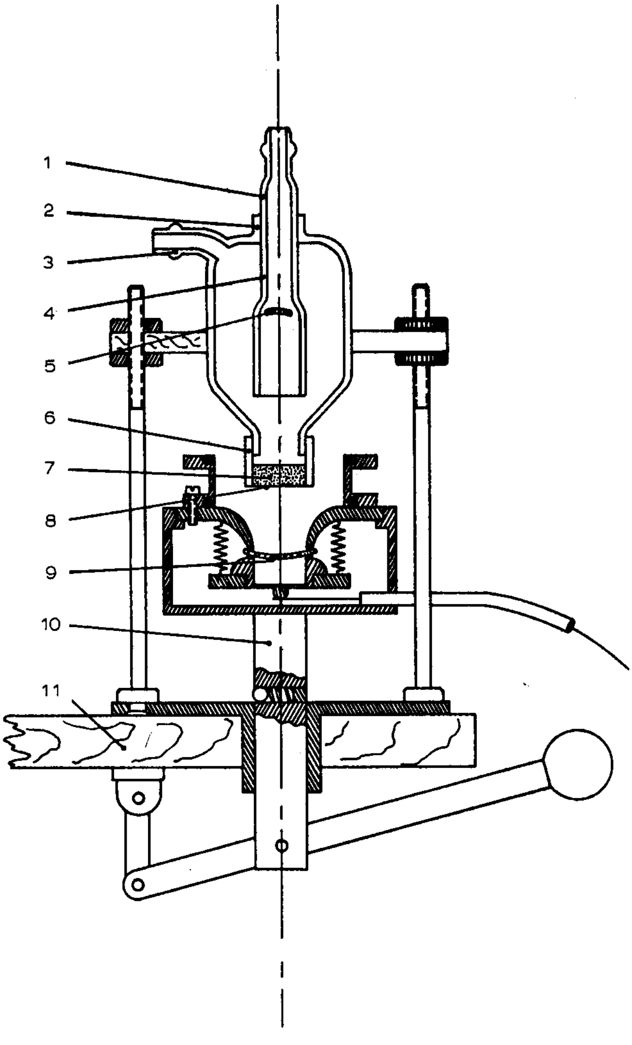

Fig. 3. Ultrasonic nebulizer with glass spray-chamber and polyethylene sample holder.

In order to obtain reproducible results, it is essential to have the surface of the solution exactly at the same height for each determination, before the oscillator is switched on. This is accomplished by mounting the sample holder, the coupling liquid and the crystal on a rod (10) which can be lowered by means of a lever system, or accurately replaced in the focal plane.

An air current *via* tube 1 forces the aerosol out of the spray-chamber (2) through tube 3 *via* a Tygon tube to the flame. The larger droplets are stopped by a spherical arrester (5) inside tube 1, and returned to the sample holder so as to keep the surface height as constant as possible. In the first design (Fig. 2), the sample holder (6) and the spray-chamber (2) were made of Perspex. However, in order to be able to work with organic solutions as well, a second apparatus (Fig. 3) was built. In this, the spray-chamber (2), the in- and outlets, and the arrester (5) were made of glass, and the sample holders of polyethylene tubing; these fitted firmly over the lower end of 2. The bottom of the sample holders were made of polyethylene sheet with the same thickness as in the perspex model.

Air and aerosol inlets for ultrasonic nebulizer

Several such sample holders were made beforehand, ready for use. When the samples are interchanged, tube 4 must be washed with distilled water to avoid contamination. This process takes about 1 min with the first design and 2 min with the glass model.

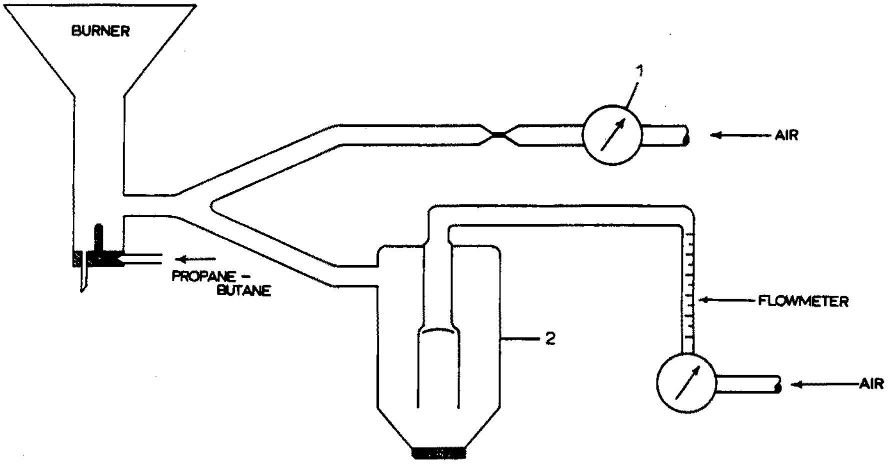

Fig. 4. Air and aerosol inlets for ultrasonic nebulizer.

The air and aerosol inlets to the burner are shown in Fig. 4. Enough air for the flame could be sent through the flowmeter *via* the nebulizer (2) alone, but the sample feed rate was then too high and resulted in a decrease in absorption, as was shown by parameter adjustments. For this reason, additional air was fed to the flame *via* regulator 1.

Parameter adjustments of the ultrasonic nebulizer

The nebulized droplet size for a specific liquid does not appreciably depend on the energy input. The rate at which the sample nebulizes does, however, depend on the energy input. In the present case, it reached a wide maximum when the input power to the oscillator was in the range, 20–45 W.

It is essential also to keep the liquid height constant for reproducible results. As a practical approach, each determination was started with the liquid height slightly higher than the focal plane. As the nebulization proceeded and the surface lowered, a maximum could easily be observed and was noted for each determination.

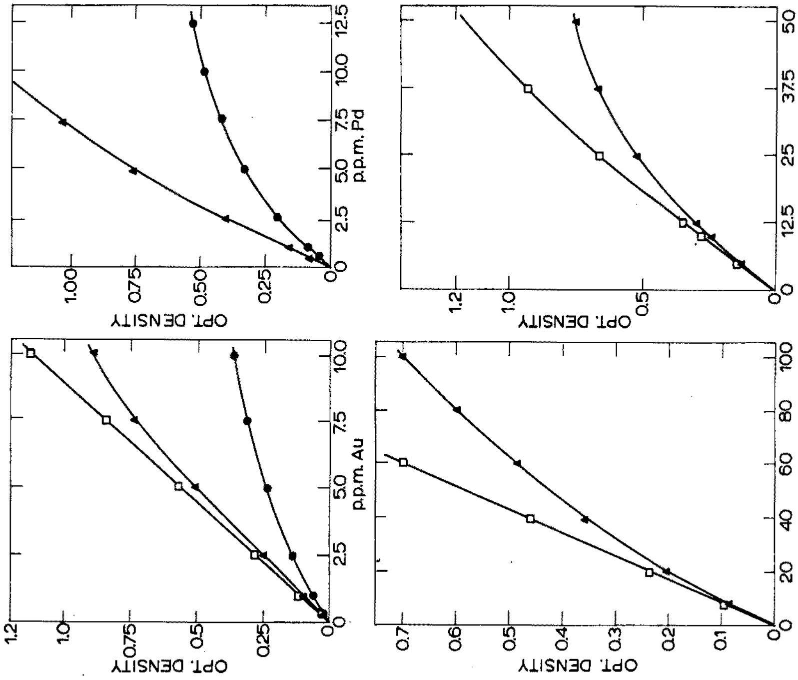

Fig. 5. Calibration curves for Au, Pd, Pt and Rh in aqueous solns. (□) Selective modulation; (▲) high intensity; (●) hollow cathode.

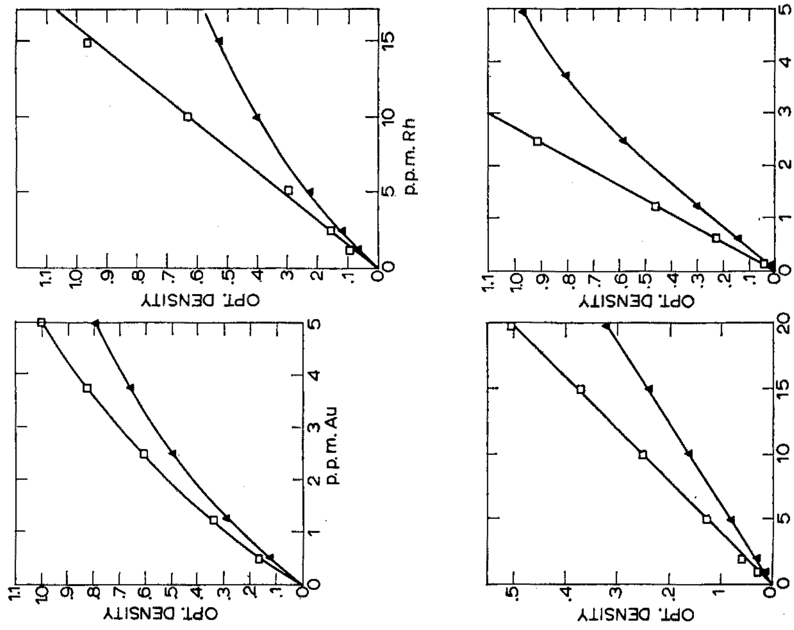

Fig. 6. Calibration curves for Au, Rh, Pt and Pd in 95% acetone. (□) Selective modulation; (▲) high intensity.

In determining the optimum working conditions, it must be borne in mind that the absorption depends on the amount of sample introduced per second into the flame. If the sample feed rate is too high, too much flame energy is used in evaporating the sample and the remaining reduction steps are inefficient. On the other hand, if the feed rate is too low, the production of neutral atoms is low in any case, and the corresponding absorption signal is weak. To find the optimum working conditions, the propane–butane pressure was changed in steps of 10 mmW* from 30 mmW to 80 mmW, the air-input was changed by adjusting the air regulator (1) (Fig. 4) from 5 p.s.i. to 30 p.s.i. and the absorption was then measured for each of the above combinations with air-flows of 3, 4.2, 5 and 6 l/min through the nebulizer chamber. These observations were made for various regions in the flame and for power inputs of 20, 25, 30, 35, 40 and 45 W to the oscillator. The optimum working conditions for the four elements are listed in Table I.

TABLE I

OPTIMUM WORKING CONDITIONS FOR THE VARIOUS NOBLE METALS

(Power input to oscillator: 35 W)

Element	*Fuel gas pressure (mmW)*	*Air-flow through nebulizer (l/min)*	*Air regulator reading (p.s.i.)*
Pd	50	5	15
Au	60	5	20
Rh	50	5	15
Pt	50	4.2	15

Standards and calibration curves for aqueous solutions

Standards for aqueous solutions were obtained from Specpure Johnson, Matthey & Co. solutions which were of the ammonium chloro type. Stock solutions containing 1000 p.p.m. of the noble metal in 10% hydrochloric acid were prepared. The stock solutions were diluted to the required concentration with 10% hydrochloric acid.

Working curves were drawn for the conventional hollow-cathode lamp, the high-intensity lamp and the latter supplemented by selective modulation. In some cases the signals obtained with the conventional lamp were too weak and only the others are then shown. The results are shown in Fig. 5.

Standards and calibration curves for organic solutions

The above work was repeated for organic solvents. Various mixtures of acetone and the alcohols, up to butanol, in water were tried. Acetone and methanol were the only solvents which nebulized satisfactorily and it was found that the best nebulization occurred when the percentage of acetone or methanol was as high as possible. The other alcohols showed very little, and in some cases no, nebulization.

When organic solvents were sprayed the propane–butane flow was reduced until the flame became non-luminous. In this way the flame size and shape were kept the same for all the solvents used. For solutions which contained 95% acetone, no fuel gas was used. A solution which contained 95% acetone showed a slightly

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* mmW = mm H_2O

better sensitivity than one containing 95% methanol. Accordingly, all further work was carried out with solutions containing 95% acetone.

Stock solutions containing 500 p.p.m. of the noble metal in 95% acetone were prepared from Johnson-Matthey Specpure solutions. The various standards were obtained by diluting the stock solutions with a 95% acetone solution. The optimum working conditions were again determined as described above and the calibration curves were drawn for the high-intensity lamps and for the high-intensity lamps supplemented by selective modulation. These curves are shown in Fig. 6.

Detection limits and coefficients of variation

In order to investigate the reproducibility of the method, two standard solutions of different concentrations for each element were analysed 30 times and the coefficients of variation were calculated for each solution. This was done for aqueous and organic solutions, with high-intensity lamps with and without selective modulation. The results are shown in Table II.

TABLE II

COEFFICIENTS OF VARIATION OBTAINED FOR THE NOBLE METALS AT DIFFERENT CONCENTRATIONS WITH AN ULTRASONIC NEBULIZER

Element	*Resonance wave length (Å)*	*Aqueous solns.*			*Organic solns.*		
		Concn. (p.p.m.)	*Coeff. of variation*		*Concn. (p.p.m.)*	*Coeff. of variation*	
			High-int. (%)	*Sel. mod. (%)*		*High-int. (%)*	*Sel. mod. (%)*
Au	2428	0.5	6.1	6.7	0.5	4.4	4.6
		5.0	3.0	3.3	1.25	4.1	4.2
Pd	2448	0.5	5.2	—	0.1	9.2	9.3
		5.0	2.0	—	2.5	3.9	4.1
Pt	2659	4.0	7.1	8.0	1.0	12.0	10.3
		20.0	3.1	3.7	10.0	4.8	5.2
Rh	3435	1.0	6.9	7.1	0.4	9.1	9.2
		10.0	2.6	3.2	10.0	4.3	4.8

TABLE III

DETECTION LIMITS FOR THE NOBLE METALS OBTAINED BY THE VARIOUS METHODS

Element	*Resonance wave length (Å)*	*Detection limits (concn. in p.p.m. giving 0.004 O.D.)*		
		Aqueous solns.		*Organic solns.*
		Pneumatic nebulizer	*Ultrasonic nebulizer*	*Ultrasonic nebulizer*
Au	2428	0.13	0.03	0.009
Pd	2448	0.09	0.02	0.012
Pt	2659	1.10	0.30	0.21
Rh	3435	0.15	0.09	0.06

The concentration that gave an optical density of 0.004 was taken as the detection limit. These limits were determined for each element in the two media. The results are given in Table III. The detection limits given are the average of the results obtained with high-intensity lamps and selective modulation. These values did not differ much for the two methods.

The detection limits for aqueous solutions determined with a conventional pneumatic nebulizer are also listed in Table III. Apart from the different nebulizers the experimental conditions were the same.

DISCUSSION

Table III shows that the detection limits obtained with an ultrasonic nebulizer are much lower than those obtained with a conventional pneumatic nebulizer. The detection limit for gold, for example, is about 4 times better, thus illustrating the importance of small droplet size for greater sensitivity. This feature and the fact that the sample feed rate can be varied over a wide range are amongst the chief advantages of the ultrasonic nebulizer. The results in Table II prove that the ultrasonic nebulizer can be successfully used for the analysis of noble metals.

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SUMMARY

The use of a multi-element high-intensity hollow-cathode lamp with selective modulation and a 2-MHz ultrasonic nebulizer for the determination of Au, Pt, Pd and Rh by atomic absorption spectroscopy is described. The sensitivities for the various elements in aqueous and organic media were studied. Only some organic solutions could be nebulized satisfactorily; a solution containing 95% acetone proved to be the best. For aqueous solutions, the detection limits (concn. giving 0.004 O.D.) were as follows: Au, 0.03 p.p.m.; Pd, 0.02 p.p.m.; Pt, 0.3 p.p.m.; and Rh, 0.09 p.p.m. For a 95% acetone solution the detection limits were: Au, 0.009 p.p.m.; Pd, 0.012 p.p.m.; Pt, 0.20 p.p.m. and Rh, 0.06 p.p.m. The coefficients of variation for aqueous and organic media were satisfactory.

RÉSUMÉ

On décrit l'utilisation d'une lampe à cathode creuse multi-élément, de forte intensité, avec modulation sélective et d'un nébuliseur ultrasonique 2-MHz, pour le dosage de l'or, du platine, du palladium et du rhodium par spectroscopie d'absorption atomique. On examine les sensibilités de divers éléments en milieux aqueux et organiques. Une solution contenant 95% d'acétone semble convenir le mieux. Les limites de détection en milieu aqueux sont les suivantes: Au 0.03 p.p.m., Pd 0.02 p.p.m., Pt 0.3 p.p.m. et Rh 0.09 p.p.m.; en milieu acétone 95% nous avons: Au 0.009 p.p.m., Pd 0.012 p.p.m., Pt 0.20 p.p.m. et Rh 0.06 p.p.m. Les coefficients de variation pour les milieux aqueux et organiques sont satisfaisants.

ZUSAMMENFASSUNG

Die Verwendung einer hochintensiven Hohlkathodenlampe mit mehreren Elementen, einer selektiven Modulation und einem 2-MHz-Ultraschallzerstäuber zur Bestimmung von Au, Pt, Pd und Rh mit der Atomabsorptionsanalyse wird beschrieben. Die Empfindlichkeiten für die verschiedenen Elemente in wässrigen und organischen Medien werden untersucht. Nur einige organische Lösungen konnten befriedigend zerstäubt werden; Lösungen, die 95% Aceton enthielten, waren am günstigsten. Für wässrige Lösungen betrugen die Nachweisgrenzen 0.03 p.p.m. Au, 0.02 p.p.m. Pd, 0.3 p.p.m. Pt, 0.09 p.p.m. Rh; für eine 95%ige acetonische Lösung: 0.009 p.p.m. Au, 0.012 p.p.m. Pd, 0.20 p.p.m. Pt, 0.06 p.p.m. Rh. Die Standardabweichungen waren für wässrige und organische Lösungen zufriedenstellend.

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AN OXYGEN STANDARD FOR THE DETERMINATION OF OXYGEN IN STEEL BY 14-MeV NEUTRON ACTIVATION ANALYSIS

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A neutron generator can be considered as a disk neutron source, hence an important flux gradient exists as a function of the distance between the neutron source and the irradiated sample. For samples with finite dimensions the highest activity will be induced at the face nearest to the tritium target. Furthermore, as the counting efficiency of the NaI(Tl) detector is also influenced by the distance between sample and crystal, the most activated face of the sample must be nearest to the detector to achieve the highest possible counting rate. In this way the highest sensitivity is obtained. Several authors[1-6] prefer to spin the samples during activation and (or) counting in order to achieve isotropic irradiation and (or) measurement. This method lowers the obtainable sensitivity as the mechanical setup increases the distance between sample and neutron generator and (or) γ-detector. An additional disadvantage is the difficulty of constructing a reliable instrument to spin heavy samples.

A simple solution for these geometry problems was achieved by applying a transport system with aluminium tubes of rectangular cross-section[7]. In this way, the samples necessarily present the same face to the neutron generator and to the detector. Additional advantages of this pneumatic system are the possibility of transporting the samples without a container and of analysing both sides, thus allowing the detection of important oxygen inclusions.

As usual, a relative method was adopted, the oxygen concentration of the sample being measured by comparison with a standard of known oxygen content. In most published procedures, standard and sample are irradiated successively, whilst the neutron flux or a related quantity is measured. Afterwards, the induced activities in sample and standard are corrected for differences in the neutron output of the generator.

Two possibilities can be applied for the flux monitoring: either the activity induced in a suitable target simultaneously with the sample or standard is measured, or direct neutron counting during the irradiation is done. In the first case, the reaction ^{63}Cu(n,2n)^{62}Cu ($T_{\frac{1}{2}}=9.9$ min, $\sigma=0.5$ b) is generally used[8]. Direct neutron counting can be achieved with organic plastic scintillators[1,3,9] or with a low-geometry BF$_3$ counter surrounded with paraffin to thermalize the neutrons[10-13]. Measurement of ^{16}N formed by the ^{16}O(n,p)^{16}N reaction on the target cooling water has also been proposed[14]. In this work, sample and standard were irradiated together. This reference sample system was recommended by IDDINGS[15].

Although it is possible to irradiate sample and standard next to each other[4,16],

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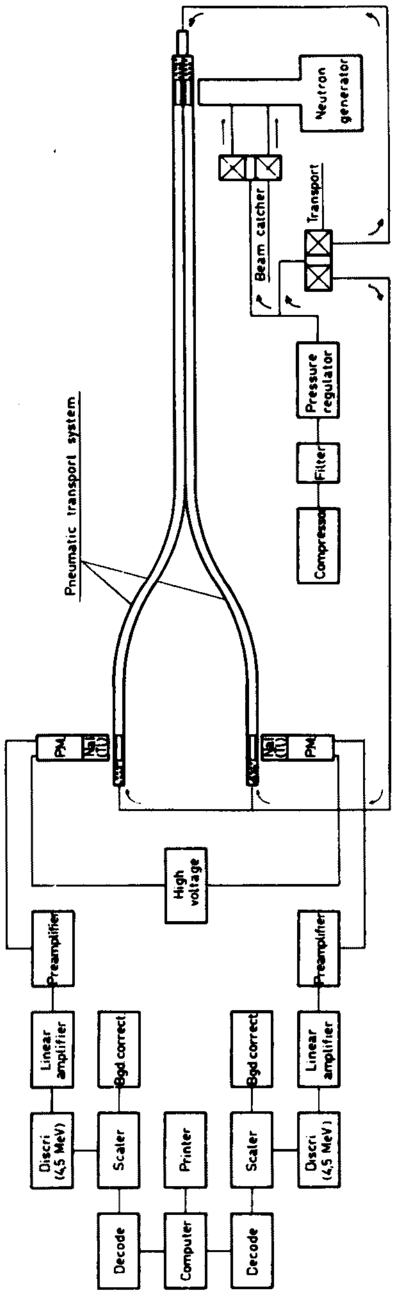

Fig. 1. General design of the system.

in this work the standard was placed behind the sample (see Fig. 1). Thus, the sample, placed at a distance of 3 mm from the target (position 1) is subjected to the highest neutron flux, whereas the smaller flux in the standard (position 2) is easily compensated by introducing a high oxygen quantity. The problem of flux gradients, geometry factors and absorption of neutrons and γ-rays must obviously be considered. Afterwards, the activities of sample and standard are measured simultaneously with two separate but nearly identical detector systems. The oxygen content in the unknown sample is then computed by the classical activation analysis formula

$$w_X = (w_S/K) \cdot (A_X/A_S) \qquad (1)$$

where the subscripts X and S indicate sample and standard respectively; A is the induced ^{16}N activity, w the oxygen weight and K a factor which depends on the ratio of the neutron flux in X and S (including the flux gradient and neutron absorption in the sample) and on the difference in counting efficiencies of the two counting systems (including the geometry, the discriminator setting and the self-absorption of the β- and γ-rays in the sample and standard (see below)).

Duplication of the rectangular transport system is fully compensated by minimisation of the errors in standardisation, the simplicity of automatic computation of the results and the omission of a spinning system.

EXPERIMENTAL

Instrumentation

The *neutron generator* used in this work was a SAMES Type J 150-kV 1.5-mA accelerator with a 80 MHz–60 W RF ion source and a constant field acceleration tube (10 electrodes). Focalisation provides a beam with a diameter of 10–30 mm. Targets of different origin (2 to 5 Ci) were used with a useful diameter of 18 mm. The neutron production is controlled by a pneumatic water-cooled removable tantalum screen, hence the accelerator is continuously in working conditions, which enhances the reproducibility of the neutron output.

Counting is performed by two separate but identical γ-counting systems, consisting of a common high-voltage supply, 3 × 3 in NaI(Tl) detectors, preamplifiers, linear amplifiers with discriminators and scalers. An automatic background correction is included: the reset at the start of the counting is made on the complement of the adjustable background (*ca.* 40 counts per 30 sec). The discriminator is set at 4.5 MeV.

Pneumatic transport system. Aluminium tubes with rectangular section (26.5 × 9.5 mm) were used. At the irradiation site the tubes of sample and standard are placed one after the other, the sample being nearest to the tritium target; at the measuring site the tubes are separated at a distance of *ca.* 100 cm. Concrete shielding screens the detectors from each other.

In the system described previously[7] rectangular *samples* of 20 × 17 × 7 mm were used. For industrial routine analysis preference was given to cylindrical samples of diameter 26 mm and thickness 9 mm. The samples are transferred without any container. In order to avoid excessive wear of the aluminium walls and to ensure reliable pneumatic transport, tolerances on the size must be kept within –0.1 mm. For an air pressure of 1.5 atm, a transport time of less than 1 sec is obtained for a distance of *ca.* 6 m. A detailed description of the apparatus is given in ref. 7.

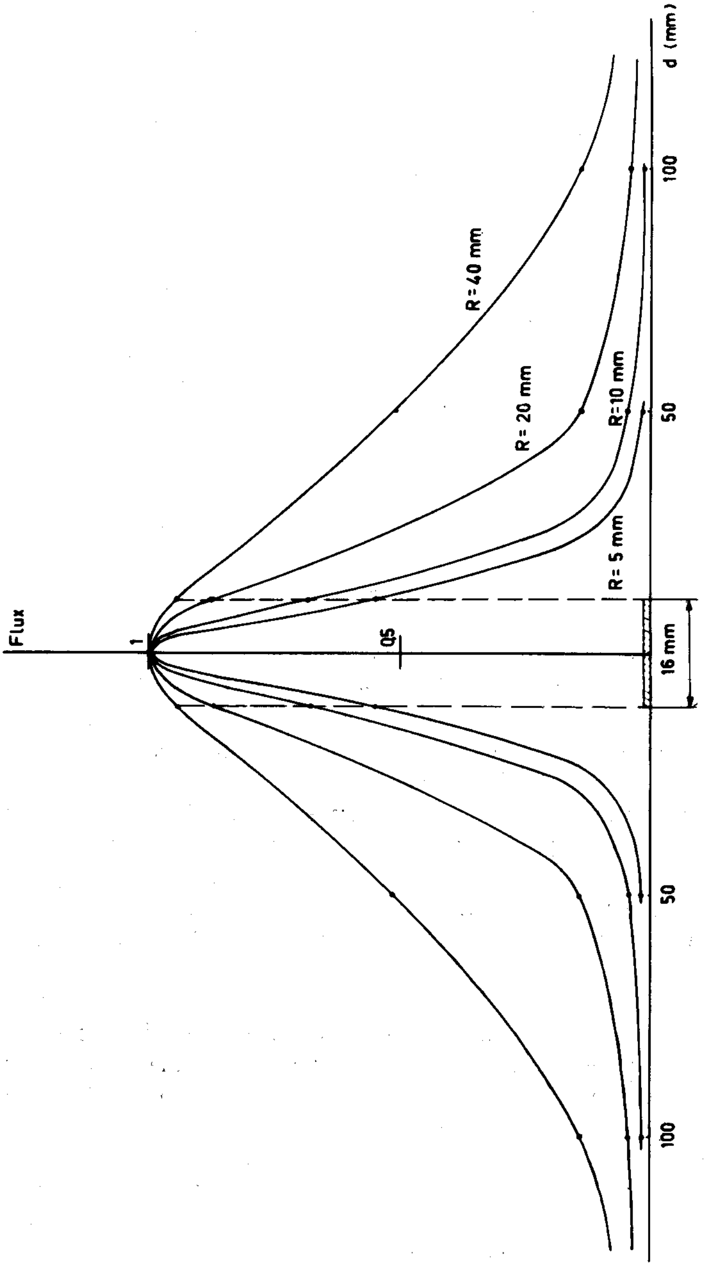

Fig. 3. Lateral gradient in planes parallel to the target, normalized to flux = 1, as a function of distance from target axis[17].

Standards

Important lateral and axial flux gradients exist at the irradiation position, as appears from Figs. 2 and 3. Consequently, the specific activity produced by irradiation in the standard (position 2) will be lower by a factor of 3 to 4 than that in the sample. To minimize the statistical error in counting A_S, the standard must contain a sufficient amount of oxygen, *e.g.* between 300 and 400 mg. Moreover, the oxygen in the standards must be as homogeneously distributed as possible. However, steel with such a high and accurately known oxygen content is not available. Nylon, plexiglass, etc., cannot be used since their oxygen content is not sufficiently well known and is not always homogeneously distributed.

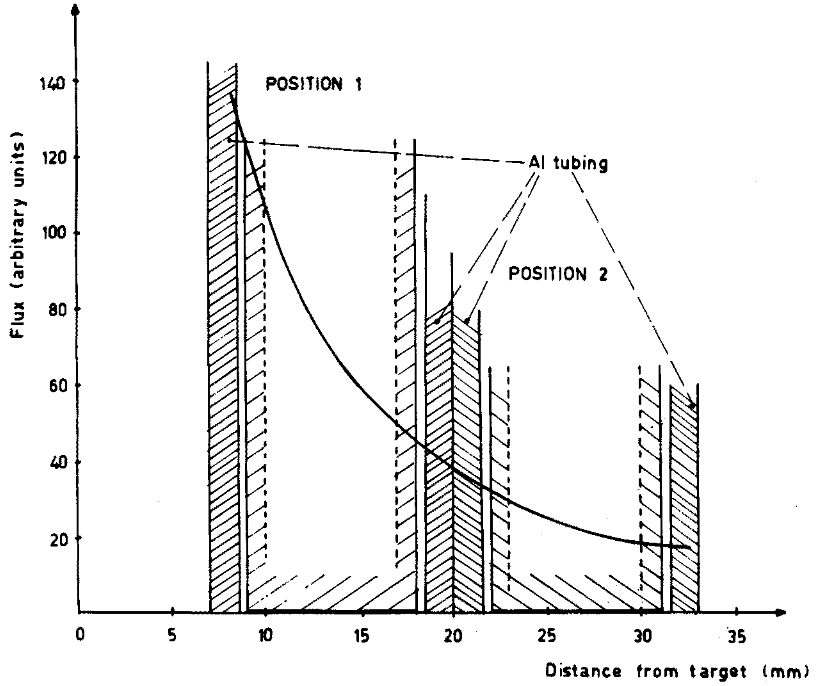

Fig. 2. Axial flux gradient.

Therefore, the standards used in this work were cylindrical capsules in ordinary steel, machined to the following dimensions (see Fig. 4): internal diameter 22.00 ± 0.02 mm, internal thickness 7.00 ± 0.02 mm; external diameter 26.0 mm and external thickness 9.00 ± 0.02 mm. The wall thickness of bottom and cover should be 1.00 ± 0.01 mm. These tolerances must be kept as strictly as possible, as appears from the following examples. A standard with walls of 0.79 and 1.42 mm for cover and bottom respectively gave rise to a difference of 15% in measured activity (normalized to the same flux) when irradiated with either side towards the target. For walls of 0.65 and 1.15 mm, this difference was 11%; for 0.87 and 1.14 mm, 5%; for 0.97 and 0.99 mm, 2% (see also Table I).

The relatively large volume of these capsules does not allow a complete filling with a homogeneous and pure substance of known oxygen content, since the induced

^{16}N activity will overload the counting apparatus. A mixture with graphite (National, spec pure, grade SP-1 suitable for pressing pellets) is proposed, as this substance is available in very high purity and does not give rise to interfering activities; it has a small blank value (oxygen content) and is suitable for making pellets. This mixture is directly pressed into the capsules, see Fig. 5.

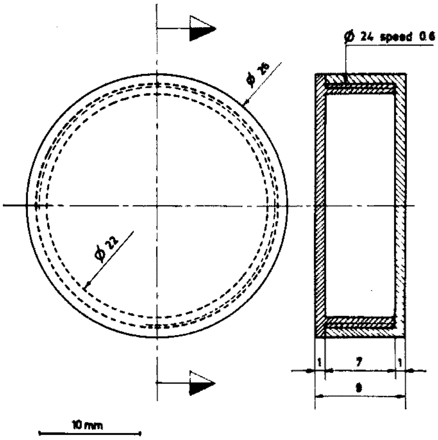

Fig. 4. Standard capsule.

TABLE I

COMPARISON OF TWO OXYGEN STANDARDS

Position 1	*Position 2*	*k*[a]
St. 1 (c)	St. 2 (c)	4.00±0.04[b]
St. 1 (c)	St. 2 (b)	4.00±0.04[b]
St. 2 (b)	St. 1 (b)	4.00±0.04[b]

[a] *k* = ratio of measured ^{16}N activities.
[b] Average value of 20 determinations; the reproducibility is expressed in terms of the standard deviation for a single determination.
(b) = bottom side facing the tritium target.
(c) = cover side facing the tritium target.

Choice of oxygen compound. Oxalic acid, $(COOH)_2 \cdot 2H_2O$, an acidimetric and oxidimetric primary standard is not available as a finely divided powder and cannot directly be mixed with graphite. Moreover, partial dehydration is possible because of local heating during grinding. *Benzoic acid* primary standard is finely divided but shows a tendency to "coagulate" after pressing, even after thorough mixing with graphite. Finally *iron(III) oxide* was chosen since it is a very finely divided powder of definite composition; it can be mixed homogeneously with graphite and is easily pressed into pellets.

Purity control of iron oxide standard

Iron(III) oxide (Fe_2O_3, pro analysi, Merck; Urtitersubstanz zur Eisenbestimmung mit $KMnO_4$ in salzsaurer Lösung) was used. Gravimetric analysis with urea

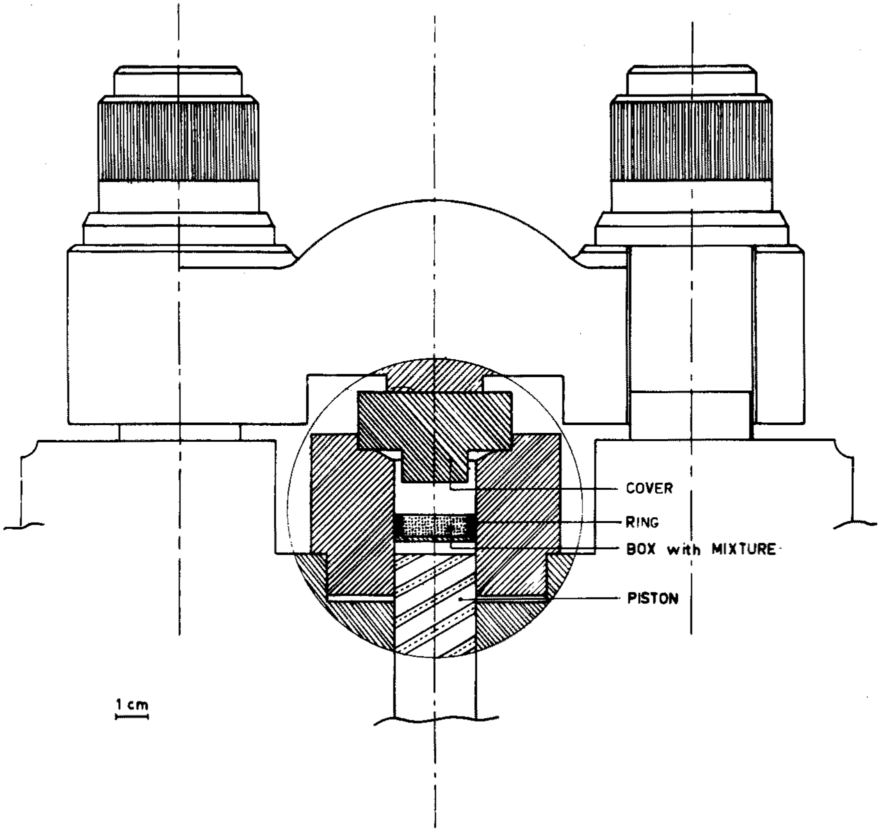

Fig. 5. Pressing of the standard mixture in the capsule.

and ignition of the hydroxide at 700° to constant weight yielded 100.25% (average value of 3 determinations) of the weighed sample.

The homogeneity after mixing with graphite was checked as follows: *ca.* 200 mg of the mixture was boiled for 30 min with 3 ml of concentrated hydrochloric acid, the graphite was filtered off, and iron was precipitated with ammonia and urea; the precipitate was also ignited at 700°. For 3 determinations, differences varying from 0 to −0.3% (*i.e.* 0 to 0.13 mg) were found between the theoretical and experimental values.

These data show that, in the most unfavourable case, the compound used should contain 98.4% Fe_2O_3 and 1.60% FeO, *i.e.* the oxygen can be too low by at most 0.4%.

Preparation of the mixture

Mix 11.0075 g of graphite and 3.9925 g of Fe_2O_3 homogeneously by shaking with plexiglass beads for at least 45 min. The mixture thus contains 26.62% Fe_2O_3 or 80.00 mg of oxygen per g. Fill the bottom of the capsule with the mixture (see Fig. 5); after pressing for 20 sec at 1000 psi, remove the cover, fill the box again, and press under the same conditions. Repeat this procedure until the box is completely filled, *i.e. ca.* 7 times. At this stage the homogeneity of the mixture can be checked by observing the surface of the pellet with a microscope (8×10). Two standards having the same thickness (wall 1.00 mm, pellet 7.00 mm) can be observed with the same focussing. After weighing, grease the screw thread with vaseline and close the capsule.

The box contains 4.92 g of the mixture, *i.e.* 394 mg of oxygen. The blank value of a box, filled with a pure graphite pellet, was 4.3–4.5 mg of oxygen as determined by activation analysis.

To be of practical value, a standard must be completely symmetrical; both sides facing the tritium target must yield the same activity. Moreover, two identical standards should be available, in order to determine the *k*-factor (see below). This was checked by irradiating two standards and counting the induced ^{16}N activity. Some typical results are given in Table I. The data show that the standards are identical and symmetrical, hence they are completely interchangeable and reversible. Note that this also eliminates manipulation errors.

THEORETICAL CONSIDERATIONS

Calibration of the system ("determination of k")

At the end of the irradiation, the measured ^{16}N activity for a standard, irradiated in position 1 (nearest to the target) is given by

$$A_S(1) = \sigma[\bar{\varphi}_1] w_S \theta N_A S C_S C_1 / M \qquad (2)$$

where σ = 14-MeV cross-section of the reaction $^{16}O(n,p)^{16}N$;
θ = isotopic abundance of ^{16}O;
N_A = Avogadro's number;
M = atomic weight of oxygen;
S = saturation factor $= 1 - \exp(-\lambda t_b)$;
$[\bar{\varphi}_1]$ = average 14-MeV neutron flux in the capsule at position 1 (diameter 22 mm, thickness 7 mm);
C_1 = detection efficiency, including the setting of the discriminator and the detection efficiency of the detector for the γ-rays of interest at measuring station 1;
C_S = "transmission factor", which takes into account the absorption of neutrons in the standard during activation and the self-absorption of γ-rays during the counting.

The measured activity for a standard, irradiated in position 2 is given by

$$A_S(2) = \sigma[\bar{\varphi}_2] w_S \theta N_A S C_S C_2 \exp(-\Sigma_S d) / M \qquad (3)$$

where $[\bar{\varphi}_2]$ is the average 14-MeV neutron flux in the box at position 2. The factor $\exp(-\Sigma_S d)$ takes into account the 14-MeV neutron absorption by a simultaneously irradiated standard in position 1. Σ_S is the macroscopic cross-section for effective removal of fast neutrons[18] for 2 mm of steel plus 7 mm of graphite mixture; $d = 9$ mm.

The absorption of neutrons and γ-rays in both the standards is the same (C_S). Discriminator setting and counting geometry for measuring station 2 are taken into account by C_2.

The measured activity ratio k is given by

$$k = A_S(1)/A_S(2) = [\bar{\varphi}_1]C_1/[\bar{\varphi}_2]C_2 \exp(-\Sigma_S d) \tag{4}$$

NARGOLWALLA *et al.*[19] found that the neutron absorption by a sample was indeed directly proportional to its macroscopic cross-section for effective removal of fast neutrons.

Oxygen analysis in steel

The measured ^{16}N activity, induced in a steel sample, irradiated in position 1, is given by:

$$A_{Fe}(1) = \sigma\bar{\varphi}_1 w_X \theta N_A S C_{Fe} C_1/M \tag{5}$$

where: $\bar{\varphi}_1$ = the average flux in a cylinder of 9 mm thickness and 26 mm diameter (dimensions of the steel sample);
w_X = the unknown oxygen weight in the steel sample;
C_{Fe} = the "transmission factor" for steel.

For the standard, which is irradiated simultaneously in position 2, one can write:

$$A_S(2) = \sigma[\bar{\varphi}_2] w_S \theta N_A S C_S C_2 \exp(-\Sigma_{Fe} d)/M \tag{6}$$

since the standard is shielded by a steel sample. Σ_{Fe} is the macroscopic fast-neutron removal cross-section for iron and $d = 9$ mm.

From eqns. (5) and (6), one obtains:

$$\frac{A_{Fe}(1)}{A_S(2)} = \frac{\bar{\varphi}_1 w_X C_1 C_{Fe}}{[\bar{\varphi}_2] w_S C_2 C_S \exp(-\Sigma_{Fe} d)} \tag{7}$$

After multiplying nominator and denominator by $[\bar{\varphi}_1]$ and substituting eqn. (4) into eqn. (7), one obtains

$$w_X = \frac{w_S}{k} \cdot \frac{A_{Fe}(1)}{A_S(2)} \cdot \frac{C_S}{C_{Fe}} \cdot \frac{\exp(-\Sigma_{Fe} d)}{\exp(-\Sigma_S d)} \cdot \frac{[\bar{\varphi}_1]}{\bar{\varphi}_1} \tag{8}$$

k is determined experimentally in step (i); $A_{Fe}(1)$ and $A_S(2)$ are determined experimentally in step (ii); w_S is known, namely, 394 mg of oxygen, not including the blank value. Calculation of w_X is possible, if C_S/C_{Fe}, $\exp(-\Sigma_{Fe} d)/\exp(-\Sigma_S d)$ and $[\bar{\varphi}_1]/\bar{\varphi}_1$ are known.

EXPERIMENTAL DETERMINATION OF $\exp(-\Sigma_{Fe} d)/\exp(-\Sigma_S d)$

In position 2 an oxygen standard is irradiated and its activity measured with a steel sample or an oxygen standard in position 1. The neutron output is measured by means of a BF_3 counter, surrounded by 5 cm of paraffin wax. This setup allows the determination of the ratio of the fast-neutron removal for a steel sample of 9 mm thickness to that for a standard (2 mm steel plus 7 mm graphite–iron oxide mixture).

The average value for 6 × 20 determinations was found to be

$$\exp(-\Sigma_{Fe} d)/\exp(-\Sigma_S d) = 0.949 \pm 0.006 \text{ (S.D. of the mean).}$$

It should be noted that no measurable difference was observed between steel and stainless steel.

Calculated value. From the density of the graphite–iron oxide mixture (1.3), the composition of the mixture (*ca.* $\frac{3}{4}$ graphite and $\frac{1}{4}$ Fe_2O_3), and the experimental 14-MeV neutron mass-attenuation coefficients Σ/δ for carbon, iron and oxygen, it can be calculated, according to ZOLLER[18], that

$$\Sigma_{\text{mixture}} \simeq \delta_{\text{mixture}} \left[\frac{3}{4}\left(\frac{\Sigma}{\delta}\right)_{\text{C}} + \frac{1}{4}\left(\frac{111.6}{159.6}\right)\left(\frac{\Sigma}{\delta}\right)_{\text{Fe}} + \frac{1}{4}\left(\frac{48.0}{159.6}\right)\left(\frac{\Sigma}{\delta}\right)_{\text{O}}\right] = 0.048 \text{ cm}^{-1}.$$

The neutron attenuation for a steel sample is thus given by

$$\varphi/\varphi_0 = \exp(-\Sigma_{\text{Fe}}d) = \exp(-0.156 \times 0.9) = 0.867$$

and for a steel capsule containing a 7-mm layer of the standard graphite mixture

$$\varphi/\varphi_0 = \exp(-0.156 \times 0.2)\exp(-0.048 \times 0.7) = 0.937$$

Hence one calculates $\exp(-\Sigma_{\text{Fe}}d)/\exp(-\Sigma_{\text{S}}d) = 0.867/0.937 = 0.93$. This value is in reasonable agreement with the experimental value of 0.949.

EXPERIMENTAL DETERMINATION OF C_S/C_{Fe}

This ratio includes both the absorption of 14-MeV neutrons in the sample during activation and the absorption of the γ-rays of ^{16}N during the counting. It can be considered as a transmittance factor[12].

Seven steel disks, 22.0 mm in diameter and 1 mm thick and cellophane foils of the same diameter were alternately piled to a height of 7 mm and placed in a standard capsule.

Afterwards, seven aluminium disks 22.0 mm in diameter and 1 mm thick and the same cellophane papers (on the same place in the capsule to avoid differences due to inhomogeneities in the cellophane) were used.

These samples were consecutively irradiated in position 1, while the neutron flux was monitored with a BF_3 counter. After correction for the blank value of capsule and Fe or Al disks (*i.e.* without cellophane), the following ratio was found

$C_S/C_{Fe} = 1/(0.939 \pm 0.005)$ (s.d. for the average value of 7 × 20 determinations).

Calculated value. Considering 0.1-cm layers of steel ($d \simeq 0.8$ g.cm^{-2}; $\mu \simeq 0.03$ cm^2.g^{-1}), one calculates for the absorption of the ^{16}N γ-rays by the cover (or bottom) of the box and 7 steel disks:

for ^{16}N in the first cellophane paper: $I_1 = I_{0_1} \exp(-\mu d) = 108 \exp(-0.03 \times 0.8)$
$= 105.5$ arbitrary units;

for ^{16}N in the second cellophane paper: $I_2 = I_{0_2} \exp(-2\,\mu d) = 94 \exp(-0.03 \times 1.6)$
$= 89.5$ arbitrary units;

etc.... eighth cellophane paper: $I_8 = I_{0_8} \exp(-8\,\mu d) = 49 \exp(-0.192)$
$= 40.4$ arbitrary units.

The values of I_0 are read from Fig. 2 (flux gradient).

$$\sum_1^8 I/\sum_1^8 I_0 = 532.0/584 = 0.9129 \text{ arbitrary units.}$$

For seven Al disks (0.1 cm $=0.26$ g.cm^{-2}; $\mu \simeq 0.025$ cm^2.g^{-1}) in an iron box, similar calculations can be made:

$I_1 = 108 \exp(-0.03 \times 0.8) = 105.5$ arbitrary units (steel cover)

$I_2 = 94 \exp(-0.03 \times 0.8) \exp(-0.025 \times 0.26) = 91.3$ arbitrary units (steel cover +1 Al disk)

etc...

$I_8 = 49 \exp(-0.03 \times 0.8) \exp(-0.025 \times 1.82) = 45.7$ arbitrary units (steel cover +7 Al disks)

$\sum_1^8 I / \sum_1^8 I_0 = 560.5/584 = 0.9598$ arbitrary units.

Hence: $C_{Al}/C_{Fe} = 1/0.949$.

This calculated value is in reasonable agreement with the experimental value of 1/0.939.

Note. Aluminium was used instead of the graphite–Fe_2O_3 mixture, because the latter contains too much oxygen. Pure graphite could not be used, since it is very difficult to make layers of exactly 1 mm between two successive cellophane disks.

The use of aluminium in the cylindrical iron capsule is justified, as its absorption for 14-MeV neutrons equals that of the graphite–Fe_2O_3 mixture within *ca.* 1%, in agreement with the calculated value (*cf.* $\exp(-\Sigma_{Al}d)/\exp(-\Sigma_S d) = 1.012$ for a pure aluminium sample and an oxygen standard). For C_{Al}/C_S one calculates in a similar way as above, $560.5/565.45 \simeq 0.99$ using $d = 0.13$ g.cm^{-2} for a 0.1-cm layer of the mixture, and $\mu \simeq 0.026$ cm^2.g^{-1}.

The absolute error caused by replacing the graphite–iron oxide mixture with aluminium is thus estimated to be about 1% ($1/(0.939 \pm 0.01)$).

EXPERIMENTAL DETERMINATION OF $[\bar{\varphi}_1]/\bar{\varphi}_1$

This ratio takes into account the different 14-MeV "neutron density" in a capsule (internal diameter 22.00 mm, thickness 7.00 mm) and in a normal sample (diameter 26.0 mm, thickness 9.0 mm). The factor actually takes into account two factors.

(a) Decrease in thickness

As can be seen from Fig. 2, this decrease (9.00 mm $- 2 \times 1.00$ mm $= 7.00$ mm) lowers the average 14-MeV "neutron density", and thus the specific activity. Its contribution was determined as follows: 7 steel disks (22.0 mm in diameter and 1 mm thick) are placed in a standard capsule and irradiated in position 1 (see Figs. 1 and 2). After irradiation the induced ^{56}Mn activity of each disk is measured on a flat 3 × 3″ NaI(Tl) detector. The measured activity, corrected for decay, is directly proportional to the flux and is plotted as a function of distance from the target (*cf.* Fig. 2). The average flux in the capsule is $\left(\sum_1^7 A_i\right)/7$ arbitrary units. Extrapolation 1 mm towards and 1 mm away from the target allows calculation of the average flux over a sample of 9 mm thickness, namely, $(\sum_1^9 A_i)/9$ arbitrary units.

Similar series of experiments were done with 7 steel disks (26 mm in diameter and 1 mm thick), placed symmetrically in the pneumatic tube at position 1. The same result was found.

Average value $\frac{1}{7}\sum_{1}^{7} A_i / \frac{1}{9}\sum_{1}^{9} A_i = 0.974 \pm 0.001$

(standard deviation of the average of 11 series of measurements).

(b) Decrease in radius

As can be seen from Fig. 3, the decrease in radius (13.00 mm − 2.00 mm = 11.00 mm) increases the average 14-MeV "neutron density", and thus the specific activity of ^{16}N in the capsule.

This contribution was determined as follows: steel disks (26 mm in diameter and 1 mm thick) were irradiated and the central parts (22 mm diameter) cut out. The resulting disks and rings were dissolved in hydrochloric acid, the solutions diluted to 25 ml and the ^{56}Mn activity measured. After decay corrections, the ratio (sum of specific activities of central parts)/(sum of specific activities of central parts + rings) was computed. The average value was 1.070 ± 0.005 (standard deviation of the average of 9 determinations).

The most important factor, which makes the measured specific ^{16}N activity different in standards and samples, is the radial contraction. Note that the factor $\exp(-\Sigma_{Fe}d)/\exp(-\Sigma_S d)$ and C_S/C_{Fe} approximately compensate each other. The overall correction factor is

$$\frac{(0.949 \pm 0.006)}{(0.939 \pm 0.005)}(0.974 \pm 0.001)(1.070 \pm 0.005) = 1.053 \pm 0.01$$

Hence the amount of oxygen in the steel sample can be calculated from the following equation:

$$w_X = \{(1.053\, w_S + b)/k\} \cdot \{A_{Fe}(1)/A_S(2)\} \qquad (9)$$

The calculations for routine analyses are done with a small ratio computer (see Fig. 1).

The relative error of the correction factor 1.053 is *ca.* 1%. The absolute systematic error is estimated to be within the same limits. For a standard containing 394 mg of oxygen (as Fe_2O_3 in graphite), this means that the apparent oxygen weight which has to be used for oxygen analysis in steel is (394 mg × 1.053) + 4.3 mg or 419.2 mg; 4.3 mg is the blank value for the steel capsule and for the graphite.

RESULTS

Accuracy tests on the standard. Comparison between activation analysis and reducing fusion

The oxygen content in 6 different steel samples was determined by activation analysis (A.A.) and the results compared with those obtained by reducing fusion analyses (R.F.A.) in three or four selected laboratories of the E.S.C.C. High Authority. Sampling was done as indicated in Fig. 6[20].

Sample 1 contained 0.072% C, 0.34% Mn, 0.009% P and 0.023% S.

Sample 2: 0.066% C, 0.31% Mn, 0.15% P, 0.015% S, 0.053% Cu, 0.018% Cr, 0.032% Ni, 0.005% Sn, 0.042% As and 0.002% N.

Sample 3: 0.069% C, 0.30% Mn, 0.011% P, 0.017% S, 0.027% Cu, 0.014% Cr, 0.028% Ni, 0.005% Sn, 0.017% As and 0.002% N.

Sample 4: 0.050% C, 0.032% Mn, 0.030% P, 0.021% S, 0.03% Cu and 0.005% N[20].

Samples 57 and 68 were non-killed chromium–manganese steels. Only one sample from these steel blocks was available for activation analysis (top). Results are given in Table II. For each laboratory the average value of these reducing fusion analyses is given (top, middle, bottom). The overall average value is also indicated with the standard deviation for a single determination. In the case of activation analysis, the average value of 9 analyses for each of the two samples (see Fig. 6) is

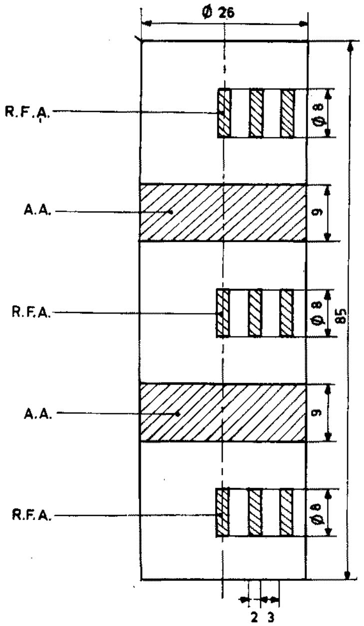

Fig. 6. Sampling for activation analysis (A.A.) and reducing fusion analysis (R.F.A.)[20].

TABLE II

COMPARISON BETWEEN RESULTS OF ACTIVATION ANALYSIS AND FUSION ANALYSIS (IN p.p.m. OXYGEN)

Sample	*R.F.A. average value for*				*R.F.A.*[a] *overall average*	*A.A.*[a] *average*	*A.A. − R.F.A. (p.p.m.)*
	Lab. I	*Lab. A*	*Lab. E*	*Lab. M*			
1	269	265	254	—	263±8	285±17	+22
2	169	145	149	—	154±13	183±12	+29
3	146	144	137	—	142±7	148±7	+6
4	322	329	301	—	317±25	316±15	−1
57	943	910	952	901	929±27	935±25	+6
68	1230	1205	1275	1233	1240±35	1253±40	+13

[a] = Standard deviation for a single determination.

given; the *ca.* 35-g disks were analyzed on both sides, but no substantial heterogeneity was observed.

The agreement of the results obtained by the two methods is satisfactory, although there is a tendency to find higher results with activation analysis (see samples 1 and 2).

Long-term reproducibility

Sample 57 (a chromium–manganese steel) was regularly analyzed over a period of 6 months, using the same oxygen standard. The results are given in Table III. Each value is the mean of 5 determinations; the standard deviation for a single determination is given. It can be seen that essentially the same result was found over a long period, the average value being 941 p.p.m.

The correction factor 1.053 (see eqns. (8) and (9)) contains the geometrical factor $[\bar{\varphi}_1]/\bar{\varphi}_1$, which varies slightly as a function of distance from the target and as a function of the diameter of the deuteron beam.

TABLE III

LONG-TERM REPRODUCIBILITY (RESULTS FOR SAMPLE 57—FRONT SIDE)

Date	*p.p.m. oxygen*	*Date*	*p.p.m. oxygen*
30-06-67	933±13	09-11-67	936±21
03-07-67	943±36	09-11-67	936±13
04-07-67	929±27	17-11-67	944±45
04-10-67	951±22	23-11-67	946±35
10-10-67	950±20	23-11-67	934±35
25-10-67	944±15	07-12-67	915±47
25-10-67	944±15	07-12-67	944±45
27-10-67	936±40	08-12-67	949±26
27-10-67	931±37	13-12-67	934±43
30-10-67	934±17	14-12-67	945±55

Mean long-term standard deviation: ±30 p.p.m. (±3.2%)
Lowest value ±13 p.p.m. (±1.4%)
Highest value ±55 p.p.m. (±5.8%)

TABLE IV

INFLUENCE OF BEAM DEFOCALISATION AND DISTANCE OF SAMPLE TO TRITIUM TARGET ON ANALYTICAL RESULT

Date	*Diaphragm current*	*Distance to target as compared with normal position*	*p.p.m. O in sample 57*
10-10-67	normal (< 5 μA)	+1.8 mm	953±5 943±47
09-11-67	15–25 μA	Normal	926±10 944±39
09-11-67	normal (< 5 μA)	+6.0 mm	921±16 936±39
09-11-67	15–25 μA	+6.0 mm	959±23 949±20
17-11-67	15–25 μA	Normal	944±20
17-11-67	10–20 μA	+3.5 mm	939±12 930±26 951±19

These effects are, however, not very important, as appears from Table IV, where the oxygen content is given for sample 57, as calculated from eqn. (9) (average of 5 determinations, standard deviation for a single determination). The average value of 941 p.p.m. agrees with that of Table III for the normal working conditions, which were also used for the calibration of the oxygen standard.

This means that the positioning of the accelerator and the defocalisation of the deuteron beam is not critical.

Note. Analyses of sample 57 were also performed with a tritium target of 28 mm effective diameter. It appeared that oxygen results higher by 1.5% were obtained in comparison with the target of 18 mm effective diameter. Although this observation deserves further investigation, the difference is probably due to a difference in the correction factor for the decrease in radius.

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SUMMARY

A relative method for the determination of oxygen in steel via the $^{16}O(n,p)^{16}N$ reaction by means of 14-MeV neutrons is described. A standard is irradiated immediately behind the sample and the induced activities are counted simultaneously with two separate but identical detector systems. The standard mixture (*ca.* 5 g of graphite plus iron oxide containing 80 mg of oxygen per g) is compressed into a steel capsule of the same external dimensions as the samples (26 mm diameter, 9 mm thick). Dimensional tolerances, choice and purity control of the oxygen compound and preparation of the standard mixture are discussed. Fast neutron shielding, absorption of fast neutrons, self-absorption of the ^{16}N γ-rays and the average neutron flux in sample and standards are considered and a total correction factor is established. Flux inhomogeneities and differences in counting geometry and discriminator setting can be determined by irradiation and counting of two identical standards. The accuracy of this method was checked by comparison of the results with those of the reducing fusion method; satisfactory agreement was observed, although the activation results tended to be slightly higher. The mean long-term standard deviation for analysis of a given sample over a period of 6 months was found to be $\pm 3\%$.

RÉSUMÉ

On décrit une méthode pour le dosage de l'oxygène dans l'acier via la réaction $^{16}O(n,p)^{16}N$ au moyen de neutrons 14 MeV. Un standard est irradié immédiatement derrière les disques d'échantillons; les activités induites sont comptées simultanément avec deux systèmes détecteurs séparés mais identiques. Le mélange étalon (5 g de graphite plus oxyde de fer renfermant 80 mg d'oxygène par gramme) est comprimé dans une capsule d'acier. On prend en considération la formation de neutrons rapides, l'absorption des neutrons rapides, la self-absorption des rayons $^{16}N\gamma$ et le flux moyen de neutrons dans l'échantillon et les étalons. On a examiné l'exactitude de cette méthode par comparaison des résultats avec ceux obtenus par la méthode de fusion réductrice; les résultats par activation tendent à être légèrement plus élevés. L'écart type pour l'analyse d'un échantillon donné sur une période de 6 mois est de ±3%.

ZUSAMMENFASSUNG

Eine Relativmethode zur Bestimmung von Sauerstoff in Stahl durch die Reaktion $^{16}O(n,p)^{16}N$ mittels 14 MeV-Neutronen wird beschrieben. Dabei wird ein Standard unmittelbar hinter der Probe bestrahlt und die induzierten Aktivitäten werden gleichzeitig mit 2 getrennten, aber identischen Detektorsystemen gezählt. Der Standard besteht aus einer Mischung von etwa 5 g Graphit und Eisenoxid, das 80 mg Sauerstoff pro Gramm enthält. Er wird in eine Stahlkapsel gepresst, die dieselben äusseren Dimensionen wie die Probe besitzt. Aufgrund der Diskussion der Toleranzen bei den geometrischen Abmessungen der Kapsel, der Wahl und der Reinheit der Sauerstoffverbindungen, der Präparation des Standards, der Absorption der schnellen Neutronen und des mittleren Neutronenflusses wird ein Korrektionsfaktor aufgestellt. Unterschiede im Neutronenfluss, der Zählgeometrie und der Diskriminatoreinstellung können durch Bestrahlung und Zählung 2 identischer Standards bestimmt werden. Die Richtigkeit der Methode wurde durch Vergleich der Ergebnisse mit denen der Reduktions-Schmelzmethode überprüft und eine befriedigende Übereinstimmung festgestellt, obwohl die Ergebnisse der Aktivierung zu etwas höheren Werten tendierten. Für eine bestimmte Probe wurde in einem Zeitraum von 6 Monaten durch wiederholte Messungen eine Standardabweichung von ±3% gefunden.

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THE DETERMINATION OF SILICON IN STEEL BY 14-MeV NEUTRON ACTIVATION ANALYSIS

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In industry, the determination of silicon in steel is mostly performed either by wet analysis, which is accurate but time-consuming, or by instrumental methods as emission spectrometry, X-ray fluorescence, colorimetry etc., usually with less accurate results.

With 14-MeV neutrons, a non-destructive determination of silicon can, in principle, be carried out in a few minutes, via the reaction ^{28}Si(n,p)^{28}Al. This determination has already been described by KUSAKA AND TSJUJI[1] and WOOD AND ROPER[2].

Irradiation of silicon and iron with 14-MeV neutrons gives rise to a number of possible reactions as summarized in Table I. From this it appears that the most convenient silicon determination can be expected from the measurement of ^{28}Al produced by a (n,p) reaction on ^{28}Si. In this way, one can take advantage of high abundance, important cross-section and suitable half-life, while the relatively energetic γ-rays (1.78 MeV) will be relatively free of interferences.

With a NaI(Tl) detector, however, the 1.78-MeV γ-energy of ^{28}Al cannot be

TABLE I

NUCLEAR REACTIONS

Element	*Reactions*	*Abundance (%)*	*Cross-section (mb)*[3,4]	*Half-life*	*Energy (MeV) and abundance*[5]
Si	^{28}Si(n,p)^{28}Al	92.2	250	2.3 min	1.78 (100)
	^{29}Si(n,p)^{29}Al	4.7	100	6.6 min	1.28 (94); 2.43 (6)
	^{30}Si(n,α)^{27}Mg	3.1	45–185	9.5 min	0.84 (69); 1.01 (30.4); 0.18 (0.6)
Fe	^{54}Fe(n,2n)^{53}Fe	5.82	12	8.9 min	β^+/0.38 (38)
	^{54}Fe(n,p)^{54}Mn	5.82	350	303 d	0.84 (100)
	^{54}Fe(n,α)^{51}Cr	5.82	130	27.8 d	0.32 (9)
	^{56}Fe(n,2n)^{55}Fe	91.7	440	2.6 y	E.C.
	^{56}Fe(n,p)^{56}Mn	91.7	115	2.58 h	0.84 (98.7); 1.81 (29.3); 2.11 (15.5); 2.52 (1.1); 2.66 (0.7); 2.95 (0.5); 3.37 (0.2)
	^{57}Fe(n,p)^{57}Mn	2.2	60	1.7 min	Several low energy gammas
	^{58}Fe(n,p)^{58}Mn	0.33	23	1.1 min	
	^{58}Fe(n,α)^{55}Cr	0.33	21.5	3.5 min	

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distinguished from the 1.81 MeV γ-energy of ^{56}Mn. ^{56}Mn is obviously the most important radionuclide produced in the iron matrix. In principle a correction for this activity can be made in different ways.

Method I. Two successive counts of the complex photopeak at 1.8 MeV can be made. Within a short time interval, the decay of ^{56}Mn is negligible. The count difference between the two measurements is thus proportional to the ^{28}Al activity. The spectra of a 3% silicon steel, irradiated for 5 sec at 300 μA and measured 1 and 4 min after the irradiation, are represented in Fig. 1. For very low silicon contents, the ^{56}Mn decay should be taken into account. During the time interval of 3 min, the ^{56}Mn activity has decayed 1.33%, causing an error of about 0.005% of silicon for an iron sample.

Method II. Simultaneous counting of the complex photopeak at 1.8 MeV and of the ^{56}Mn photopeak at 2.11 MeV is possible. If k_{Fe}, the ratio of the activities under the photopeaks at 1.81 and 2.11 MeV in a pure ^{56}Mn spectrum is known (*ca.* 2) the contribution of ^{56}Mn in the 1.8-MeV peak can be calculated. The net ^{28}Al activity is given by

$$\mathrm{Act}_{^{28}\mathrm{Al}} = \mathrm{Act}_{1.8\ \mathrm{MeV}} - k_{\mathrm{Fe}} \times \mathrm{Act}_{2.1\ \mathrm{MeV}}$$

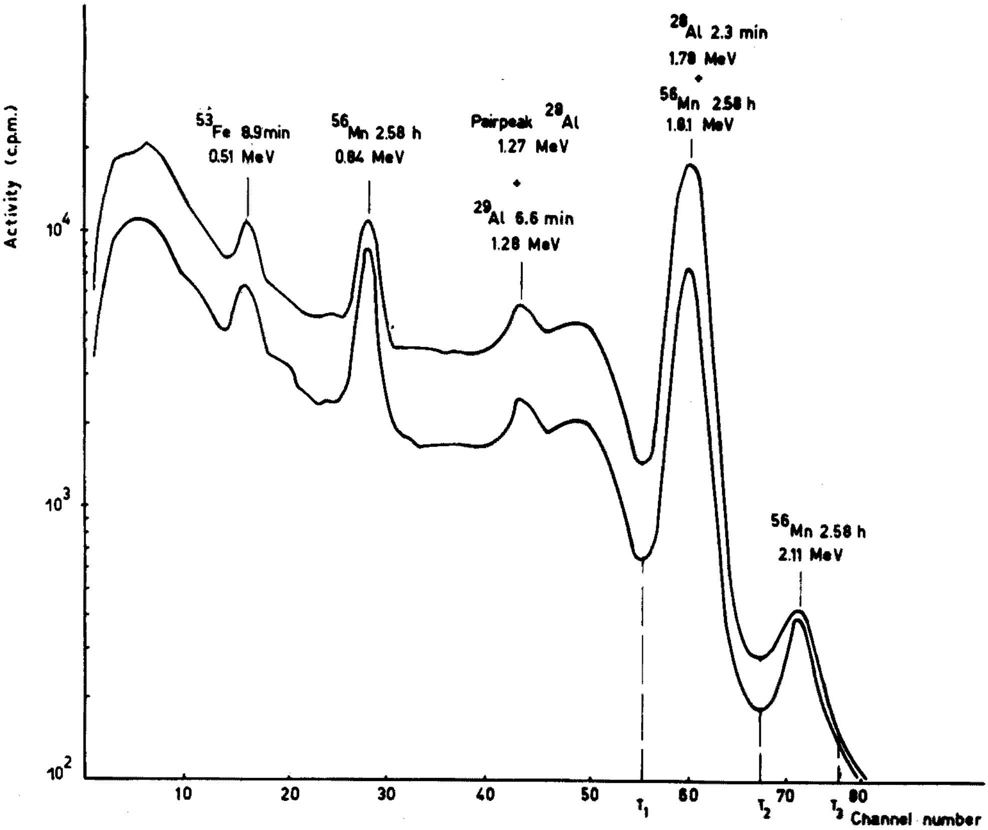

Fig. 1. γ-Spectrum of irradiated steel sample containing 3% of silicon, 1 min and 4 min after irradiation.

Method III. Simultaneous counting of the complex photopeak at 1.8 MeV and the ^{56}Mn photopeak at 0.84 MeV allows the net ^{28}Al activity to be calculated from a set of two equations. The Compton scattering of a number of radionuclides formed from possible alloy elements giving a photopeak in the 0.8–1.8 MeV range, *e.g.* chromium, manganese, aluminium, will interfere at 0.84 MeV. This method is thus unfavourable for steels of varying composition, and will not be discussed here.

STANDARDS AND FLUX MONITORING

To avoid errors due to different neutron and gamma absorption and to obtain an identical geometry in samples and standards, steel samples (with ±3% Si) were used as standards. The silicon content was determined chemically by the perchloric acid method described by the A.S.T.M.[6].

In order to carry out precise determinations, a correction for flux variations is required. The ^{56}Mn activity induced in the iron matrix, can only be used as an internal standard[2], for samples with a known or constant iron content. As steels can vary widely in iron content, the internal standard method was not applied and preference was given to neutron monitoring to normalise the results.

Various types of flux monitoring are available, such as a BF_3 counter[7–11], plastic scintillator[12,13], measurement of ^{16}N formed by the reaction $^{16}O(n,p)^{16}N$ in the target cooling water[14] and α-particle counting of the $^{3}H(d,n)^{4}He$ reaction[15,16].

In the comparator sample technique, the standard and sample are irradiated together and then transferred to different detectors. IDDINGS[17] and VOLBORTH AND BANTA[18] recommend this system as being the most accurate one. Since a dual-transfer system had already been built in the authors' laboratory for oxygen analysis[19,20] this technique could easily be applied to the present problem.

Oxygen is a very suitable flux monitor for 5-sec irradiations; by a (n,p) reaction, ^{16}N is produced with a good yield. As oxygen flux monitor, an iron box was used, with the same external dimensions as the samples and filled with *ca.* 1.3 g of Fe_2O_3 diluted with graphite. This oxygen standard has been described in detail by GIJBELS *et al.*[20]. In this work, it was applied as a flux monitor, to allow normalisation of the ^{28}Al activity. As for the oxygen determination, the standard was irradiated behind the sample and the ^{16}N activity induced in it was counted for 30 sec, with an automatic start 2.3 sec after the end of the irradiation. It was assumed that the neutron flux distribution is constant and that the positioning of the sample and the flux monitor is reproducible at the irradiation and at the detection places. Variations of 2–3% were, however, observed, when two oxygen flux monitors were irradiated simultaneously, so that the eventual reproducibility is determined by this instrumental error and by the counting statistics.

INTERFERENCES

Phosphorus

The (n,α) reaction on ^{31}P yields ^{28}Al, which, of course, cannot be distinguished from ^{28}Al produced by the reaction $^{28}Si(n,p)^{28}Al$. It was found experimentally that pure phosphorus yields 60% of the ^{28}Al activity that would be induced in the same weight of pure silicon. This agrees quite well with the value, calculated from the

14-MeV neutron cross-sections[3,4], which are respectively 140 mb and 250 mb, while the abundances are respectively 100% and 92.2%.

In the present paper, this correction was taken into account, using the phosphorus content as determined by emission spectrometry.

Aluminium

^{28}Al can be produced via the reaction ^{27}Al(n,γ)^{28}Al. The cross-section is *ca.* 0.5 mb for 14-MeV neutrons; moreover, some slowing down of the neutrons can occur. It appeared, however, that in the irradiation system used, about 5% of aluminium in the sample causes an apparent silicon content of 0.01% only. For most steels, the interference of aluminium is thus negligible.

Chromium

The most important radionuclide produced in chromium by 14-MeV neutrons is ^{52}V (half-life 3.8 min, γ-rays of 1.44 MeV, β-rays of 2.5 MeV). Without precautions, a positive error of *ca.* 0.08% (absolute) was found for steels containing 20% of chromium, when method I was used. This interference was partially due to pile up, since it could be reduced to about 0.035%, for 20% of chromium, by decreasing the integral count-rate from about 550,000 counts/min to 100,000 counts/min during the first counting. When a beryllium absorber (8 mm thick) was used, the error did not significantly decrease. Moreover, no photopeak was found in the 1.8-MeV range when irradiated chromium was counted, even when a high-resolution Ge(Li) detector was used. It also appeared that the activity in the 1.8-MeV range was significantly higher than that expected from a Gaussian distribution of a photopeak at 1.44 MeV. The half-life was *ca.* 4 min, which closely approximates the half-life of ^{52}V.

Therefore, Bremstrahlung in the 9-mm thick sample itself was considered to be responsible for the remaining error of +0.03% of silicon in steels containing 20% of chromium.

No systematic error was observed with method II, even for high count rates and for different detector systems (*e.g.* different resolution of NaI(Tl) crystal and/or slightly different discriminator settings).

From the shape of a γ-spectrum of ^{52}V in which pile up and Bremstrahlung occur, it appeared that the ratio 1.8 MeV/2.1 MeV is *ca.* 2, which approximates the k_{Fe}-value for a pure ^{56}Mn spectrum. Hence compensation of errors occurs.

Experimental evidence for the formation of Bremstrahlung in the samples was found by comparing the results of Methods I and II for samples of different thicknesses. For a 6-mm thick stainless steel sample, the difference between the two methods was 0.015% (absolute) higher than for a 1-mm thick sample. Hence, one can expect that the use of a 9-mm thick sample instead of an infinitely thin one, will introduce a positive error of 0.02–0.03%.

Manganese

^{52}V can also be formed by the reaction ^{55}Mn(n,α)^{52}V. The reaction rate is, however, about 5 times smaller than for chromium. Hence, for most steels no interference is found.

Nickel

After short irradiations of nickel, the Ge(Li) gamma spectrum shows photopeaks at 0.127, 0.511 and 1.37 MeV (36 h ^{57}Ni) and at 1.130, 1.164, 1.173, 1.726, 2.032 and 2.313 MeV. Measuring the decay by integral γ-counting yields a composite decay curve with components whose half-lives are 1.7 and 13.2 min. Hence, they were attributed to 1.6 min ^{62m}Co, formed by the reaction ^{62}Ni(n,p)^{62m}Co ($\sigma > 2.0 \pm 0.5$ mb[21], $\theta(^{62}\text{Ni}) = 3.66\%$) and to 13.9 min ^{62}Co, formed by the reaction ^{62}Ni(n,p)^{62}Co ($\sigma < 3.3 \pm 0.02$ mb).

Another radionuclide of 2 min, which can be formed, is ^{64m}Co; the cross-section for the reaction ^{64}Ni(n,p)^{64m}Co, however, is only about 0.45 mb, and the isotopic abundance of ^{64}Ni is 1.16%, so that the reaction rate should be *ca.* 12 times lower than for ^{62m}Co. Because of the short half-life of ^{62m}Co, method I cannot correct for this interference; in the case of a sample containing 20% nickel, the error is +0.01%.

For method II, no significant systematic error can be observed, owing to partial compensation of the interference.

Other elements

The effect of the presence of boron, carbon, cobalt, lead, magnesium, nitrogen, oxygen, sulphur, tin, tungsten, zinc, zirconium was found to be completely negligible for the concentrations normally occurring in steel; 1% of copper, molybdenum and titanium introduce a positive error of 0.001% of silicon via method I.

EXPERIMENTAL

Apparatus

14-MeV neutrons were produced by a SAMES Type J accelerator (150 kV, 1.5 mA, 4 Ci tritium target). The neutron production was controlled by means of a pneumatically operated removable tantalum target. Cylindrical steel samples were used, with a diameter of 26 mm and a thickness of 9 mm, weighing *ca.* 37 g. A double pneumatic transfer system was employed allowing two samples to be irradiated simultaneously behind each other.

The accelerator, transfer system and counting equipment have been described in detail by HOSTE, DE SOETE AND SPEECKE[19].

A 400-channel analyser with multiscaler program unit was included as a supplementary facility. The detector was a 3 × 3'' NaI(Tl) crystal with a resolution of 8.0%.

To avoid shifts in base line and bias settings, the counting room was thermostatted at 23 ± 0.5°.

Method I

The experimental setup is shown in Fig. 2. The sample activity was counted with a 400-channel analyser or a linear amplifier–discriminator. The analysis cycle was essentially as follows.

After pushing the start button:

(1) Pneumatic transfer of the sample and oxygen flux monitor to the irradiation positions within less than 1 sec at an air pressure of 1.6 atm.

(2) Simultaneous irradiation of the sample and the oxygen flux monitor behind each other during 5 sec (at a beam intensity of 300 μA) by pneumatic removal of the tantalum target. (For stainless steels: 70 μA to avoid any pile up.)

(3) Pneumatic transfer of sample and monitor to the counting positions. After 2.3 sec, automatic start of the counting during 30 sec of the ^{16}N activity induced in the oxygen flux monitor. The bias voltage of the discriminator is regulated to correspond to an energy of 4.5 MeV. Count rate: 12,000 counts per 30 sec per 400 mg oxygen, for 300 μA.

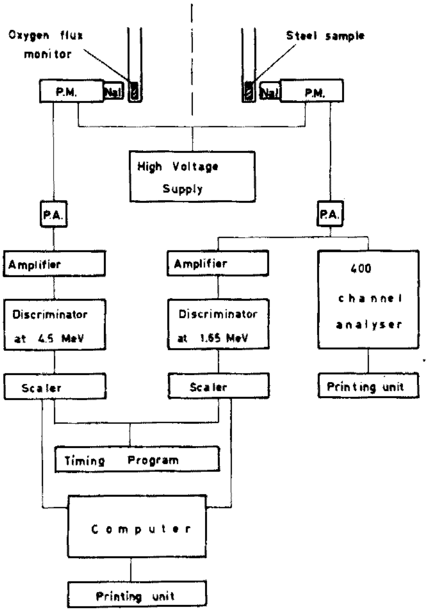

Fig. 2. Counting equipment.

(4) 1 min after the end of the irradiation, automatic start of the first counting during 1 min of the 1.8-MeV photopeak on the multichannel analyser or via a discriminator set to count all pulses above 1.65 MeV. (For stainless steels: counting was extended to 2.5 min to improve statistics.) Count rate: 20,000 counts for 1% of silicon (300 μA).

(5) 4 min after the end of the irradiation: automatic start of the second counting during 1 min. (For stainless steels: 6 min after the end of the irradiation during 2.5 min.) Count rate: 10,000 counts for 1% of silicon (300 μA).

Standards of known silicon content allow the normalized specific ^{28}Al activity, and hence, the weight of silicon in the samples to be calculated. Standardisation was checked approximately every 30 min, to correct for possible drift in the electronics. This drift was usually within 2 to 3% in an 8-h working period.

From this, it appears that the system can be readily automated completely, if the equipment developed for the oxygen determination[19], is available. If the second count of the silicon chain is subtracted electronically from the first count, this result can be divided by the ^{16}N count, by an analysis factor K and by the weight of the sample, to obtain the silicon percentage.

The analysis factor K represents:

$$K = \{A_s(1) - A_s(2)\}/A_O \times W_s \times \%\ \mathrm{Si}_s$$

with $A_s(1)$: number of counts during the first counting of the ^{28}Al activity of the standard;

$A_s(2)$: number of counts during the second counting;

A_O : number of counts of the ^{16}N in the oxygen flux monitor, irradiated simultaneously with the standard;

W_s : weight of the standard sample;

% Si_s: silicon content of the standard.

With appropriate modifications in the timing unit, this system can be used for the simultaneous determination of oxygen and silicon in steel.

Method II

The same setup was used as for Method I, but the detector of the silicon chain was connected to two single-channel analysers, selecting the energy ranges of T_1–T_2 and T_2–T_3 respectively (Fig. 1), or to a multichannel analyser.

Again, the counts were automatic:

(1) 2.3 sec after the end of the irradiation, counting during 30 sec of the ^{16}N activity, induced in the oxygen flux monitor. Count rate: about 12,000 counts.

(2) 1 min after the end of the irradiation: simultaneous counting during 1 min of the complex photopeak at 1.8 MeV (count rate: 20,000 counts for 1% of silicon), and of the 2.11-MeV peak of ^{56}Mn (count rate: 2,000 counts).

Every 30 min, standardisation was checked and the analysis factor K was calculated, where

$$K = \{A_s(1.8) - k_{Fe} \times A_s(2.1)\}/A_O \times W_s \times \%\ Si_s$$

with $A_s(1.8)$: number of counts in the 1.8-MeV energy range for the standard;

$A_s(2.1)$: number of counts in the 2.1-MeV energy range;

k_{Fe} : ratio 1.8 MeV/2.1 MeV for a spectrum of pure irradiated iron.

RESULTS

Results and standard deviations for a single determination are listed in Table II. Samples of different industrial origin were analysed: CA ... CK, IA ... IO, and TA ... TJ. For these samples, the total content of alloy elements other than silicon did not exceed 2%.

The maximum contents of other elements were 0.1% aluminium, 0.4% carbon, 0.2% chromium, 0.2% copper, 0.8% manganese, 0.7% nickel, 0.1% phosphorus and 0.1% sulphur.

For these series, the functional relationship between activation analysis and chemical determination was calculated (Table III).

The mean of the six calibration graphs is

$$\%\ \text{Act.anal.} = (0.009 \pm 0.019)\% + (0.998 \pm 0.014) \times (\%\ \text{chem.anal.})$$

which is quite satisfactory.

T-tests[22] show the non-zero intercept to be significant at the 90% probability level for the CA ... CK and TA ... TJ series, both for method I and method II. The slope differs significantly from 1 for series CA ... CK (Method I) and for series IA ... IO (Method II).

TABLE II

RESULTS FOR THE ACTIVATION ANALYSES OF LOW-ALLOY STEEL SAMPLES

Sample	*% Si chemical*	*% P*	*% Si found (activation analysis)*	
			Method I	*Method II*
CA	0.183	0.008	0.206±0.027 (3)[a]	0.190±0.006 (2)
CB	0.188	0.028	0.240±0.017 (4)	0.226±0.010 (2)
CC	0.203	0.026	0.205±0.007 (8)	0.201±0.013 (2)
CD	0.224	0.026	0.229±0.009 (5)	0.228±0.010 (2)
CE	0.593	0.013	0.598±0.017 (5)	0.599±0.016 (2)
CF	0.800	0.005	0.819±0.025 (2)	0.813±0.020 (2)
CG	1.06	0.005	1.078±0.030 (5)	1.096±0.020 (2)
CH	1.08	0.022	1.090±0.030 (3)	1.108±0.003 (2)
CI	1.41	0.006	1.466±0.037 (4)	1.440±0.040 (2)
CJ	3.09	0.008	3.039±0.050 (6)	3.084±0.011 (2)
CK	3.17	0.015	3.136±0.055 (4)	3.137±0.070 (2)
IK	0.10	0.026	0.115±0.018 (5)	0.104±0.011 (3)
IC	0.12	0.021	0.141±0.011 (4)	0.129±0.016 (3)
IB	0.17	0.014	0.182±0.011 (6)	0.180±0.008 (3)
IA	0.28	0.012	0.323±0.013 (5)	0.298±0.017 (3)
ID	0.63	0.022	0.688±0.048 (5)	0.669±0.014 (3)
IE	0.90	0.085	0.920±0.028 (6)	0.88 ±0.040 (3)
IL	0.98	0.050	1.04 ±0.02 (4)	1.01 ±0.03 (3)
IM	1.06	0.032	1.13 ±0.08 (4)	1.08 ±0.04 (3)
IF	1.07	0.023	1.08 ±0.05 (5)	1.07 ±0.03 (3)
IG	1.56	0.105	1.59 ±0.04 (5)	1.57 ±0.01 (3)
IO	2.75	0.022	2.87 ±0.10 (5)	2.79 ±0.17 (3)
IH	2.98	0.037	3.01 ±0.14 (5)	2.91 ±0.15 (3)
II	3.07	0.024	3.12 ±0.05 (4)	3.14 ±0.08 (3)
IN	3.81	0.032	4.07 ±0.09 (3)	3.95 ±0.02 (3)
TA	0.01	0.045	0.006±0.004 (6)	0.003±0.006 (3)
TB	0.02	0.021	0.009±0.003 (6)	0.003±0.013 (3)
TC	0.02	0.025	0.010±0.006 (4)	0.005±0.012 (3)
TD	0.03	0.095	0.025±0.006 (6)	0.022±0.007 (3)
TE	0.09	0.084	0.090±0.008 (6)	0.080±0.006 (3)
TF	0.12	0.057	0.096±0.006 (6)	0.091±0.012 (3)
TG	0.12	0.041	0.109±0.003 (4)	0.094±0.003 (3)
TH	0.22	0.050	0.202±0.004 (6)	0.198±0.007 (3)
TI	0.23	0.063	0.212±0.007 (6)	0.212±0.006 (3)
TJ	1.03	0.031	1.01 ±0.030 (6)	1.02 ±0.026 (3)

[a] Number of analyses.

Positive and negative deviations from chemical analyses were observed. Moreover, in a given series, the deviation was found to be of the same sign for both methods. One can thus conclude that the observed differences are rather due to the different chemical techniques applied in the different industrial laboratories than to the activation analyses.

A series of stainless steels was also analysed (Table IV). To avoid pile up, irradiations were performed at a beam intensity of 70 μA. To improve statistics in this case, the irradiation cycle for method I was changed as mentioned above.

No phosphorus correction was made as the content was not exactly known. In most cases, the phosphorus content is 0.015–0.025%, so that the correction should be −0.01% to −0.015%.

In the case of Method I, the Bremstrahlung interference of chromium was

TABLE III

FUNCTIONAL RELATIONSHIP BETWEEN ACTIVATION ANALYSIS AND CHEMICAL ANALYSIS

Method I	
CA ... CK:	% Act. anal. = (0.026±0.012)% + (0.982±0.008) × (% chem. anal.)
IA ... IO:	% Act. anal. = (0.032±0.029)% + (1.012±0.013) × (% chem. anal.)
TA ... TJ:	% Act. anal. = −(0.010±0.003)% + (0.987±0.008) × (% chem. anal.)
Method II	
CA ... CK:	% Act. anal. = (0.020±0.010)% + (0.990±0.006) × (% chem. anal.)
IA ... IO:	% Act. anal. = (0.002±0.017)% + (1.016±0.008) × (% chem. anal.)
TA ... TJ:	% Act. anal. = −(0.014±0.004)% + (1.000±0.012) × (% chem. anal.)

TABLE IV

RESULTS FOR THE ACTIVATION ANALYSIS OF STAINLESS STEELS

Sample	*Spectroscopical*			*% Si found (activation analysis)*	
	% Cr	*% Ni*	*% Si*	*Method I*	*Method II*
HA	26.3	21.0	0.38	0.386±0.015 (5)[a]	0.394±0.021 (3)
HB	18.3	33.5	0.45	0.442±0.019 (5)	0.457±0.015 (3)
HC	23.1	13.5	0.46	0.452±0.013 (4)	0.467±0.015 (3)
HD	12.6	31.1	0.60	0.626±0.021 (8)	0.620±0.028 (2)
HE	19.1	58.8	0.78	0.794±0.018 (4)	0.778±0.008 (3)
HF	12.3	19.9	1.81	1.783±0.007 (3)	1.826±0.004 (3)
HG	10.5	19.0	2.29	2.267 (1)	2.248±0.033 (3)

[a] Number of analyses.

corrected by subtracting 0.03% for 20% of chromium, and the nickel interference by subtracting 0.01% for 20% of nickel.

The maximum contents of other elements were 0.3% carbon, 0.2% copper, 0.2% molybdenum and 2% manganese.

CONCLUSION

Activation analysis appears to be a satisfactory and rapid method for silicon contents down to 0.02–0.05% depending on the phosphorus content. A precision of about 3% can easily be obtained for silicon contents above 1%, whereas the precision is *ca.* 7% for silicon contents of 0.1%. The two methods described appear to be equally precise, while the sensitivity of method I is somewhat better.

The counting equipment for method I is simpler (only one amplifier–discriminator for the ^{28}Al counting), but method II allows a shorter analysis time (*ca.* 2 min), and compensates more or less for the chromium interference.

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SUMMARY

A fast (2–5 min) non-destructive determination of silicon in steel by 14-MeV neutron activation is described. The 1.78-MeV ^{28}Al activity, induced by the reaction ^{28}Si(n,p)^{28}Al, is counted on a NaI(Tl) detector. An oxygen flux monitor is used to normalise to the same neutron flux.

Two methods are described to correct for the ^{56}Mn activity (2.58 h), induced into the iron matrix via ^{56}Fe(n,p)^{56}Mn. Nuclear interferences of phosphorus and aluminium have been examined. Special attention has been paid to stainless steels. A sensitivity of 0.02 to 0.05% of silicon is obtained. The precision is 2 to 3% for steels containing above 1% silicon, and 7% for 0.1% of silicon.

RÉSUMÉ

On décrit un dosage non-destructif rapide (2–5 min) du silicium dans l'acier par activation au moyen de neutrons 14-MeV. L'activité 1.78-MeV ^{28}Al, induite par la réaction ^{28}Sn(n,p)^{28}Al est comptée sur un détecteur NaI(Tl). Deux méthodes sont décrites pour correction de l'activité ^{56}Mn (2.58 h) induite dans la matrice de fer via ^{56}Fe(n,p)^{56}Mn. On examine les interférences nucléaires du phosphore et de l'aluminium, et tout spécialement les aciers inox. On arrive à une sensibilité de 0.02–0.05% de silicium. La précision est de 2–3% pour des aciers renfermant plus de 1% de silicium et 7% pour 0.1% de silicium.

ZUSAMMENFASSUNG

Es wird eine schnelle (2–5 min) zerstörungsfreie Bestimmung von Silicium in Stahl durch Aktivierung mit 14-MeV-Neutronen beschrieben. Die durch die Reaktion ^{28}Si(n,p)^{28}Al induzierte Aktivität des ^{28}Al von 1.78 MeV wird mit einem NaJ(Tl)-Detektor gezählt. Ein Sauerstoff-Fluss-Monitor wird zur Normalisierung desselben Neutronenflusses verwendet. Zur Korrektur der ^{56}Mn-Aktivität (2.58 h), welche durch die Reaktion ^{56}Fe(n,p)^{56}Mn in der Eisenmatrix hervorgerufen wird, werden 2 Methoden beschrieben. Störungen durch Phosphor und Aluminium wurden geprüft. Besondere Aufmerksamkeit wurde den rostfreien Stählen gewidmet. Das Verfahren besitzt eine Empfindlichkeit von 0.02 bis 0.05% Silicium und eine Reproduzierbarkeit von 2 bis 3% für Stähle, die mehr als 1% Silicium enthalten und von 7% für Gehalte von 0.1% Silicium.

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THE PREPARATION OF PRECISELY DEFINED LITHIUM ISOTOPE MIXTURES

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Although better than 1% reproducibilities on the mass spectrometric determination of $^{6}Li/^{7}Li$ ratios are achieved in many laboratories, spreads of several percent in the reported measurements are a widely recognized fact. These variations are assumed to be caused by isotopic effects during chemical treatment or isotopic measurements (fractionation in the ion source), or geological variations in the isotopic composition of the samples. In recent times even commercial lithium chemicals show unmentioned depletion in the ^{6}Li isotope, and subsequent change in atomic weight. In this laboratory, a depletion of the ^{6}Li concentration from 7.5 to 3.75% was observed. This increases the atomic weight of lithium (6.939) by 0.5%, whereas the International Committee on Atomic Weights allows an uncertainty of only 0.02%. Lithium chemicals used in analytical laboratories should consequently be labelled as "natural". It would be still better if their atomic weight were indicated. An important need for absolute lithium isotopic measurements arises from the use of ^{6}Li as a reference material for measurements of thermal neutron fluxes, because of its large absorption cross section (about 950 barn). A relative accuracy of 0.1% on the ^{6}Li concentration would be highly appreciated in this field.

THE ACCURATE MEASUREMENT OF LITHIUM ISOTOPIC COMPOSITIONS

$^{6}Li/^{7}Li$ ratios can be determined by mass spectrometry or by optical spectroscopy. The former method, which involves either electron bombardment of gaseous compounds or thermal ionization of solid salts, is the earliest and most widely used method. However, to achieve accuracies of the order of 0.1%, samples with well known $^{6}Li/^{7}Li$ ratios are necessary to calibrate the mass spectrometer used.

Such samples can be prepared by weighing and mixing fractions of precisely defined solutions of pure ^{6}Li and ^{7}Li.

This implies:

1. starting solutions of sufficiently enriched ^{6}Li and ^{7}Li;
2. precise chemical definition of these solutions;
3. precise mass spectrometric definition of these solutions;
4. a precise metrological blending technique.

To calibrate a mass spectrometer by means of isotopic blends, synthetic mixtures of different compositions have to be prepared. These enable one to establish the dependence (if any) of the bias upon isotopic composition and to correct — by extrapolation — the isotopic measurements of the starting solutions.

The preparation of blends containing 2–7.0–7.5–8.0–20–50–80–92.5% ^{6}Li was planned for this particular project at CBNM.

Isotopic enrichments of the starting materials

Ultimately an accurate isotopic blend provides a determination of the systematic error of the mass spectrometer concerned:

$$K=(R_{AB})\text{ true}/(R_{AB})\text{ observed} \tag{1}$$

The general relation[1] governing the blending of isotopes is:

$$q=\frac{N_A}{N_B}=\frac{R_B-R_{AB}}{R_{AB}-R_A}\times\frac{1+KR_A}{1+KR_B} \tag{2}$$

where N is the number of atoms of the element concerned and where R_A,R_B and R_{AB} are the measured isotope ratios of enriched ^{6}Li, enriched ^{7}Li and blend solutions. q can be experimentally determined as

$$q=N_A/N_B=C_AM_A/C_BM_B$$

where M and C are the mass and chemical concentration of the isotopically enriched solutions. Attention is drawn to the fact that only the ratio of chemical concentrations as well as ratios of masses are required. Equation (2) assumes K constant, *i.e.* independent of R. This assumption has been verified for boron[2] and a few other elements[3,4].

It can be seen that

$$K=\frac{q(R_{AB}-R_A)-(R_B-R_{AB})}{(R_B-R_{AB})R_A-q(R_{AB}-R_A)R_B} \tag{3}$$

To answer the question about the values of the necessary isotopic enrichment of the starting materials R_A and R_B, it is useful to consider the dependence of the statistical uncertainties:

$$\sigma(K)=\mathrm{F}[q,R_{AB},R_A,R_B,\sigma(q),\sigma(R_{AB}),\sigma(R_A),\sigma(R_B)].$$

It is possible to compute an *a priori* estimate of attainable accuracies on K by normal propagation of error calculation:

$$\left[\frac{\sigma(K)}{K}\right]^2=\left[\frac{(1+R_A)(1+R_B)}{(R_A-R_B)}\right]^2\times\left[\frac{\sigma(q)}{q}\right]^2+\left[\frac{R_{AB}(1+R_A)(1+R_B)}{(R_{AB}-R_A)(R_B-R_{AB})}\right]^2\times\left[\frac{\sigma(R_{AB})}{R_{AB}}\right]^2$$
$$+\left[\frac{(1+R_{AB})R_A(1+R_B)}{(R_{AB}-R_A)(R_A-R_B)}\right]^2\times\left[\frac{\sigma(R_A)}{R_A}\right]^2+\left[\frac{(1+R_A)(1+R_{AB})R_B}{(R_A-R_B)(R_B-R_{AB})}\right]^2\times\left[\frac{\sigma(R_B)}{R_B}\right]^2 \tag{4}$$

Assuming that mass spectrometric measurements of lithium isotope ratios can be made with a relative precision ε of 0.1% and that a blending error $\beta=\sigma(q)/q$ of 0.03% can be obtained, one can compute roughly from eqn. (4) that K can be determined with an accuracy better than 0.15% with all the blends mentioned, if enrichments of $\geq$98% for ^{6}Li and $\geq$99.9% for ^{7}Li are available. For the two blends with lowest and highest ^{6}Li content, the dependence of $\sigma(K)/K$ upon R_A and R_B is given in Table I for discrete values of the latter.

TABLE I

UNCERTAINTIES ON K FOR $\varepsilon = 0.1\%$ AND $\beta = 0.03\%$

R_B / R_A	$\frac{96}{4}$	$\frac{98}{2}$	$\frac{99}{1}$	$\frac{99.9}{0.1}$
For a blend $R_{AB} = 2/98$	%	%	%	%
1/99	0.24	0.24	0.24	0.23
0.5/99.5	0.15	0.15	0.15	0.14
0.1/99.9	0.11	0.11	0.11	0.11
0.01/99.99	0.11	0.11	0.11	0.10
For a blend $R_{AB} = 92.5/7.5$				
1/99	0.26	0.14	0.12	0.11
0.5/99.5	0.26	0.14	0.12	0.11
0.1/99.9	0.26	0.14	0.12	0.11
0.01/99.99	0.26	0.14	0.12	0.11

Accuracy of the chemical definition of the starting solutions

If the estimations $R_A = 98/2$, $R_B = 0.1/99.9$ and $\varepsilon = \sigma(R)/R = 0.1\%$ are introduced into eqn. (4), a more precise calculation shows that a K determination within 0.15% requires an accuracy on $q \leq 0.05\%$ in the worst case ($R_{AB} = 92.5/7.5$).

Any other blend will yield an accuracy on K of $\leq 0.12\%$. This value as well as the $\varepsilon = 0.1\%$ in the observed R (see eqn. 1) show that the accuracy of the blend will then be

$$\sqrt{0.12^2 - 0.10^2} = 0.06\% \quad \text{(Fig. 1).}$$

This assumes a chemical determination of the starting solutions with a precision of 0.035% on each solution. The metrological uncertainty ($\leq 0.006\%$) is negligible compared to the uncertainty involved in the chemical assay. To avoid the two solutions being subject to a different systematic error (caused, for example, by chemical impurities at a different level in the solutions), it is strongly recommended to prepare both solutions in the same way, and to use a minimum of two or, better, three assay methods. On the other hand, systematic errors inherent to each of the methods will cancel in the calculation of the ratios of the concentration of the two solutions.

From the above considerations, it can be concluded that to obtain a final accuracy of 0.15% on ^{6}Li/^{7}Li isotope ratio measurements, the following conditions are essential:

1. solutions of ^{6}Li and ^{7}Li isotopically enriched to at least 98% and 99.9%, respectively;
2. different chemical methods for the determination of lithium with precisions of $\leq 0.035\%$, and giving results agreeing within the reproducibility of each method;
3. a mass spectrometric method of determination of lithium isotope ratios allowing precisions of 0.1% over a wide range;
4. an accuracy of $\leq 0.005\%$ on the weighing of the fractions to be blended.

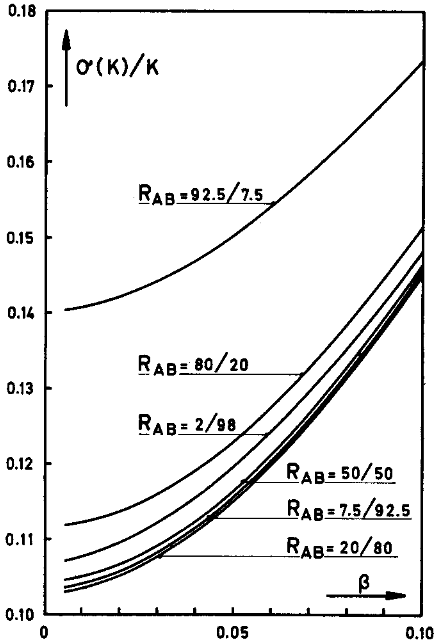

Fig. 1. Uncertainties on K as a function of the uncertainty β, with $R_A=98/2$, $R_B=0.1/99.9$ and $\varepsilon=0.1\%\cdot(\sigma(K)/K$ in $\%)$

THE STANDARDIZATION OF LITHIUM HYDROXIDE SOLUTIONS

For the preparation of well defined isotope mixtures, starting with precisely analyzed solutions of enriched ^{6}Li and ^{7}Li, lithium hydroxide solutions are most suitable. For the standardization of these solutions, four methods were applied that are sufficiently precise: titration with hydrochloric acid, titration with benzoic acid, and gravimetry of lithium as sulphate or as carbonate.

Experimental procedures

The hydrochloric acid titration: The titration of lithium hydroxide with hydrochloric acid was done potentiometrically, with a combined glass-saturated calomel electrode and a recording pH-meter for the location of the end-point. Lithium hydroxide and hydrochloric acid — about 20 g of a 0.1 M solution — were weighed to 0.1 mg in weight burettes and mixed until an excess of lithium hydroxide and a pH value of 8–9 were obtained. Nitrogen was passed through the titration cell to avoid interference from carbon dioxide. The end-point was precisely located by back-titration with 0.1 M hydrochloric acid from a calibrated microburette.

Silver metal was used as primary standard for the standardization of the hydrochloric acid.

The benzoic acid titration: The titration of lithium hydroxide with benzoic acid was carried out under the same conditions and with the same equipment as for hydrochloric acid. About 350 mg of benzoic acid (NBS standard no. 350) was weighed to 0.01 mg and quantitatively transferred to the titration cell with 20 ml of ethanol.

Lithium hydroxide was added until a pH value of 9.5–10 was reached and a back-titration was done as above.

The lithium sulphate method: 20 g of 0.1 *M* lithium hydroxide was weighed to 0.1 mg and quantitatively transferred to a platinum crucible. After the conversion of lithium to the sulphate with a small excess of sulphuric acid, the solution was slowly evaporated and dried at 750°. The lithium sulphate was weighed to 0.01 mg.

The lithium carbonate method: 65–75 g of 0.1 *M* lithium hydroxide was weighed to 0.1 mg and converted to lithium carbonate by passing a flow of carbon dioxide for 1–2 h. The solution was then quantitatively transferred to a platium crucible, carefully evaporated and dried at 350–375°. The lithium carbonate is weighed to 0.01 mg.

Systematic errors

Systematic errors caused by impurities are given in Table II. The influence of absorption of carbon dioxide in the lithium solution on the results of the titrations was experimentally determined as being $-(0.005 \pm 0.001)\%$ per 0.1 eq% of carbonate present for the hydrochloric acid titration[5], and $-(0.015 \pm 0.003)\%$ per 0.1 eq% of carbonate present for the benzoic acid titration[5].

TABLE II

SYSTEMATIC ERRORS CAUSED IN THE DIFFERENT METHODS BY IMPURITIES IN THE LITHIUM HYDROXIDE SOLUTION

Element	*Effect caused by 1 µg impurity/g lithium*		
	Titrations (%)	*Sulphate method (%)*	*Carbonate method (%)*
Na	+ 0.000030	+ 0.000038	+ 0.000043
K	+ 0.000018	+ 0.000028	+ 0.000034
Mg	+ 0.000058	+ 0.000064	+ 0.000066
Ca	+ 0.000034	+ 0.000044	+ 0.000047
Si	——	− 0.000018	+ 0.000022

RESULTS AND CONCLUSIONS

A comparison of the results obtained for the analysis of a pure lithium hydroxide solution (made from 99.98% pure Li) is given in Table III. The molarity of

TABLE III

COMPARISON OF THE RESULTS OBTAINED BY THE FOUR METHODS FOR A PURE 0.1 *M* LiOH SOLUTION

Method[a]	*Uncorrected experimental mean value (M)*	*Corrected values (M)*	*Coefficient of variation (%)*	*Overall mean*	*Difference from overall mean (%)*
A	0.105610	0.105616	0.014		− 0.018
B	0.105650	0.105663	0.010	0.105635 *M*	+ 0.027
				Coeff. of variation	
C	0.105642	0.105638	0.030	0.020 %	+ 0.003
D	0.105628	0.105623	0.022		− 0.011

[a] A, hydrochloric acid titration; B, benzoic acid titration; C, gravimetry as sulphate; D, gravimetry as carbonate.

hydrochloric acid used was (0.09712 ± 0.00005) M, and the carbonate content of lithium hydroxide was 0.16 eq% [5]. The benzoic acid titration was corrected for traces of acid in the ethanol and for the purity of the benzoic acid. The sulphate method was corrected for ash residues in the sulphuric acid.

Table III shows that the molarity of a 0.1 M lithium hydroxide solution can be determined with good precision (0.01–0.03%) by each of the four described methods. When corrections for systematic errors are applied, it can be concluded that the accuracy of the results is consistent with the analytical uncertainty. For 99.98% pure lithium, the coefficients of variation of these corrections were mostly negligible ($\leq$ 20%) compared with those of the methods themselves.

THE PREPARATION OF PURE HYDROXIDE SOLUTIONS OF ISOTOPICALLY ENRICHED LITHIUM

The four methods of analysis of 0.1 M lithium hydroxide solutions described above are unselective, but had to be applied to ^{6}LiOH and ^{7}LiOH solutions which are needed for the preparation of synthetic isotopic mixtures. Accordingly, as no chemically pure isotopes were available, a purification method was developed. The purity of the final lithium hydroxide solutions must be such that neither cationic nor anionic impurities affect the precision and accuracy of ± 0.02% of the analytical methods. In the method described below lithium is first purified until less than 50 p.p.m. of alkali elements remain, and then all anions are eliminated with a strongly basic anion-exchanger.

The purification is carried out on a cation-exchanger of the Dowex 50W-type, with a high divinylbenzene content ("X16"). With such a resin good separations of lithium from the other alkali metals and the alkaline earth metals can be obtained in dilute hydrochloric acid medium[6].

Although the cation-exchanger used was of analytical grade (AG 50W-X16/Bio Rad), further purification proved necessary. Good results were obtained by successive batch operations with LiOH–EDTA solutions and concentrated hydrochloric acid, followed by a final elution with 1 M hydrochloric acid to eliminate any natural lithium contamination that might have occurred.

The purified lithium was then quantitatively converted to sulphate, dissolved in carbonate-free twice-distilled water, and converted to the hydroxide by batch operations with AG1-X8(OH^-). For this exchange, special attention had again to be paid to the anionic and cationic purity of the anion-exchanger used. Its hydroxyl content had to be brought to at least 99.8% by extended washings with concentrated base solutions. Successive elutions with large quantities of carbonate-free twice-distilled water lowered the present cationic contaminations to a tolerable limit[7].

Procedure for the preparation of 0.1 M isotopically enriched lithium hydroxide

The purification of AG 50W-X16. Twice-distilled water was used in *all* processes. 150 g (≈450 meq) of AG 50W-X16 (50/100 mesh) were purified by four batch operations with:

(*a*) 150 mmol of EDTA and 1050 mmol of lithium hydroxide dissolved in 750 ml of water; (*b*) 150 mmol of EDTA and 600 mmol of lithium hydroxide dissolved in 750 ml of water; (*c*) 750 ml of 30% "Suprapur" hydrochloric acid (Merck AG, Germany); and (*d*) 750 ml of 30% "Suprapur"hydrochloric acid. After the first three batch operations, the ion-exchanger was washed with 0.4 l of water; after the last one this wash was repeated three times. Then a 3-cm diameter quartz column was filled with a quantity equivalent to 80 g of the oven-dried resin ($\approx$400 meq), and eluted with successively 3 l of 1 *M* hydrochloric acid and 0.5 l of water. Hydrochloric acid (1 *M*) was prepared from 30% "Suprapur" acid and twice-distilled water. The whole operation was done in a glove box to avoid contamination from the atmosphere.

The purification of lithium. 0.5 g of lithium was dissolved in 20–25 ml of water, and mixed for 30 min with 25 g ($\simeq$80 meq) of air-dried unpurified AG 50W-X16. After settling of the lithium-loaded resin, the supernatant solution was decanted, and the wet resin transferred to the top of the cation-exchange column. Elution was performed with (1.00 ± 0.02) *M* hydrochloric acid ("Suprapur"). The eluates were collected in 50-ml polyethylene bottles. Aliquots of 1 ml were analysed by conversion to sulphate and weighing. The lithium was largely recovered (80–90%) in fractions 7–9 or 8–10 of the eluate, with a maximum concentration in fraction 8 or 9.

The elimination of anionic and cationic impurities from AG1(OH^-). 80 g (100 meq) of air-dried AG 1-X8 (20/50 mesh, hydroxyl form) were transferred to a teflon column, and 12.5 l of carbonate-free 2 *M* lithium hydroxide and 1–2 l of carbonate-free water were passed through. Lithium hydroxide was prepared from 99.98% pure metallic lithium (Koch & Light Laboratories, England).

After complete elution, the anion exchanger was transferred to a clean teflon column, and washed with 40 l of carbonate-free water.

The whole treatment was done in a glove box filled with argon. Twice-distilled water was directly distilled into this box.

The conversion of purified lithium to 0.1 M lithium hydroxide

Lithium, purified as described above, was transferred to a platinum crucible, quantitatively converted to the sulphate with "Suprapur" sulphuric acid (Merck AG, Germany), and calcined at 750° for a few minutes. The lithium sulphate was then redissolved in 0.5 l of carbonate-free water, transferred to a teflon bottle, and treated in 3 batch operations with respectively 50, 25 and 25 meq of purified AG 1-X8.

RESULTS AND DISCUSSION

Lithium hydroxide (2 l) isotopically enriched to 99% in ^{6}Li, and lithium hydroxide (2 l) isotopically enriched to 99.99% in ^{7}Li, were prepared by the above method.

The cationic impurity content of both the ion-exchangers used was considerably lowered (Table IV). The higher silicon content of the purified AG 50W-X16 is due to the use of a quartz column for the elutions. The residual chloride ions in AG 1 were lowered from 1% to 0.15%. The cationic content of the purified lithium chloride was less than 100 μg/g Li. During the conversion to the hydroxide, lithium was contaminated by impurities from the anion-exchanger. Nevertheless, the lithium hydroxide solutions prepared with these resins contained only 100-125 μg alkalis/g lithium, and the alkaline-earth content was as low as 50 μg/g lithium (cf. Table V). Further anionic impurities (except carbonate and silicate) were of the order of 0.01 eq%. The carbonate content of the solutions was ca. 0.2 eq%.

This purity level is largely sufficient for the preparation of lithium sulphates and carbonates which are not hygroscopic and can be weighed to 0.01% and to allow

TABLE IV

COMPARISON OF THE IMPURITY LEVELS OF THE ORIGINAL ION-EXCHANGERS AND THE PURIFIED ONES (IN P.P.M./OVEN-DRIED RESIN)

	AG 50W-X16		AG 1-X8	
Element	*Original*	*Purified*	*Original*	*Purified*
Na	10	< 0.05	50–150	< 0.06
K	8	< 0.1	< 2	0.04
Mg	4	0.5	2.5	0.6
Ca	1000	0.15–0.3	15	< 0.06
Ba	4	< 0.15	< 2	< 2
Sr	4	< 0.1	< 2	< 2
Si	1	2.5	50	4
Fe	≤ 4	0.3	3	0.5
Al	4	1	7	1–2
Cu	4	0.5	1.5	0.4

TABLE V

PURITY OF LITHIUM CHLORIDE AFTER PURIFICATION AND CONVERSION TO THE HYDROXIDE

Element	*LiCl sol. (μg/g Li)*	*LiOH sol. (μg/g Li)*
Na	10–25	50–75
K	5–25	50
Mg	15	15–30
Ca	< 5	35
Si	≤ 50	60–150
Al	< 50	≈ 100
Fe	20–50	≈ 100
other elements	not detectable by emission spectrography	

TABLE VI

FINAL RESULTS OF THE CHEMICAL ANALYSES OF THE ^{6}LiOH AND ^{7}LiOH STARTING SOLUTIONS

Method[a]	*Concn.* ^{6}*LiOH (M)*	*Concn.* ^{7}*LiOH (M)*	*Ratio* C_6/C_7	*St. Dev.* C_6/C_7
A	0.099346	0.092425	1.07488	0.00005
B	0.099341	0.092411	1.07499	0.00005
C	0.099347	0.092435	1.07478	0.00014
D	0.099371	0.092452	1.07484	0.00025
Mean	0.099351	0.092431	1.07487	
95% CL	0.021%	0.028%	0.014%	

[a] A, hydrochloric acid titration; B, benzoic acid titration; C, gravimetry as sulphate; D, gravimetry as carbonate.

a chemical assay of lithium with an accuracy of 0.02%. The ratios of the concentrations of both prepared solutions, calculated for each of the four methods of analysis individually, agreed within ± 0.01% (Table VI). From these solutions a series of isotope mixtures with nominal values of 2–7–7.5–8–20–50–80–92.5% ^{6}Li were made by the metrological service of the CBNM.

Finally, attention must be drawn to the fact that even with isotopic enrichments as high as 99.0% ^{6}Li and 99.99% ^{7}Li, no change in this isotopic concentration, which could have been due to contamination with natural lithium, could be detected by thermal emission mass spectrometry.

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SUMMARY

The need for accurate ($< 0.06\%$) isotopic blends of ^{6}Li and ^{7}Li is explained and their preparation is discussed. It is shown that lithium must be determined at an accuracy level better than 0.035%. Four methods — acid–base titration with hydrochloric acid or benzoic acid, and weighing as sulphate or carbonate — were tested and improved for the precise and accurate analysis of lithium hydroxide solutions. The results of these four methods for a 0.1 *M* solution agreed within ± 0.02%. The preparation of pure isotopically enriched lithium hydroxide solutions, with specially purified cation- and anion-exchangers, is described. The prepared products contain as little as 100 µg of other alkali metals and 50 µg of alkaline-earth metals per gram of lithium, and are sufficiently free of anions to permit accurate chemical assay of lithium. No changes in the isotopic compositions of 99% ^{6}Li or 99.99% ^{7}Li were detected during the treatment.

RÉSUMÉ

La nécessité de mélanges isotopiques précis ($<0.06\%$) de ^{6}Li et ^{7}Li est signalée, ainsi que leur préparation. Le lithium doit être dosé avec une précision supérieure à 0.035%. Quatre méthodes—titrage acide–base avec acide chlorhydrique ou acide benzoïque; pesée comme sulfate ou carbonate—ont été essayées et mises au point pour effectuer un dosage précis et exact de solutions d'hydroxyde de lithium (±0.02% pour une solution 0.1 *M*). On décrit une préparation de solutions d'hydroxyde de lithium enrichies, isotopiquement pures, en utilisant un échangeur cations-anions spécialement purifié. On n'observe pas de variation de compositions isotopiques de ^{6}Li 99% ou ^{7}Li 99.9% au cours du traitement.

ZUSAMMENFASSUNG

Die Notwendigkeit zur Herstellung genau zusammengesetzter Mischungen aus den Isotopen ^{6}Li und ^{7}Li wird begründet und ihre Herstellung diskutiert. Es zeigt sich, dass Lithium mit einer Genauigkeit von weniger als 0.035% bestimmt werden muss. Für die genaue Analyse von Lithiumhydroxidlösungen wurden folgende 4 Methoden geprüft: Säure-Basen-Titration mit Salzsäure oder Benzoesäure, Wägung als Sulfat oder Carbonat. Die Ergebnisse dieser 4 Methoden stimmen bei einer 0.1 *M* Lösung innerhalb ±0.02% überein. Die Darstellung von reinen an Isotopen an-

gereicherten Lithiumhydroxidlösungen geschieht mit besonders gereinigten Kationen- und Anionenaustauschern. Die so hergestellten Produkte enthalten weniger als 100 µg anderer Alkalimetalle und 50 µg Erdalkalimetalle pro Gramm Lithium. Sie sind weitgehend frei von Anionen, so dass eine genaue chemische Prüfung möglich ist. Ein Wechsel der Isotopenzusammensetzung von 99% ^{6}Li oder 99.99% ^{7}Li wurden während der Untersuchungen nicht festgestellt.

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THE DETERMINATION OF LOW LEVELS OF POLONIUM-210 IN ENVIRONMENTAL MATERIALS

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Monitoring polonium-210 in effluent and natural waters requires a method which is both rapid and sensitive. The study of radioactive disequilibrium in rocks and minerals calls for a method which is precise and applicable to samples of considerable chemical complexity. A survey of existing methods indicated that the most widely used technique is the spontaneous deposition of polonium on to silver from weakly acidic solutions. This method is subject to interference from oxidants, organic materials, and elements that also deposit on silver. Precipitation has usually been employed to remove these interferences as well as concentrate the ^{210}Po before plating. SMALES *et al.*[1] used calcium tannate precipitation and plated for 3 h from hydrochloric acid solution to obtain good recoveries from effluent samples; plating both sides of the silver disc considerably reduced sensitivity and increased the counting time. For the determination of ^{210}Po in biological materials, RUNDO[2] proposed a sodium hypophosphite precipitation with tellurium as a carrier. The precipitate was then dissolved and the tellurium separated from the ^{210}Po by precipitation with hydrazine hydrochloride. Plating was carried out in a special cell on to one side only of a silver disc, thus enhancing sensitivity and reducing counting time; recoveries were 80–85% for plating at 80° for 90 min. To determine the ^{210}Po content of zircons and uranium-rich minerals, MILLARD[3] plated directly from solution without a preliminary separation. The disc was suspended in the solution with one side coated with glyptal, and yields of 93–95% were obtained after plating overnight at room temperature. RUSHING[4] used tin(II) chloride to coprecipitate ^{210}Po with tellurium for water analyses, and counted directly from the precipitate after leaving for 24 h to allow ^{222}Rn products to decay.

This paper describes a method for the spontaneous deposition of ^{210}Po in the presence of large quantities of foreign ions. Plating is carried out by suspending a silver disc in 50 ml of hydrochloric acid solution adjusted to pH 2.0 and containing 0.5 g of sodium citrate, 1.0 g of hydroxylamine hydrochloride, and 10 mg of bismuth hold-back carrier; at 85–90°, deposition is complete in 1 h. No preliminary separation is required and essentially quantitative recoveries are obtained from standard solutions containing as little as 0.02 pCi ^{210}Po. The accuracy of the method has been demonstrated by the analysis of rocks and ores of known uranium content.

EXPERIMENTAL

Apparatus

Polonium deposition cell. A perspex disc holder was specially designed to fit 150–500 ml beakers (Fig. 1).

Counter. A.E.R.E. 1-in diameter low background head, coupled to an A.E.R.E. 1430 H.F. head amplifier and main amplifier, with an A.A.E.C. type 2 scaler. With argon counting gas, the efficiency with a standard ^{239}Pu source was 50.4%. The background was 1.0 count/h.

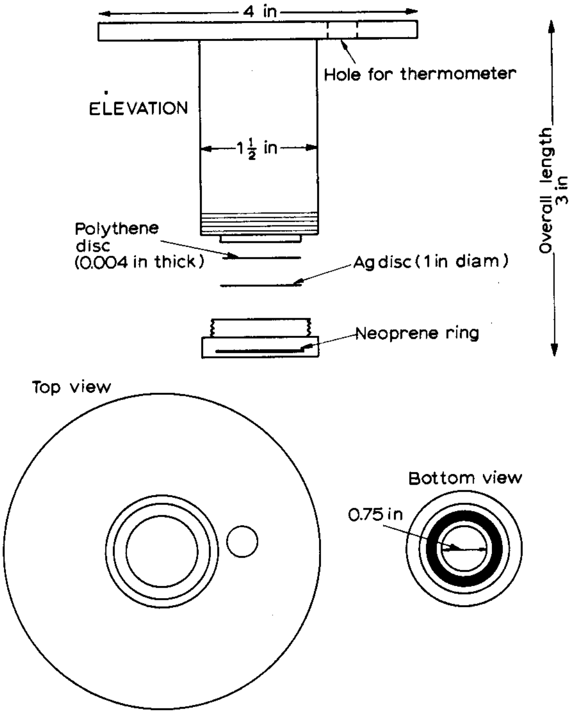

Fig. 1. Perspex disc holder.

Standard and reagents

Polonium-210 standard solution. A solution was obtained from the Radiochemical Centre, Amersham, and standardised by evaporation on to a silver disc at about 100°, and counting to an accuracy of ±1%. Good agreement was obtained by plating from standard solution for 3 h at 85–90°.

Silver foil. 0.005-in thick, cut into discs of 1 in diameter.

Bismuth carrier. (10 mg Bi^{3+}/ml) 2.32 g of $Bi(NO_3)_3 \cdot 5\,H_2O$ was dissolved in 5 ml of concentrated nitric acid and diluted to 100 ml.

Sample pre-treatment

Effluents. Add 10 ml of concentrated nitric acid and 10 ml of 70% perchloric acid to a 1-l aliquot. Evaporate to the first signs of white fumes, and then take to dryness under infrared heating at about 120°. Add 5 ml of concentrated hydrochloric acid, heat to dissolve and transfer to a 150-ml beaker. Rinse with a further 5 ml of boiling concentrated hydrochloric acid and transfer to the 150-ml beaker.

Rocks. Weigh accurately about 1.0 g in a platinum dish. Evaporate to dryness with 40% hydrofluoric acid and concentrated nitric acid on a water bath. Add 5 ml of concentrated nitric acid and again take to dryness. Warm with 5 ml of concentrated hydrochloric acid to dissolve the residue and transfer to a 150-ml beaker. Rinse by heating with a further 5 ml of concentrated hydrochloric acid and transfer to the 150-ml beaker.

Low-grade uranium ores. Weigh accurately 0.1–0.2 g in a platinum dish. Treat with hydrofluoric and nitric acids as described for rocks. Then warm with 20 ml of concentrated hydrochloric acid to dissolve the residue and transfer to a 100-ml volumetric flask. Rinse with a further 20 ml of hydrochloric acid, transfer to the volumetric flask and make to the mark. Transfer an aliquot of 10 ml to a 150-ml beaker.

Plating procedure

To the sample in the 150-ml beaker add 5 ml of 20% hydroxylamine hydrochloride, 2 ml of 25% sodium citrate solution, and 10 mg of bismuth carrier. Adjust the pH to 2.0 with concentrated ammonia solution. Dilute to 50 ml, place on a hot-plate magnetic stirrer, heat to 85–90° and stir with a 1-in Teflon stirrer bar for 2–3 min to reduce any Fe^{3+}, Cr^{6+} or other oxidants that may be present. Place the holder with a silver disc into the beaker, and remove any air bubbles trapped beneath the disc by manipulation of the stirrer bar. Stir for 75 min at 85–90°. Remove the disc, wash with demineralized water and methanol, dry and count.

DISCUSSION

From earlier reports it was evident that rapid and efficient deposition depended on elevated temperature and low volume. Accordingly, the volume was kept to a minimum by plating in an almost enclosed environment in order to reduce loss by evaporation. Mechanical stirring with a glass rod caused excessive splashing, owing to the difficulty of regulation at low speed, hence a combined hot-plate magnetic stirrer was used. The silver disc had then to be suspended in the solution, to allow clearance for the stirrer bar. Evaporation loss was reduced to a minimum by using the beaker itself as a support for the disc holder. Maximum counting sensitivity was obtained by ensuring that only one side of the silver disc was exposed to the solution.

Previous reports showed that some plating had been done from hydrochloric acid solution, and some from nitric acid solution. Because of the possibility of nitric acid attacking the perspex holder and the silver disc, it was decided to use hydrochloric acid media. A preliminary study of deposition from 50 ml of solution at 85–90° showed that the greatest efficiency was obtained from 1–2 N hydrochloric acid solutions. A further study of volume and temperature indicated that full recovery could be obtained in 3 h by plating from 50 ml of solution at 85–90°. In attempting to avoid a preliminary separation of tellurium by the use of a complexing agent, it was found that sodium citrate facilitated plating. Full recovery of ^{210}Po was proved possible in 60 min by plating at 85–90° in presence of 0.5 g of sodium citrate; recoveries were unaffected by further plating time up to at least 3 h. The interference of iron(III), chromium(VI) and other oxidants was eliminated by addition of hydroxylamine hydrochloride, excess of which did not interfere with plating efficiency. Tellurium and selenium in milligram quantities deposited on the silver and decreased plating efficiency but as much as 10 mg of these metals could be tolerated by raising the pH to 2.0.

Further study of pH showed that full recovery of ^{210}Po was achieved in 1 h up to pH 2.5; between pH 2.5 and 3.0, recoveries decreased quite rapidly to *ca.* 85% and then decreased slowly between pH 3 and 6. When citrate and hydroxylamine hydrochloride were present at pH 2, it was found that plating for 1 h at 25° gave only 40% recovery, the recovery then increasing with temperature up to 80°. Increasing the volume of the solution above *ca.* 70 ml caused low recoveries. Under the recommended conditions, the amount of sodium citrate present could vary from 0.2 to 2 g without affecting the results.

Subsequent determinations carried out at pH 2.0 with 1 g of hydroxylamine hydrochloride, 0.5 g of sodium citrate and 10 ml of concentrated hydrochloric acid gave good recoveries of ^{210}Po in the presence of many different ions (Table I). Various representative α-emitters were shown not to deposit in significant amounts (Table II). Thorium precipitated at pH 1.0 but this was prevented by the addition of a small quantity of sulphate. The ^{212}Bi decay product of ^{232}Th was found to deposit, but addition of 10 mg of bismuth carrier prevented the ^{212}Bi deposition. ^{212}Bi was identified by plating from a solution containing 100 mg of thorium and counting the activity at regular intervals over 6 h; a half-life of *ca.* 60 min proved the presence of ^{212}Bi.

The determination of ^{210}Po in low-grade uranium ores in which equilibrium was assumed, showed good agreement with spectrophotometric results obtained for

TABLE I

EFFECT OF VARIOUS ELEMENTS ON THE RECOVERY OF ^{210}Po

(*ca.* 0.5 pCi ^{210}Po/ml present)

Foreign ion	*Amount taken (g)*	*Added as:*	*Recovery (%)*	*Foreign ion*	*Amount taken (g)*	*Added as:*	*Recovery (%)*
Ag^+	0.001[a]	$AgNO_3$	98	PO_4^{3-}	0.10	KH_2PO_4	98
Al^{3+}	0.10	$AlCl_3$	99	Ru^{3+}	0.02[a]	$RuCl_3$	100
Bi^{3+}	0.10	$Bi(NO_3)_3$	100	Sb^{3+}	0.10	$SbCl_3$	100
Ca^{2+}	0.10	$CaCl_2$	96	Se^{4+}	0.01[a]	SeO_2	98
Ce^{4+}	0.10	$Ce(SO_4)_2$	99	Sn^{2+}	0.005[a]	$SnCl_2$	98
Co^{2+}	0.10	$Co(NO_3)_2$	103	Te^{4+}	0.01[a]	K_2TeO_3	100
Cr^{6+}	0.10[b]	Na_2CrO_4	101	Th^{4+}	0.10	$Th(NO_3)_4$	100
Cu^{2+}	0.10	$Cu(NO_3)_2$	99	U^{6+}	0.10	$UO_2(NO_3)_2$	98
Fe^{3+}	0.10[b]	$FeCl_3$	100	V^{5+}	0.10	Na_3VO_4	97
F^-	2.5[a]	HF	98	Zn^{2+}	0.10	$ZnCl_2$	100
Hg^{2+}	0.01[a]	$HgCl_2$	97	Zr^{4+}	0.10	$ZrOCl_2$	98
I^-	0.75	KI	100	$HClO_4$	8.0		97
Mg^{2+}	0.10	$MgCl_2$	98	KNO_3	1.0		98
Mn^{2+}	0.10	$MnCl_2$	102	KCl	1.0		99
Ni^{2+}	0.10	$NiSO_4$	98	$(NH_4)_2SO_4$	1.0		100
Pb^{2+}	0.10	$Pb(NO_3)_2$	98				

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[a] Maximum permissible amount of ion for determination.
[b] Extra $NH_2OH \cdot HCl$ required.

TABLE II

ACTIVITY FOUND AFTER PLATING FROM STANDARD SOLUTIONS OF VARIOUS RADIONUCLIDES

Nuclide	*Activity added (d.p.m.)*[a]	*Activity found (d.p.m.)*[a]
^{241}Am	1100	0.2
^{237}Np	750	0.8
^{231}Pa	515	0.8
^{239}Pu	680	0.4
^{226}Ra	400	0.2
^{230}Th	450	0.1
^{232}U	440	0.7

[a] d.p.m. = disintegration/min.

TABLE III

COMPARISON OF URANIUM ORE ANALYSES[a]

Sample	*% U*		
	Spectrophotometric[b]		*^{210}Po deposition*
	DBM[c]	*NH$_4$SCN*	
Carnotite	0.348	0.347	0.340
Uraninite	0.321	0.312	0.304
Torbernite (Spain)	0.263	0.265	0.264
Torbernite (Australia)	0.397	0.398	0.405

[a] I.A.E.A. comparison samples.

[b] Analyses by P. PALKANS AND B. MCALLISTER, A.A.E.C., Lucas Heights, Australia.

[c] Dibenzoylmethane.

TABLE IV

COMPARISON OF ANALYSES OF STANDARD ROCKS[a]

Sample	*U (p.p.m.)*				*Th (p.p.m.)*
	γ-Spectrometry[5]	*Neutron activation*[6]	*Delayed neutron*[7]	*^{210}Po deposition*	
Andesite (AGV-1)	1.9 ± 0.2	2.17 ± 0.02	2.09 ± 0.06	1.72 ± 0.06	6.4
Basalt (BCR-1)	1.6 ± 0.1	1.81 ± 0.14	1.80 ± 0.05	1.92 ± 0.08	6.0
Granite (G-2)	2.1 ± 0.3	2.16 ± 0.07	2.07 ± 0.03	1.80 ± 0.10	25
Granodiorite (GSP-1)	1.7 ± 0.8	—	2.68 ± 0.04	2.75 ± 0.05	106

[a] Courtesy of F. J. FLANAGAN, U.S. Geological Survey.

uranium (Table III). Initial dissolution with 1:1 nitric acid for 5 h gave low results, but with hydrofluoric plus nitric acid, 100% recovery was obtained for all but the carnotite ore. Dissolution with hydrofluoric acid at room temperature overnight gave only 75% recovery; with hydrofluoric and perchloric acids on heating recoveries were only about 85%. The high vanadium content of carnotite ore seemed to indicate that oxidation to vanadium(V) was necessary for full recovery.

Estimation of ^{210}Po in standard rocks in which equilibrium was also assumed, showed that the method was accurate. The addition of bismuth(III) as a hold-back carrier was also shown to be effective in preventing deposition of the ^{212}Bi from the ^{232}Th present (Table IV).

The method of standard addition was used to determine that full recovery of ^{210}Po was possible from effluent samples.

Polonium-210 is adsorbed strongly on to glass, and standard solutions were kept in polythene bottles in 2 *N* hydrochloric acid. Dilution of samples in glass volumetric flasks was unavoidable but to prevent adsorption solutions were kept at 4–5 *N* hydrochloric acid. Glassware was decontaminated by boiling with 15 *M* nitric acid. At about 150°, ^{210}Po is volatile and loss from beakers taken to dryness on a hot plate at about 450° was 60% in 15 min. Consequently, all evaporations were carried out at 120°, or less, to avoid loss.

The silver discs were used many times by cleaning with metal polish. Some loss of efficiency was evident when the discs became too thin. After plating in the presence of tellurium or selenium, a slight black deposit was evident which was not entirely removed by metal polish, causing a drop in plating efficiency for the next sample. Cleaning with fine steel wool was effective in removing this contamination.

SUMMARY

A method is presented for the determination of polonium-210 at very low levels in the presence of many different ions. Essentially quantitative recoveries were obtained in 60 min by deposition on to a silver plate in a special holder from 50 ml solution at 85–90° with sodium citrate present.

RÉSUMÉ

On propose une méthode pour le dosage du polonium-210, en très faibles teneurs, en présence de nombreux ions étrangers. Des rendements quantitatifs sont obtenus en 60 minutes par déposition sur une plaque d'argent avec support spécial. On utilise 50 ml de solution à 85–90° en présence de citrate de sodium.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Polonium-210 bei sehr geringen Konzentrationen in Gegenwart zahlreicher verschiedener Ionen beschrieben. Durch die Abscheidung auf einer Silberplatte in einem Spezialhalter bei 85–90° aus 50 ml Lösung, die Natriumcitrat enthält, konnte das Polonium nahezu quantitativ zurückgewonnen werden.

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OPTICAL NITROGEN-15 ANALYSIS OF SMALL NITROGEN SAMPLES WITH A MIXTURE OF HELIUM AND XENON TO SUSTAIN THE DISCHARGE IN AN ELECTRODELESS TUBE

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Many spectrographic methods have been reported for measuring nitrogen-15 enrichment. Some work involves the use of nitrogen-15 as a tracer. To date, the amount of sample nitrogen analyzed in electrodeless tubes has been not less than about 5 μg[1]. However, methods are currently needed for the study of nitrogen uptake by plants, for example, to determine the excess of nitrogen-15 in samples containing submicrogram quantities of nitrogen.

A previous communication[2] reported that noble gases showed promise in sustaining a discharge of submicrogram quantities of nitrogen gas in an electrodeless discharge tube. The work reported here is a continuation of this investigation.

EXPERIMENTAL

Preparation of an electrodeless tube containing nitrogen, and the noble gases, helium and xenon

A conventional vacuum line[3] with dosing volumes and with containers of noble gases and nitrogen of spectroscopic purity, was employed for the preparation of the electrodeless tubes containing nitrogen, xenon and helium. An Autovoc gauge, Model No. 3294B, was attached to the vacuum line to measure gas pressures. The discharge tubes used (8–10 cm long, 2 mm i.d.) were made of quartz. To prepare a tube of this dimension containing the gases of interest, the following technique was employed. A quartz tube, about 25 cm long, closed at one end, was attached to the vacuum line with Apiezon W. About 15 cm of the closed end of the tube was thoroughly flamed for about 10 min and the impurities exhausted. Subsequently, some 5 torr of xenon was introduced into the tube, and then the tube was flamed, before evacuation, for another 10 min at this pressure and cooled to room temperature in order to adsorb xenon on the wall of the tube. Next, appropriate amounts of nitrogen, helium, and xenon were admitted into the clean, xenon-treated tube. Finally, the tube was sealed with a flame, about 10 cm from the closed end, and pulled off the vacuum line. A recorder tracing obtained with an excited blank tube, treated with xenon and containing a mixture of helium and xenon, showed no nitrogen or impurity

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bands in the spectral region employed to measure the nitrogen bands of interest (2977 and 2983 Å).

Excitation and readout system

A 100-Mc generator[4], operating at *ca.* 50 W, was used to excite the gases in the discharge tube. Light from the discharge tube was focussed by a 64-mm lens on to a 100-μ entrance slit, reduced to a length of 9 mm, of a Hilger Watts quartz spectrograph, Model No. E 742, modified at this laboratory[5] for photometric work. Light from the 100-μ exit slit was directed to à RCA 1P28 photomultiplier tube. A commercially available readout system (power supply, amplifier and recorder) was employed to trace the signal from the photomultiplier tube. The discharge tube was air-cooled during operation. As a result, the Döppler widths of the nitrogen band-heads at 2977 and 2983 Å used were reduced, and the life of the nitrogen was prolonged. The use of a rare gas to sustain a low pressure nitrogen discharge also reduced the self-pressure widths of the nitrogen bands.

RESULTS

The study of optical spectroscopy has shown that nitrogen is adsorbed when it is excited in a quartz discharge tube[6]. This problem is not serious when large quantities of nitrogen are available for analysis. However, when only submicrogram quantities of nitrogen are present, the adsorption of nitrogen is a serious problem. For example, when 1 torr (0.4 μg) of nitrogen was excited alone, under the excitation conditions described above, in a tube cleaned by flaming, the nitrogen discharge lasted about 2 min. Further, the discharge could not be started again by resting the tube for several hours, or by flaming the tube in attempt to drive the nitrogen off the wall. From this it was concluded that a gas was needed not only to sustain a discharge of small quantities of nitrogen, but also to keep it from being adsorbed quickly by the quartz. A noble gas appeared a likely choice, since it would not react with nitrogen.

Choice of a noble gas to sustain a nitrogen discharge and prevent rapid adsorption of nitrogen

Discharge tubes, cleaned by flaming, were prepared containing 1 torr of nitrogen and 1 torr of helium, neon, argon, krypton and xenon, respectively. Studies of discharges from each tube indicated that all noble gases sustained a nitrogen discharge. The heaviest gas, xenon, sustained a nitrogen discharge for a longer period of time than the other gases, but the intensities of the bands of interest were weak. Conversely, the lightest gas, helium, sustained a nitrogen discharge for a short period of time, but the intensities of the bands were strong. The following conclusions were derived from these observations.

(*a*) Xenon is adsorbed by the quartz more strongly than other gases. It retards nitrogen from being adsorbed rapidly on the quartz. As a result the nitrogen lifetime is long. Since the ionization potential of xenon is lower than that of the nitrogen molecule, nitrogen is weakly excited.

(*b*) Helium is not strongly adsorbed by quartz; hence, nitrogen is adsorbed by the quartz rapidly, and the nitrogen lifetime is short. Since the ionization potential of helium is higher than that of the nitrogen molecule, nitrogen is strongly excited.

It was decided therefore to use xenon in the tube to prevent the nitrogen from being adsorbed rapidly, and helium to sustain the nitrogen discharge.

The use of xenon to "plug" a quartz surface and helium to sustain a nitrogen discharge

To see if xenon was an effective "plugger" a discharge tube, treated with xenon as described earlier, was made containing 1 torr (0.4 µg) of nitrogen. When this tube was excited, it emitted a bright nitrogen discharge that lasted for more than 15 min, as opposed to about 2 min without the xenon treatment. Repeated tests on a number of duplicate tubes showed similar results. Thus xenon was used to "plug" quartz tubes.

The smallest quantity of nitrogen that could sustain a discharge in a tube pretreated with xenon, was determined by making a number of tubes containing 0.1–2.0 µg of nitrogen. Table I shows the results of this investigation. It is clear that 0.2 µg of nitrogen in a xenon-treated tube is an insufficient amount of gas to carry a discharge long enough for a nitrogen-15 analysis.

The use of helium to sustain 0.2 µg of nitrogen was attempted. Xenon-treated tubes were made containing 0.2 µg of nitrogen and 1, 2, 4, 8, 12 and 16 torr of helium, respectively. The nitrogen discharge that was obtained with tubes at pressures of 4 torr of helium or more was bright, but the lifetime of nitrogen was not long enough to obtain accurate nitrogen-15 results. A lifetime of 3 min is the minimum time

TABLE I

LIFETIME AND RELATIVE INTENSITIES OF SMALL AMOUNTS OF NITROGEN EXCITED IN A XENON-PRETREATED TUBE WITHOUT A MIXTURE OF HELIUM AND XENON

Nitrogen pressure (torr)	*Nitrogen (µg)*	*Life (min)*	I_0 *(av)*
0.25	0.1	<1	—
0.50	0.2	<1	—
0.75	0.3	3	40
1.0	0.4	>15	45
2.0	0.8	>15	35
5.0	2.0	>15	15

TABLE II

LIFETIME AND RELATIVE INTENSITIES OF 0.2 µg OF NITROGEN EXCITED IN A XENON-PRETREATED TUBE CONTAINING A MIXTURE OF HELIUM AND XENON

Helium pressure (torr)	*Xenon pressure (torr)*					
	0.10		*0.15*		*0.20*	
	Life (min)	I_0 *(av)*	*Life (min)*	I_0 *(av)*	*Life (min)*	I_0 *(av)*
1	<1	—	<1	—	<1	—
2	<1	—	1	42	1	40
4	2	50	8	30	14	20
8	12	44	10	47	14	43
12	8	45	10	40	8	35
16	6	40	8	44	10	25

required for a reasonable measurement, and 5–10 min is necessary for a precise measurement. The probable reason for the short lifetime was that the nitrogen was still adsorbed by the quartz even though it was treated with xenon.

Mixtures of helium and xenon, instead of pure helium, were tried for sustaining 0.2 μg of nitrogen for a longer period of time in xenon-treated tubes. It was thought that the addition of xenon to helium would retard the adsorption of nitrogen still further, since experience showed that the adsorption of nitrogen was slowed down when xenon was used. Table II shows the pressures of helium and xenon used with 0.2 μg of nitrogen, respectively. The results indicate that the optimum brightness and lifetime of nitrogen was obtained for accurate nitrogen-15 abundance measurements when the xenon-pretreated tubes contained 0.1–0.2 torr of xenon and 8–12 torr of helium.

To determine the natural nitrogen-15 abundance and to obtain a measure of the precision for this technique, three xenon-treated tubes were prepared, containing 0.5 torr (0.2 μg) of nitrogen, 0.15 torr of xenon and 10 torr of helium. Some ten recorder tracings were obtained for the three tubes. The determined nitrogen-15 abundance (Table III) was 0.370 ± 0.005 at-% which is in good agreement with the accepted value of 0.366 at-%.

TABLE III

DETERMINATION OF NATURAL ABUNDANCE OF NITROGEN-15 BY EXCITING 0.2 μg OF NITROGEN IN A XENON-PRETREATED TUBE CONTAINING A HELIUM–XENON MIXTURE

Recorder tracing no.	*Natural nitrogen-15 abundance (at-%)*	*Dev. from mean (at-%)*	*(Dev.)²*
1	0.370	0.000	0.0000
2	0.400	+0.030	0.0009
3	0.370	0.000	0.0000
4	0.350	−0.020	0.0004
5	0.360	−0.010	0.0001
6	0.380	+0.010	0.0001
7	0.360	−0.010	0.0001
8	0.370	0.000	0.0000
9	0.390	+0.020	0.0004
10	0.350	−0.020	0.0004
	Av 0.370		Sum 0.0024
	0.370 ± 0.005[a]		

[a] Calcd. according to standard error mean method: std. error = $[\Sigma d^2/n(n-1)]^{\frac{1}{2}}$, where d = deviation from average and n = number of traces.

The analysis of nitrogen-15 in plant and liquid samples

Two different plants and one ammonium chloride solution were analyzed for nitrogen-15.

Plant samples. Three pieces of a rice leaf, slightly enriched in nitrogen-15, were analyzed individually. The Dumas method as used by FAUST[7] was used to release the nitrogen from the sample. The sample weighed some 25 μg and contained about 0.5 μg of total nitrogen. The excess of nitrogen-15 was 0.013 at-% as determined by mass spectrometric techniques at this laboratory. The chemicals (CaO + CuO) used to decompose the sample and to trap the unwanted gases were briquetted into a pellet (*ca.* 1.5 mm^3) to simplify handling and to keep them intact in the discharge tube. The degassed chemicals and dried sample were sealed in a xenon-treated tube containing helium and xenon. The average excess of nitrogen-15 obtained by this spectrographic technique was $0.02_5 \pm 0.01$ at-%. This is in reasonable agreement with the mass spectrometric value, considering the slight enrichment.

A Polythricum pod weighing some 100 μg and containing normal nitrogen, an expected 1 μg, was analyzed for nitrogen-15. The technique described above was used to release the nitrogen gas from the sample. The nitrogen-15 abundance obtained was 0.370 ± 0.005 at-%.

Ammonium chloride. An enriched ammonium chloride solution that contained 0.4 μg of total nitrogen (10.6 at-% of nitrogen-15) was analyzed a number of times. The Dumas method was used to release pure nitrogen gas. Ammonium chloride solution (10 μl) was taken up by a flame-cleaned glass capillary (i.d. 1 mm, o.d. 1.5 mm). The capillary with the solution and the briquetted chemical were dried and degassed, respectively, in the quartz tube that was attached to the vacuum line. Subsequently, the capillary and chemical were sealed in a section of this tube, which was treated with xenon and contained a mixture of helium and xenon. The average excess amount of nitrogen-15 obtained was 10.3 ± 0.3 at-%. This result is slightly low, probably because of trace nitrogen contamination in the solution. The elimination of trace quantities of nitrogen, especially in a chemical solution, is an extremely difficult problem.

DISCUSSION AND CONCLUSION

The bands at 2977 and 2983 Å were used for this work for the reasons given by LEICKNAM *et al.*[8]. Other workers[9] have used these bands and obtained satisfactory results.

Helium not only sustains a nitrogen discharge but also enhances the intensities of the bands used. When two clean tubes, not treated with Xe, were prepared with 1 torr of helium plus 1 torr of nitrogen and 1 torr of nitrogen, and excited, the intensities of the bands obtained with the former tube were almost twice as great as the intensities of the bands with the latter tube. A helium line at 2945 Å is also useful for monitoring purposes. For example, it can be employed to check the helium dosing procedure and excitation power, because a tracing of it is easily and quickly obtained when the nitrogen and xenon disappear.

The reason that the nitrogen bands are enhanced when nitrogen is excited in helium is not obvious. Often, simple stable molecules in rare gases exhibit unusual radiation spectra when excited in a discharge tube. For instance, HERMAN AND HERMAN[10] found that bands of neutral oxygen are strongly developed in an excess of xenon, but are normally unobservable in pure oxygen and suppressed by helium or argon as diluent gases for oxygen. PEARSE AND GAYDON[11] also indicate that several molecules are known to emit somewhat different molecular spectra in the presence of rare gases, and that the mechanism in most cases is still somewhat obscure.

It appears, therefore, that when nitrogen is excited in the presence of noble gases, the resulting nitrogen molecular spectra are dissimilar. A careful investigation of these nitrogen spectra for possible strong bands with appreciable isotope shifts, might be useful for improving the present lower limit of nitrogen analysis and/or accuracy.

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SUMMARY

A spectrographic technique has been developed for the determination of the nitrogen-15 abundance, with a mixture of rare gases, helium and xenon, to sustain the nitrogen discharge. The average natural abundance obtained with 0.2-μg samples of nitrogen was 0.370 ± 0.005 at-%. Preliminary work indicates that this method is applicable directly to plant and liquid samples.

RÉSUMÉ

Une technique spectrographique est développée pour la détermination de l'azote-15 en présence d'un mélange de gaz rares, hélium et xénon, comme support de l'azote. L'abondance naturelle moyenne obtenue avec des échantillons de 0.2 μg d'azote est de 0.370 ± 0.005 atome %. Un travail préliminaire indique que cette méthode est applicable directement aux plantes et aux échantillons liquides.

ZUSAMMENFASSUNG

Es wurde eine spektrographische Technik zur Bestimmung von Stickstoff-15 entwickelt unter Verwendung einer Mischung von Helium und Xenon, die die Stickstoffentladung unterstützen sollen. Das mittlere natürliche Vorkommen, welches mit 0.2 μg Proben ermittelt wurde, betrug 0.370 ± 0.005 at-%. Vorhergehende Untersuchungen zeigten, dass diese Methode direkt für Pflanzenmaterial und flüssige Proben anwendbar ist.

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NEUE VERVIELFACHUNGSMETHODEN IN DER MASSANALYSE

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Es gibt zwei Wege zur Lösung des Problems, sehr kleine Probenmengen zu analysieren: Der eine, übliche, ist, eine geeignete Methode zu finden, die das Arbeiten mit so kleinen Mengen erlaubt; die zweite Möglichkeit ist, die sehr kleine zu bestimmende Substanzmenge (oder deren Aequivalent) durch eine Multiplikationsmethode zu "vergrössern".

Bisher gibt es relativ wenige Beispiele für diese Art der Mikroanalyse. Die bekannte Jodid-Bestimmung nach der sogenannten LEIPERT-Methode[1] muss hier erwähnt werden. Wir haben bereits über eine Kombination dieser Jodid-Vervielfachung mit elektrolytischer Abscheidung zur Vervielfachung einiger Metalle berichtet[2]. BELCHER hat kürzlich eine Übersicht über derartige Vervielfachungsreaktionen veröffentlicht[3]. Zweifellos wäre es wünschenswert, wenn mehr allgemein anwendbare Methoden verfügbar wären.

Bereits 1933 wies EMICH in einem Vortrag darauf hin[4], dass man, "anstatt die Messeinheit zu verkleinern, auch die Masse der Bestimmungsform vergrössern" könne. Der zu bestimmende Stoff sollte solchen stöchiometrischen Umwandlungen ausgesetzt werden, "die sein Gewicht nach und nach erhöhen". EMICH hat seine Anregungen niemals durch praktische Versuche verwirklicht. Wir haben diese Idee in Verbindung mit halbquantitativen Bestimmungen auf dem Ringofen angewandt[5]. Die dabei erhaltenen guten Ergebnisse legten die Annahme nahe, dass das gleiche Verfahren auch in der Massanalyse Anwendung finden könnte, worauf bereits früher hingewiesen wurde. Es sei an dieser Stelle ausdrücklich betont, dass im weiteren *nur solche* Reaktionsfolgen als "Vervielfachungen" bezeichnet werden sollen, die mehrfach—zumindest theoretisch beliebig oft—wiederholbar sind.

Im folgenden sollen drei Systeme beschrieben werden, die sich experimentell gut bewährt haben; mit ihrer Hilfe konnten mehrere Ionen vervielfacht werden.

DAS SYSTEM CHROMAT–SILBERCHLORID

Dieses Vervielfachungssystem sei am Beispiel der Bestimmung von Chromat erläutert:

Das Chromat wird als Silberchromat gefällt, filtriert und gewaschen. Wird der Niederschlag dann mit Bariumchloridlösung umgesetzt, so entsteht aus dem Silberchromat einerseits schwerlösliches Silberchlorid und andererseits schwerlösliches

Bariumchromat. Wir haben nun eine Silberchloridmenge, die der Menge des ursprünglich vorhandenen Chromats äquivalent ist, und *zusätzlich* eine Menge an Bariumchromat, die ebenfalls der ursprünglichen Chromatmenge äquivalent ist. Nun wird der Niederschlag mit Silbernitratlösung behandelt; dies lässt natürlich das Silberchlorid unverändert, wandelt aber das *Barium*-Chromat in eine äquivalente Menge *Silber*-Chromat um. Sorgfältiges Auswaschen der Niederschläge ist stets notwendig, ehe man wieder Reagenslösung zufügt. Wird dann wieder Bariumchloridlösung hinzugefügt und das Verfahren wie eben beschrieben fortgesetzt, so wird stets eine Silberchloridmenge dazu addiert, die dem ursprünglich vorhandenen Chromat äquivalent ist.

Wird diese Reaktionsfolge beispielsweise zehnmal wiederholt, erhalten wir schliesslich eine Silberchloridmenge, die dem zehnfachen Aequivalent des ursprünglich vorhandenen Chromats entspricht. Das Silberchlorid wird in Ammoniak gelöst und das Silber in geeigneter Weise titriert. Das Resultat wird duch 10 oder—besser gesagt—durch die Anzahl der durchgeführten Multiplikationen dividiert; aus der so gefundenen Silbermenge kann das ursprünglich vorhanden gewesene Chromat errechnet werden.

Diese Schritte—Auswaschen des Niederschlages, Umsetzen mit Silbernitratlösung usw.—werden auf der Glassinterplatte (G 4) eines Chromatographierohres (10 mm ∅) ausgeführt.

Durch das System Chromat–Silberchlorid können Silber und Chromat vervielfacht werden, ebenso auch Phosphat; letzteres wird als Silberphosphat gefällt, zu Silberchromat umgewandelt, und dieses ist, wie wir sahen, eine "vervielfachbare" Verbindung.

Durchführung

Die chromathaltige Probelösung wird in einem kleinen Becherglas mit überschüssiger 2%iger Silbernitratlösung versetzt und nach dem Ausfallen des Silberchromatniederschlages auf *ca.* 50° erwärmt. Man lässt abkühlen und spült den Niederschlag ohne Absaugen auf die Glasfritte (G 4) einer Chromatographiesäule. Dann wird langsam abgesaugt und dreimal mit Aceton ausgewaschen. Bis zum Erreichen der gewünschten Vervielfachungszahlen werden anschliessend folgende Umsetzungen wiederholt: Zugabe von *ca.* 1 ml 20%iger Bariumchloridlösung (schwach essigsauer), dreimal auswaschen mit dest. Wasser, Zugabe von Silbernitratlösung (4%ig), dreimal waschen mit Aceton ... usw.

Jede Zugabe von Bariumchloridlösung bedeutet eine Vervielfachung. Beim letzten Schritt wird anstelle von Bariumchloridlösung mit 1 *N* Salzsäure umgesetzt und mit Wasser nachgewaschen, um das Chromat von der Fritte zu entfernen. Das Silberchlorid wird mit Ammoniak von der Säule gelöst und bestimmt.

$$CrO_4^{2-} \xrightarrow{Ag^+} Ag_2CrO_4$$

$$\text{1-fach} \xrightarrow{BaCl_2} BaCrO_4 + 2\,\mathit{AgCl}$$

$$\xrightarrow{Ag^+} Ag_2CrO_4 + 2\,AgCl$$

$$\text{2-fach} \xrightarrow{BaCl_2} BaCrO_4 + 2\,\mathit{AgCl} + 2\,\mathit{AgCl}$$

$$\xrightarrow{Ag^+} Ag_2CrO_4 + 2\,AgCl + 2\,AgCl$$

3-fach $\xrightarrow{BaCl_2} BaCrO_4 + 2\,AgCl + 2\,AgCl + 2\,AgCl$

$\xrightarrow{Ag^+} Ag_2CrO_4 + 2\,AgCl + 2\,AgCl + 2\,AgCl$

. . . . . .

. . . . . .

letzter Schritt $\xrightarrow{Cl^-} 2\,AgCl + \ldots 2\,AgCl + 2\,AgCl + 2\,AgCl$

Zur Bestimmung des Silbers stehen mehrere Möglichkeiten zur Verfügung. Am besten bewährte sich die Methode nach KAINRATH[6], welche zur Bestimmung von Jodid in Silberjodid entwickelt wurde. Die ammoniakalische Silberlösung wird mit 2%iger KJ-Lösung versetzt, mit 2 *N* Schwefelsäure schwach angesäuert, erwärmt und nach dem Absetzen filtriert; das Filtrieren des AgJ erfolgt je nach Menge durch einen G-4-Glasfiltertiegel oder durch ein Membranfilterscheibchen (Membranfiltergesellschaft Göttingen) unter Verwendung eines ursprünglich von ACKERMANN[7] konstruierten, später wenig veränderten[8] Filtriergerätes.

Der abfiltrierte Niederschlag wird jodidfrei gewaschen und mit *ca.* 50° warmer Brom–Eisessiglösung übergossen (10–20 Tropfen Br_2 auf 5 ml $CH_3COOH + 10$ ml 20%iger CH_3COONa-Lösung). Man lässt die Lösung 10–15 Min auf den Niederschlag einwirken (direkt im Glasfiltertiegel!) Dabei wird alles Jodid zu Jodat oxidiert. Dann saugt man ab, zerstört den Bromüberschuss mit wenigen Tropfen Ameisensäure, stellt auf pH 4–5 ein (H_2SO_4), fügt 10%ige KJ-Lösung zu und titriert das ausgeschiedene Jod mit 0.02 *N* $Na_2S_2O_3$-Lösung gegen Stärke mit Hilfe einer Mikro oder "AGLA"-Mikrometerbürette (je nach der Menge des zu titrierenden Jods). Auf diese Weise erreicht man natürlich noch eine zusätzliche Vervielfachung. Aus den für Jodid gefundenen Werten, der Anzahl der ausgeführten Vervielfachungsschritte, der Relation $J:Ag:CrO_4$ wird die ursprünglich vorhandene Menge an Chromat berechnet.

Die in Tabelle I angeführten Resultate (berechnet für Chrom) zeigen, dass derartige Vervielfachungsreaktionen brauchbare Ergebnisse liefern. Auf diese Weise lässt sich natürlich auch Silber vervielfachen.

TABELLE I

VERVIELFACHUNGEN VON CHROM

Gegeben (µg)	*Vervielfacht (×)*	*Gefunden (µg)*	*Gegeben (µg)*	*Vervielfacht (×)*	*Gefunden (µg)*
100.0	5	92.0	5.0	5	5.25
80.0	6	75.4		6	5.2
50.0	9	47.9		10	4.8
40.0	10	39.0	2.70	8	2.06
30.0	11	27.9			2.12
	15	27.7	1.50	10	1.46
20.0	10	19.2	1.20	17	1.22
	2	21.0	1.00	15	1.02
		19.6			0.89
		20.05		13	0.95
		19.2	0.80	17	0.80
10.0	2	9.6			
	3	8.8			
	4	9.85			

Da *Phosphat* mit Silbernitrat quantitativ gefällt werden kann und sich das so erhaltene Silberphosphat in die "vervielfachbare Verbindung" Silberchromat umwandeln lässt, kann auf diese Weise auch Phosphat indirekt vervielfacht werden:

Die Probelösung wird auf *ca.* 60° erhitzt und mit 2%iger Silbernitratlösung versetzt, nach dem Erkalten wird der Silberphosphatniederschlag durch ein Membranfilter filtriert (vgl. vorher). Nach Beendigung der Filtration wird der den Niederschlag tragende Teil des Filters mit einem Locheisen (6 mm ⌀) ausgestanzt und das so erhaltene Scheibchen mit dem Silberphosphat auf die G-4-Fritte der Säule gelegt. Anschliessend setzt man in der Säule mit *ca.* 1 ml 3%iger Kaliumchromatlösung um und wäscht überschüssiges Chromat mit dest. Wasser aus. Nunmehr hat man eine dem Phosphat äquivalente Menge Silberchromat auf der Fritte. Vervielfachung, Lösung des angehäuften Silberchlorids und Bestimmung des Silbers erfolgen in der bei Chromat beschriebenen Weise. Aus den Ergebnissen der Titration des Jods und der Anzahl der Vervielfachungsschritte lässt sich das Phosphat berechnen.

Tabelle II gibt einige Ergebnisse:

TABELLE II

INDIREKTE VERVIELFACHUNGEN VON PHOSPHAT

Gegeben (μg)	*Vervielfacht (×)*	*Gefunden (μg)*	*Gegeben (μg)*	*Vervielfacht (×)*	*Gefunden (μg)*
20.0	2	20.57	1.6	16	1.53
10.0	4	9.30	1.2	18	1.27
5.0	5	5.15	1.0	21	0.96
2.0	12	1.97	0.8	21	0.83

DAS SYSTEM HEXACYANOFERRAT(II)–SILBERCHLORID

Dieses System wurde zur Vervielfachung von Hexacyanoferrat(II), Zink und Eisen verwendet. Einige andere Ionen sollten mit dieser Reaktionsfolge ebenfalls vervielfachbar sein. Am Beispiel der Vervielfachung von Hexacyanoferrat(II) sei dieses Vervielfachungssystem dargestellt: Hexacyanoferrat(II) wird zunächst als schwerlösliches Silbersalz gefällt. Mit salzsaurer Eisen(III)chloridlösung behandelt, entsteht daraus Silberchlorid und Berlinerblau in Mengen, die natürlich jeweils dem ursprünglich vorhandenen Hexacyanoferrat(II) äquivalent sind. Den Niederschlag lässt man sodann mit Silbernitratlösung reagieren, wobei das Silberchlorid unverändert bleibt, das Berlinerblau aber wiederum in eine äquivalente Menge von Silberhexacyanoferrat(II) umgesetzt wird. Damit ist man abermals bei der vervielfachbaren Verbindung angelangt und der Zyklus kann von vorne beginnen: Hinzufügen von Eisen(III) chloridlösung und so fort. Selbstverständlich ist es auch hier nötig, nach jedem Reaktionsschritt den Niederschlag zu waschen. Es wird also jeweils eine dem Hexacyanoferrat (II) äquivalente Menge an Silberchlorid hinzuaddiert. Nach Durchführung der gewünschten Anzahl von Reaktionsschritten wird das Silberchlorid vom Filter gelöst und titriert. Alle Operationen erfolgen wieder in einer Chromatographiesäule, diesmal aber auf einer etwa 2 cm hohen Schicht von Aluminiumoxid. Dieser Träger erwies sich nach vielen Versuchen als optimal.

Durchführung

Die Probelösung wird in einem kleinen Becherglas mit 2%iger Silbernitratlösung versetzt und das ausgefällte Silberhexacyanoferrat(II) auf die 2 cm hohe Säule (Aluminiumoxid "aktiv, sauer"-Merck 1078—auf G-1-Fritte) gespült. Das überschüssige Silber wird mit stark verd. Schwefelsäure (30 ml 2 *N* H_2SO_4 ad 1000 ml dest. H_2O) durch dreimaliges kurzes Auswaschen entfernt. Je nach der gewünschten Vervielfachungszahl werden nacheinander folgende Schritte wiederholt: Zugabe von salzsaurer 0.1%iger Eisen(III)chloridlösung; dreimaliges Spülen mit je 5 ml der stark verd. Schwefelsäure (vgl. oben); Zugabe von etwa 1 ml 0.5%iger Silbernitratlösung; dreimaliges Spülen... und so fort. Beim letzten Vervielfachungsschritt statt Eisen(III)-chlorid mit 1 *N* Salzsäure umsetzen (zur Entfernung des Eisens). Das angehäufte Silberchlorid wird wieder mit Ammoniak von der Säule gelöst und, wie beim vorhergehenden System beschrieben, indirekt bestimmt. Aus den dabei erhaltenen Werten, der Zahl an Vervielfachungsschritten und der Relation J : Ag : $[Fe(CN)_6]$ kann die ursprünglich vorhanden gewesene Menge an Hexacyanoferrat(II) in einfacher Weise berechnet werden.

$$[\mathrm{Fe(CN)_6}]^{4-} \xrightarrow{\mathrm{Ag}^+} \mathrm{Ag_4[Fe(CN)_6]}$$

1-fach $3\,\mathrm{Ag_4}\,[\mathrm{Fe(CN)_6}] \xrightarrow{\mathrm{FeCl_3}} \mathrm{Fe_4[Fe(CN)_6]_3} + \mathit{12\,AgCl}$

$\xrightarrow{\mathrm{Ag}^+} 3\,\mathrm{Ag_4[Fe(CN)_6]} + 12\,\mathrm{AgCl}$

2-fach $\xrightarrow{\mathrm{FeCl_3}} \mathrm{Fe_4[Fe(CN)_6]_3} + \mathit{12\,AgCl} + \mathit{12\,AgCl}$

$\xrightarrow{\mathrm{Ag}^+} 3\,\mathrm{Ag_4[Fe(CN)_6]} + 12\,\mathrm{AgCl} + 12\,\mathrm{AgCl}$

3-fach $\xrightarrow{\mathrm{FeCl_3}} \mathrm{Fe_4[Fe(CN)_6]_3} + \mathit{12\,AgCl} + \mathit{12\,AgCl} + \mathit{12\,AgCl}$

$\xrightarrow{\mathrm{Ag}^+} 3\,\mathrm{Ag_4[Fe(CN)_6]} + 12\,\mathrm{AgCl} + 12\,\mathrm{AgCl} + 12\,\mathrm{AgCl}$

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letzter
Schritt $\xrightarrow{\mathrm{Cl}^-} \mathit{12\,AgCl} + \ldots\ldots + \mathit{12\,AgCl} + \mathit{12\,AgCl} + \mathit{12\,AgCl}$

In analoger Weise werden *Zink* und *Eisen* vervielfacht, indem das entsprechende Metallion zunächst mit 0.1%iger Kaliumhexacyanoferrat(II)-lösung gefällt und auf die Aluminiumoxidsäule gespült wird. Überschüssiges Reagens wird abgesaugt und mit wenigen Millilitern 2 *N* Schwefelsäure mehrmals nachgewaschen. Durch Umsetzung des Niederschlags mit 0.5%iger Silbernitratlösung wird Silberhexacyanoferrat gebildet und weiter wie eben vorher beschrieben verfahren. Diese Vervielfachungen sind nur möglich, da sowohl die Fällung von Zink wie auch die des Eisens mit Hexacyanoferrat(II) wohldefinierte stöchiometrische Verbindungen liefern: $K_2Zn_3[Fe(CN)_6]_2$ bzw. $Fe_4[Fe(CN)_6]_3$ (vgl. Literatur FLUCK[9], FEIGL[10]).

TABELLE III

VERVIELFACHUNGEN VON $[Fe(CN)_6]^{4-}$, Zn UND Fe

Hexacyanoferrat(II)			*Zink*			*Eisen*		
Gegeben (µg)	*Vervielfacht (×)*	*Gefunden (µg)*	*Gegeben (µg)*	*Vervielfacht (×)*	*Gefunden (µg)*	*Gegeben (µg)*	*Vervielfacht (×)*	*Gefunden (µg)*
7.44	2	7.50	1.70	6	1.61	2.30	5	2.28
	4	7.20	1.00	10	0.98	2.00	5	2.05
3.72	4	3.69			0.96	1.90	5	1.80
		3.53			1.05	1.10	153	1.085
1.86	4	1.80			0.99	1.00	10	0.94
	8	1.78		13	0.89			0.98
		1.68	0.80	13	0.80			1.01
		1.90						1.10
	19	1.75	0.50	20	0.498		88	1.19
							90	1.15
							110	1.20
						0.50	20	0.49

Titration und Berechnung der Ergebnisse erfolgen sinngemäss wie bei der Vervielfachung von Hexacyanoferrat(II) selbst, natürlich unter Berücksichtigung der entsprechenden Relationen:

$$3\ Zn^{2+} \ldots 8\ Ag^{+} \ldots 8J^{-} \text{ bzw. } 4\ Fe^{3+} \ldots 12\ Ag^{+} \ldots 12\ J^{-}$$

Wie schon erwähnt, sollten noch eine Reihe anderer Metalle auf diese Weise vervielfachbar sein. Mit *Kupfer* wurden häufig sehr fehlerhafte Resultate erhalten, was offenbar darauf zurückzuführen ist, dass die mit Hexacyanoferrat(II) erhaltenen Niederschläge nicht stöchiometrisch einheitlich sind.

So haben wir verschiedene Mengen von Hexacyanoferrat(II), Zink und Eisen vervielfacht und bestimmt. Tabelle III gibt eine Reihe von Beispielen, welche zeigen, dass derartige Methoden durchaus brauchbare Ergebnisse liefern.

Als Kuriosität sei erwähnt, dass wir 1.10 µg Fe 153 mal vervielfacht haben und dann schliesslich imstande waren, die dabei resultierende relativ grosse Menge an Silberchlorid mit Hilfe einer üblichen Makrobürette zu titrieren. Wir erhielten 1.09 µg Fe als Resultat (vgl. Tabelle III). Das ist sicherlich eine Kuriosität. Normalerweise wird man eine Probe nur so oft vervielfachen, als nötig ist, um in einen Grössenordnungsbereich zu gelangen, der zu einer Titration ausreicht.

Automatisierung der Vervielfachungen

Betrachtet man die beiden bisher beschriebenen Systeme, so erkennt man, dass immer die gleichen Prozeduren wiederholt werden: Hinzufügen von Reagens 1, Waschflüssigkeit, Reagens 2, Waschflüssigkeit, Reagens 1 usw. Dies aber sind Operationen, die bequem automatisiert bzw. mechanisiert werden können. Zu diesem Zwecke wurde eine einfache Apparatur gebaut, welche in Abb. 1 schematisch dargestellt ist: Drei Reagensbehälter (zwei für die jeweils verwendeten Reagenzien und einer für die Waschflüssigkeit) sind mit der Chromatographiesäule über Magnetventile verbunden. Eine einfache Steuerwalze gibt in geeigneten Intervallen jeweils einen Impuls zu einem der Magnetventile und aus der entsprechenden Flasche fliesst ein bestimmtes Volumen von Reagens bzw. Waschflüssigkeit auf die Säule. Die Zahl der Vervielfachungen kann an einem elektrischen Zählwerk abgelesen werden. Das Gerät ist so eingestellt, dass 4 Vervielfachungsschritte in 6 Minuten durchgeführt werden können. Nur das Aufbringen der Probe und der letzte Schritt müssen von Hand aus durchgeführt werden.

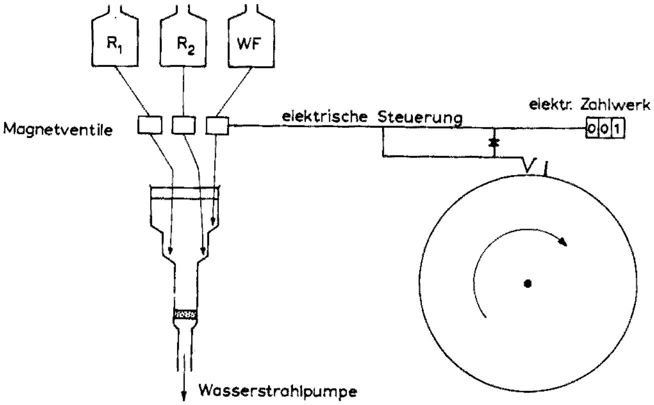

Fig. 1.

Bei kleineren Vervielfachungszahlen wird man wohl ohne diese Apparatur arbeiten, bei höheren Vervielfachungszahlen aber ist sie sicherlich von Vorteil. Wir haben diese Apparatur zunächst nur für das System Hexacyanoferrat(II)–Silberchlorid angewendet (alle in Tabelle III aufgeführten Werte für Zink und Eisen wurden auf diese Weise bestimmt), doch müsste sie nach entsprechender Umstellung natürlich auch für andere Systeme verwendbar sein.

DAS SYSTEM JODID–BARIUMJODAT

Dieses dritte bisher ausgearbeitete System liefert gute Ergebnisse bei der Vervielfachung von Silber und sollte wohl auch zur Bestimmung kleinster Mengen von Halogenen und anderen mit Silber fällbaren Ionen anwendbar sein. Es beruht wie die schon erwähnte sogen. LEIPERT-Methode gleichfalls auf der leichten Oxydierbarkeit von Jodid zu Jodat.

Behandelt man Silberjodid mit Brom–Eisessiglösung, welche gleichzeitig Bariumionen enthält, so entsteht Silberbromid und eine dem Silber bzw. dem Jodid äquivalente Menge an Bariumjodat, beides relativ schwerlösliche Verbindungen. Wird dieser Niederschlag mit Jodidlösung umgesetzt, so bleibt das Bariumjodat natürlich unverändert, während das Silberbromid wieder zu Silberjodid umgesetzt wird. Diese Umsetzungen können nun wiederholt werden.

Man addiert also jeweils eine dem Silber bzw. dem Jodid äquivalente Menge an Bariumjodat.

$$\begin{aligned} & \qquad\quad 2\,\mathrm{AgJ} \\ \text{1-fach } & \xrightarrow{\mathrm{Ba^{2+}+Br_2}} 2\,\mathrm{AgBr} + Ba(JO_3)_2 \\ & \xrightarrow{\mathrm{J^-}} \; 2\,\mathrm{AgJ} + \mathrm{Ba(JO_3)_2} \end{aligned}$$

$$\text{2-fach} \xrightarrow{Ba^{2+}+Br_2} 2\,AgBr + \mathit{Ba(JO_3)_2} + \mathit{Ba(JO_3)_2}$$

$$\xrightarrow{J^-} 2\,AgJ + Ba(JO_3)_2 + Ba(JO_3)_2$$

$$\text{3-fach} \xrightarrow{Ba^{2+}+Br_2} 2\,AgBr + \mathit{Ba(JO_3)_2} + \mathit{Ba(JO_3)_2} + \mathit{Ba(JO_3)_2}$$

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Die auf diese Weise angehäufte Menge an Bariumjodat kann einfach bestimmt werden, indem man Kaliumjodid hinzufügt und das entstandene Jod direkt mit Thiosulfat titriert.

Durchführung

Als Säulenmaterial dient eine *ca.* 3 cm hohe Schicht (auf Glasfritte G-1) von Aluminiumoxid ("Woelm neutral, zur Chromatographie"), darüber eine etwa 2 mm hohe Lage Cellulosepulver (MN-Cellulosepulver 300 nach E. Stahl zur Dünnschichtchromatographie, Macherey, Nagel u. Co., Düren) und als Abschluss nochmals etwa 5 mm Aluminiumoxid (wie oben). Diese drei Schichten werden einzeln mit 20%iger heisser Bariumnitratlösung eingeschlämmt. Diese Anordnung erwies sich nach zahlreichen Versuchen als optimal.

Die Silberlösung wird mit einigen Tropfen einer 5% igen Kaliumjodidlösung (jodatfrei!) versetzt und auf *ca.* 50° erwärmt. Nach dem Abkühlen wird der Niederschlag auf die Säule gespült und abgesaugt; dabei wird das Silberjodid von der Celluloseschicht gut festgehalten. Ueberschüssiges Jodid wird mit 1 ml 1.5 N Ammoniaklösung und Nachspülen mit 3–4 ml 20%iger Bariumnitratlösung entfernt. Sodann wird mit 3–4 ml Reagens A (5 ml Eisessig + 30 Tropfen Brom + 50 ml 20%ige Bariumnitratlösung) versetzt, dreimal mit je etwa 4 ml 20%iger Bariumnitratlösung gewaschen; hierauf 3–4 ml Reagens B (20%ige Kaliumjodidlösung + 20%ige Bariumnitratlösung 1:1) zugefügt und zunächst zweimal mit je etwa 1 ml 1.5 N Ammoniaklösung und einmal mit etwa 4 ml 20%iger Bariumnitratlösung gewaschen. Alle diese Schritte werden bis zur Erzielung der gewünschten Vervielfachung wiederholt. Es ist nötig, stets eine hohe Konzentration an Bariumnitrat auf der Säule zu haben, um Verluste von Bariumjodat zu vermeiden. Am Schluss wird schwach schwefelsaure 5%ige Kaliumjodidlösung auf die Säule gegeben und die aus der Umsetzung mit Bariumjodat entstehende

TABELLE IV

VERVIELFACHUNGEN VON SILBER

Gegeben (µg)	*Vervielfacht (×)*	*Gefunden (µg)*	*Gegeben (µg)*	*Vervielfacht (×)*	*Gefunden (µg)*
53.9	2	53.9	5.35	8	5.50
		54.9		10	5.21
21.4	2	20.8		14	5.48
	5	19.3		16	5.09
	7	19.7			
10.7	5	11.4			
		10.6			
		9.9			

Jodlösung in einer Vorlage aufgefangen und mit 0.02 *N* Natriumthiosulfatlösung titriert. Aus dem Verbrauch an Thiosulfat lässt sich unter Berücksichtigung des Vervielfachungsfaktors der LEIPERT-Methode (1 Ag ... 3 J_2) und der entsprechenden erzielten Vervielfachungszahl die ursprünglich vorhandene Silbermenge berechnen. Tabelle IV gibt einige Ergebnisse.

Die mit den drei hier beschriebenen Vervielfachungssystemen erzielten Ergebnisse zeigen, dass es möglich ist, sehr kleine Mengen verschiedener Substanzen so oft zu vervielfachen, dass sie der massanalytischen Bestimmung zugänglich werden. Zahlreiche andere Ionen sollten mit den geschilderten Systemen bestimmbar sein. Auch kann kein Zweifel darüber bestehen, dass noch neue derartige Vervielfachungssysteme möglich sind. So wurden bisher zum Beispiel keine organischen Fällungsreagenzien auf ihre Brauchbarkeit für derartige Reaktionsfolgen untersucht.

Es sollte hier zunächst nur über eine neue Möglichkeit zur Analyse sehr kleiner Probemengen berichtet werden.

An dieser Stelle sei Herrn Dr. C. TELLGMANN, Freiburg, für seine Hilfe bei Entwurf und Ausführung der Vervielfachungsapparatur bestens gedankt.

ZUSAMMENFASSUNG

Eine neue Art von Vervielfachungsreaktionen wird beschrieben, welche darauf beruht, dass durch aufeinanderfolgende, stöchiometrisch verlaufende Umsetzungen die Masse der zu bestimmenden Substanz oder deren Aequivalent vergrössert wird. Diese Reaktionsfolgen können beliebig oft wiederholt werden. Alle Reaktionen erfolgen im Chromatographierohr auf einer geeigneten Säule. Das angehäufte, vervielfachte Reaktionsprodukt wird am Schluss von der Säule gelöst und massanalytisch bestimmt. An drei Systemen wird die Methode erläutert. Vervielfacht werden direkt oder indirekt: Phosphat, Hexacyanoferrat(II), Chromat, Zink, Eisen und Silber. Es wird gezeigt, das derartige Vervielfachungen automatisiert werden können. Eine Reihe von Resultaten (Vervielfachungszahlen bis zu 153) zeigen die Brauchbarkeit der Methode.

SUMMARY

A new type of amplification reaction is described. The mass of a substance to be determined, or its equivalent, is increased by successive stoichiometric processes, the reaction sequence being repeated as often as required. All reactions are carried out on a chromatography tube on a suitable substrate. The accumulated amplified reaction product is finally dissolved from the column and titrated. The method is illustrated for three systems. Phosphate, hexacyanoferrate(II), chromate, zinc, iron and silver can be amplified directly or indirectly. The amplification technique can be automated. A series of results (with amplification factors up to 153) shows the utility of the method.

RÉSUMÉ

On décrit un nouveau type de réaction d'amplification. La masse d'une substance à doser, ou son équivalent, est augmentée par des processus stoechiométriques successifs, la séquence de la réaction est répétée aussi souvent qu'il est nécessaire. Toutes ces réactions sont effectuées sur une colonne chromatographique. Le produit de la réaction ainsi accumulé est finalement élué et titré. Phosphate, hexacyanoferrate(II), chromate, zinc, fer et argent peuvent être amplifiés directement ou indirectement. La technique d'amplification peut être rendue automatique. Une série de résultats (avec facteurs d'amplification jusqu'à 153) montre l'utilité de cette méthode.

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DETERMINATION OF TRACES OF FLUORINE OR SULFUR BY X-RAY ANALYSIS

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Because of the importance of the trace analysis of fluorine or sulfur, new, sensitive X-ray methods for the determination of these elements have been developed.

DETERMINATION OF FLUORINE

Elements with low atomic numbers such as Na, F, O, N, C, B, Be and Li cannot be determined with a conventional X-ray spectrograph. However, if a stoichiometric compound of a light element and a heavy element can be isolated for X-ray analysis, it is possible to determine the light element indirectly by measuring the amount of heavy element present[1]. Recent work in this laboratory has shown that microgram amounts of fluoride can be quantitatively precipitated with lanthanum, filtered on paper, washed free of excess lanthanum and determined by measuring the amount of lanthanum present in the precipitate[2]. In order to decrease adequately the solubility of the lanthanum fluoride, it is necessary to precipitate in 10 ml of 75% ethanol–water mixture. Under these conditions and if a suitable gathering precipitate is used, recovery of as little as 5 μg of fluoride is quantitative. Smaller amounts of fluoride will not precipitate. The lanthanum fluoride either precipitates completely or does not precipitate at all. This suggests that supersaturation occurs. In any event, in the proposed method, if 5 μg of fluoride is added to all samples, the calibration graph obtained over the range of 1 to 40 μg of added fluoride is linear and an excellent determination of as little as 1 μg of fluoride can be obtained. This indicates that the precipitation is quantitative and that it is possible to wash out the excess of lanthanum without loss of fluoride.

DETERMINATION OF FLUORINE AS LANTHANUM FLUORIDE

Reagents

Standard fluoride solutions (10 μg and 100 μg F/ml). Dissolve 0.211 g of dried reagent-grade sodium fluoride in water and dilute to 1 l (100 μg F/ml). Dilute 10.0 ml of this solution to 100 ml (10 μg F/ml). Transfer the solutions to polyethylene bottles.

Palladium solution (100 μg Pd/ml). Dissolve 16.6 mg of palladium chloride in 10 ml of hydrochloric acid (1+1) and dilute to 100 ml.

Buffer solution pH 4. Dissolve 74 g of anhydrous sodium acetate plus 286 ml of glacial acetic acid in 500 ml of water and dilute to 2 l.

Ethanol–fluoride solution. Mix 10.0 ml of sodium fluoride solution (10 μg F/ml) with 40 ml of water and dilute to 200 ml with ethanol.

Lanthanum nitrate solution. Dissolve 3 g of reagent-grade lanthanum nitrate hexahydrate in 100 ml of water and filter, if necessary.

Preparation of calibration graph

Transfer 0.0, 0.1, 0.2, 0.3 and 0.4 ml of standard sodium fluoride solution (100 μg F/ml) to 50-ml beakers. Add 2 ml of pH 4 buffer solution to each beaker followed by 0.5 ml of palladium chloride solution, 10.0 ml of ethanol-fluoride solution, 0.2 ml of lanthanum nitrate solution and 0.1 ml of dimethylglyoxime solution. Mix and allow to stand 15 minutes. Position a 25-mm, white, 2 μ disk of Millipore polyvinyl chloride (PVC; Polyvic; BSWP) and wet it with 50% ethanol solution. Clamp on a 15-ml cylindrical reservoir with a flared top. Add 2 ml of 50% ethanol solution containing a light suspension of pure carbon black to the reservoir and allow to drain. Police the beaker, containing the lanthanum fluoride, thoroughly and pour the solution as completely as possible to the reservoir. Allow to drain completely. Wash down the reservoir with 10 ml of 75% ethanol solution, added from a 50-ml beaker, and allow to drain completely. Dry the disk and take a 100-sec count on the X-ray spectrograph, using a tungsten target and a lithium fluoride crystal, at the wavelength of the Lα line of lanthanum. Plot the μg of fluoride added against the counts per sec.

Analysis of sample

Add 1 drop of phenolphthalein (ethanolic 1% solution) to the sample solution, neutralize to the pink color with 0.1% potassium hydroxide solution (w/v) and add 1 drop in excess. Evaporate in a platinum dish to about 0.5 ml. Pour and wash with 2 ml of pH 4 buffer solution to a 50-ml beaker. Add 0.5 ml of palladium chloride solution and 10.0 ml of ethanol–fluoride solution and then continue as directed in *Preparation of calibration graph*. Determine the weight of fluoride present with the help of the calibration graph.

Discussion

Precipitation of traces of lanthanum fluoride is less complete at pH 3 than at pH 4 or pH 5 and more complete in 75% ethanol–water mixture than in 50% ethanol–water mixture. Better recoveries and a more linear calibration graph are obtained if the precipitation is made in the presence of a little palladium dimethylglyoxime precipitate. The reason for this is not apparent but perhaps the organic precipitate gathers the lanthanum fluoride by occlusion or adsorption, or it may simply supply nucleation sites to initiate the precipitation. The palladium dimethylglyoxime precipitate was chosen since the organic reagent is virtually specific for palladium. It is true that when more than a few milligrams of nickel are present in the solution being analyzed, small amounts of this element will be precipitated at pH 4. However, no other elements that may be present will contaminate the fluoride precipitate. Attempts to use thorium in place of lanthanum were not successful because traces of fluoride do not precipitate.

If MF-Millipore paper is used in the filtration of ethanol solutions, the disks tend to curl badly on drying. However, it is possible to use such disks in a fluoride analysis provided that a little rhodamine B is added to the ethanol wash solution in order to stain the paper and provided that the disks are measured on the X-ray spectrograph while they are still damp. Disks made of PVC are not stained by rhodamine B and do not curl on drying.

Tests on the interference of other elements that may be present in a sample to be analyzed have shown that aluminum, even in small amounts, complexes the fluoride so strongly that it will not precipitate with lanthanum. The interference of iron(III) is less and that of borate still less. Nevertheless, in most instances, it will be necessary to resort to the use of a Willard and Winter distillation or an ion-exchange separation before attempting an analysis. After such a separation, the distillate or effluent must be made alkaline and evaporated to a small volume. According to McClure[3] this evaporation should be done in platinum ware in order to avoid loss of fluoride.

In the method described, 5 μg of fluoride is added to all samples. Another approach to the problem of correcting for the solubility of an isolated compound would be to saturate the solution in which the precipitation is to take place with the compound that is to be isolated. Such a procedure is feasible if the solubility of the compound is low and if supersaturation does not occur (see below).

Typical calibration graph data obtained with the proposed method are shown in Table I. If these data are plotted it is seen that the graph is linear.

TABLE I

CALIBRATION GRAPH DATA FOR DETERMINATION OF FLUORIDE

Fluoride added (μg)	*Counts per sec*	*Fluoride added (μg)*	*Counts per sec*
0	383	20	2346
1	480	30	3300
5	862	40	4257
10	1346		

DETERMINATION OF SULFUR

Recent semiquantitative work has shown that traces of sulfur can be determined by coprecipitation–X-ray analysis[2]. In this work the sulfur was precipitated as barium sulfate with selenate as a coprecipitant. The method has now been put on a quantitative basis. It has been shown that, if precipitation is made at pH 4 or pH 3 in 15 ml of 50% ethanol–water mixture saturated with barium sulfate, as little as 0.1 μg of sulfur can be separated and determined by X-ray measurement at the wavelength of the $K\alpha$ line of sulfur with a chromium target and a sodium chloride or graphite crystal; or that, by omitting the use of selenate as a coprecipitant, as little as 1 μg of sulfur can be determined by measuring the sulfur in the same manner or the barium at the wavelength of the $L\alpha$ line of barium using a chromium target and a lithium fluoride crystal.

The method appears to be applicable in the presence of milligram quantities of several other elements. When, however, an analysis of traces of sulfur in large samples of salts, ores, metals or alloys is desired it will be necessary to use the distillation–sulfide method for the analysis[4]. In the original distillation method, the collected H_2S is converted to lead sulfide and determined spectrophotometrically; the method is useful down to about 1 μg of sulfur. In order to gain additional sensitivity, some workers have modified the distillation apparatus by using a water-cooled condenser to prevent hydriodic or hydrochloric acid from accompanying the hydrogen sulfide. The hydrogen sulfide is collected in a buffered solution of zinc acetate and is then determined by the methylene blue spectrophotometric method. It has been shown that a much simpler way to achieve additional sensitivity is to filter the precipitated lead sulfide, wash free of excess lead and then determine the sulfur or lead in the precipitate by X-ray analysis. Even better results are obtained if cadmium is used in place of lead. As little as 0.1 μg of sulfur can be distilled and determined with good accuracy by this method.

DETERMINATION OF SULFUR AS BARIUM SULFATE

Reagents

Standard sulfur solutions. Dissolve 0.544 g of pure dry potassium sulfate in water and dilute to 1 l (100 μg S/ml). Prepare 10 μg S/ml and 1 μg S/ml solutions by volumetric dilution.

Selenate solution (200 μg Se/ml). Dissolve 48 mg of anhydrous sodium selenate in 100 ml of water.

Buffer solution pH 4. See p. 246.

Buffer solution pH 3. Mix 250 ml of pH 4 buffer solution with 200 ml of glacial acetic acid.

Ethanol–buffer solution. Dissolve 0.2 g of barium chloride dihydrate in 100 ml of water in a 1-l volumetric flask. Add 10 ml of standard sulfur solution (100 μg S/ml) plus 125 ml of pH 4 or pH 3 buffer solution plus 500 ml of ethanol. Dilute to 900 ml and cool. Then dilute to the mark and mix. Allow to stand for 3 h and then filter on a 47-mm, white, 0.8-μ Millipore paper disk using gentle suction. Discard the paper. Store the solution in a stoppered glass bottle.

Preparation of calibration graphs

Transfer aliquots of an appropriate standard sulfur solution to 50-ml beakers. The aliquots taken should not exceed 0.5 ml and, depending on the concentration range of interest, should contain 0, 0.1, 0.5 and 1.0 μg or 0, 5.0, 10.0, 20.0, 30.0 and 40.0 μg of sulfur. Add 0.25 ml of selenate solution and mix. Add 15.0 ml of ethanol-pH 4 or pH 3 buffer solution, swirl and allow to stand for 15 min, or 5 min if more than 1 μg of sulfur is present. Police the beaker thoroughly and filter with gentle suction on a carbon stained PVC disk. Allow the solution to drain completely. Then add 2 ml of 50% ethanol solution to the reservoir, pouring the solution directly onto the paper disk. Allow the solution to drain completely. Dry the disk and then take a 100-sec count on the X-ray spectrograph, using a chromium target and a sodium chloride or graphite crystal at the wavelength of the Kα line of sulfur. Prepare calibration graphs covering the appropriate range of sulfur concentration by plotting μg of sulfur added against counts per second (2).

Analysis of sample

Convert the sulfur in the sample to the sulfate form. Evaporate in a 50-ml beaker to moist dryness to expel unwanted acids. Dissolve the residue in 0.5 ml of water, cool, add selenate and proceed as directed in *Preparation of calibration graphs*. Determine the amount of sulfur present with the help of the appropriate calibration graph.

Discussion

Traces of sulfate sulfur can be quantitatively precipitated from a saturated solution of barium sulfate in 50% or 75% ethanol–water mixture containing pH 3, 4 or 5 buffer solution. However, in order to prevent hydrolysis of other metals that may be present in the sample to be analyzed, it would seem desirable to avoid the use of pH 5 buffer solution.

When selenate is used as a coprecipitant the calibration graphs obtained over the ranges 0–1 μg or 0–40 μg of sulfur are linear (Table II). The barium selenate present on the disks causes a slight but unimportant reduction in the net counts for sulfur. If selenate is not used, the sulfur content of a sample can be determined by washing the reservoir and precipitating on the paper disk with 10 ml of 50% ethanol and then measuring the X-ray counts for sulfur or barium. The calibration graphs obtained for sulfur or barium are both linear when more than 1 μg of sulfur is present. However, when the amount of sulfur present is less than 1 μg the graphs curve slightly, showing that precipitation of the sulfate is not quite complete (Table II).

TABLE II

CALIBRATION GRAPH DATA FOR PRECIPITATION OF SULFUR AS BARIUM SULFATE

Sulfur added (μg)	*Counts per sec*			
	No selenate used		*Selenate used*	
	pH 4 S (Kα)	*pH 4 Ba (Lα)*	*pH 3 S (Kα)*	*pH 4 S (Kα)*
0	35	160	53	59
0.1	40	280	62	68
0.5	78	527	91	92
1.0	140	715	140	125
5.0	470	2164	360	385
10.0	901	4123	708	734
20.0	1667	7676	1438	1460
30.0	2521	11870	2070	2176
40.0	3183	15491	2660	2800

TABLE III

PRECIPITATION OF 1 μg OF SULFATE SULFUR IN THE PRESENCE OF IRON OR NICKEL

Metal added (mg)	*Counts per sec*	
	pH 3	*pH 4*
0	116	99
0.1 Fe	118	100
1.0 Fe	114	100
5.0 Fe	113	100
1.0 Ni	110	105
5.0 Ni	114	101

The proposed method for sulfur just described will not be applicable in the presence of large amounts of other elements, but limited data show that as little as 1 μg of sulfate sulfur can be quantitatively precipitated in the presence of a few milligrams of iron or nickel (Table III). A distinct advantage of the barium sulfate method over the distillation method to be described below is that selenium(IV) causes no interference.

The effect of temperature on the solubility of barium sulfate in 50% ethanol–buffer solution is not known. Hence, it would appear wise, in those instances where the temperature in the laboratory varies widely, to filter only enough of the barium sulfate-saturated 50% ethanol–buffer solution for the analyses to be made during the day.

DETERMINATION OF SULFUR AS CADMIUM SULFIDE

Reagents

Hydriodic–hypophosphorous acid mixture. Transfer 200 ml of hydriodic acid (s.g. 1.70) plus 50 ml of 50% hypophosphorous acid to a 500-ml standard taper conical flask. Cap with a distilling head (ASTM Apparatus 6B)[5], connect to a flow of nitrogen gas (100 ml of water displaced in 1 min) and heat at 100–110° on a hotplate for 1 h. Discard the distillate. Remove the head, cover and cool.

Cadmium nitrate solution. Dissolve 0.275 g of cadmium nitrate tetrahydrate in 100 ml of water.

Preparation of calibration graphs

Transfer aliquots of standard sulfur solutions, containing 0, 0.1, 0.5 and 1.0 μg or 0, 5.0, 10.0, 20.0, 30.0 and 40.0 μg of sulfur, to 125-ml standard taper flasks and evaporate to about 0.5 ml. Cool and add 5 ml of redistilled hydrochloric acid[4] followed by 15 ml of hydriodic–hypophosphorous acid mixture, wetting the standard taper joint in the process. Cap with a distillation head and place on a 150° hotplate with a flow of nitrogen gas (100 ml of water displaced in 1 min) bubbling into the flask and thence into the bottom of a tall 25-ml graduate, containing 15 ml of ammonium hydroxide (1+2), which is resting in a 600-ml beaker filled with cold water. Allow to remain on the plate for 5 min after the first appearance of white fumes above the ammonium hydroxide solution, or for 10 min in all if such fumes do not appear.

Raise the flask off the plate and immediately pour the ammonium hydroxide solution into a 50-ml beaker containing 1 ml of cadmium nitrate solution. Swirl and filter immediately on a 25 mm, 0.8 μ, white MF-Millipore paper disk and allow to drain. Wash the reservoir and disk with 10 ml of aqueous 0.001% rhodamine B solution and allow to drain completely. Dry the disk and then take a 100-sec count on the X-ray spectrograph at the wavelength of the Kα line of sulfur using a chromium target and a sodium chloride crystal or at the wavelength of the Lβ line of cadmium using a chromium target and a lithium fluoride crystal. Prepare appropriate calibration graphs.

Analysis of sample

Prepare the sample for analysis as directed elsewhere[4]. Cool, add 15 ml of hydriodic–hypophosphorous acid mixture and proceed as directed in *Preparation of calibration graphs*.

Discussion

Calibration graph data for the precipitation of sulfide with cadmium or lead are shown in Table IV. When the cadmium sulfide data are plotted it is seen that the graphs for both sulfur and cadmium are linear. It seems probable that deviation from linearity may be encountered when more than 40 μg of sulfur is present. This deviation may be caused by attainment of infinite thickness or by absorption of sulfur radiation by the cadmium or absorption of cadmium radiation by sulfur. When the ammonium hydroxide distillate is poured into a swirled mixture of 1 ml of aqueous 0.2% (w/v) solution of hydrated lead acetate and 1 ml of aqueous 2% (w/v) solution of citric acid, the graphs obtained for lead are linear but those for sulfur are very curved, showing that lead absorbs the sulfur radiation strongly. Hence, the sulfide must be precipitated with cadmium rather than lead if the sulfur is to be determined by measurement at the Kα line of sulfur. It may be that experience will show that linearity will extend to amounts of sulfur over 40 μg when lead is used and the amount of lead present in the precipitate is measured.

TABLE IV

CALIBRATION GRAPH DATA FOR PRECIPITATION OF SULFUR AS CADMIUM OR LEAD SULFIDE

Sulfur added (μg)	*Counts per sec*			
	Cadmium sulfide		*Lead sulfide*	
	S(Kα)	*Cd(Lβ)*	*S(Kα)*	*Pb(Lα)*
0	49	128	57	210
0.1	52	138	33	189
0.5	91	215	66	258
1.0	141	310	100	336
10.0	818	1467	859	1709
20.0	1479	2738	1554	3148
30.0	2226	3946	2124	4552
40.0	2895	5150	2555	5853

In the preparation of calibration graphs it has been observed that, at times, the counts obtained for the blank sample are higher than for the sample to which 0.1 μg of sulfur has been added. It may be that this is due to the fact that the blank was usually run first and that the distillation head was cleansed of sulfur in the first run.

SUMMARY

New X-ray methods have been developed for the determination of as little as 1 μg of fluorine or as little as 0.1 μg of sulfur. Fluorine as fluoride is precipitated as lanthanum fluoride in 75% ethanol–water mixture and determined by measuring the amount of lanthanum present in the precipitate. Sulfur as sulfate is precipitated as barium sulfate from a barium sulfate saturated 50% ethanol–buffer mixture, using selenate as a coprecipitant, and determined by measuring the amount of sulfur present. Sulfur as sulfide is precipitated as cadmium sulfide and determined by measuring the amount of sulfur or cadmium in the precipitate.

RÉSUMÉ

Des méthodes aux rayons-X sont proposées pour le dosage du fluor ou du soufre en faibles teneurs (jusqu'à 1 μg de fluor et 0.1 μg de soufre). Les fluorures sont précipités sous forme de fluorure de lanthane dans l'éthanol à 75% et dosés en mesurant la quantité de lanthane présente dans le précipité. Le soufre à l'état de sulfate est précipité comme sulfate de baryum à l'aide d'une solution saturée de sulfate de baryum dans l'alcool à 50%. Le soufre à l'état de sulfure est précipité comme sulfure de cadmium. On mesure la teneur en soufre ou en cadmium dans le précipité.

ZUSAMMENFASSUNG

Es wird eine röntgenspektralanalytische Methode zur Bestimmung von 1 μg Fluor oder 0.1 μg Schwefel beschrieben. Dabei wird das Fluor aus 75%igem Alkohol als Lanthanfluorid gefällt und im Niederschlag das Lanthan bestimmt. Sulfatschwefel wird als Bariumsulfat zusammen mit Selenat aus einer gesättigten, gepufferten, 50%igen äthanolischen Lösung gefällt und im Niederschlag der Schwefel bestimmt. Sulfidschwefel wird als Cadmiumsulfid gefällt und hier entweder der Schwefel oder das Cadmium analysiert.

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A FLUORIMETRIC KINETIC METHOD FOR THE DETERMINATION OF ORGANOPHOSPHORUS AND ORGANOCARBONYL COMPOUNDS

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A colorimetric reaction for the detection and determination of nerve gases such as Sarin was first described by SCHOENEMANN[1]. This reaction is based on the principle that perphosphonates, formed in the reaction of pentavalent phosphorus compounds with peroxides, oxidize dyes such as *o*-tolidine or *o*-dianisidine at much faster rates than peroxides alone. An excellent review of the chemistry of the SCHOENEMANN reaction has been written by CRABTREE AND POZIOMEK[2]. GEHAUF *et al.*[3] have described a quantitative method for organophosphorus compounds based on this reaction, using *o*-dianisidine as dye, that had excellent specificity but lacked sensitivity.

GEHAUF AND GOLDENSON[4] proposed the use of indole as a fluorogenic dye for the SCHOENEMANN reaction, and developed a qualitative method for the nerve gas Sarin. The non-fluorescent indole was oxidized to the highly fluorescent indigo white by the perphosphonate. The peak fluorescence formed in 1 min was a qualitative measure of the Sarin present (0.05 μg detectable). Because the fluorescent compound formed, indigo white, was quickly air-oxidized to the non-fluorescent indigo blue, it was difficult to obtain good accuracy (ca. 10%) and the fluorescence had to be quickly read after the addition of reagents. Varying amounts of a phosphorus compound resulted in varying times for the production of the peak fluorescence.

In the present study a search was made for substrates, themselves non-fluorescent, which might be oxidized to highly fluorescent molecules by perphosphonates. Further, it was hoped that the SCHOENEMANN reaction could be applied to the quantitative determination of low concentrations of a wide range of organic compounds with both high precision and accuracy.

Of all the fluorogenic substrates tested, indole and homovanillic acid proved to be the best, and methods were developed for the determination of 0.01–100 μg per ml of benzoyl chloride, benzoyl bromide, DFP (diisopropylphosphorofluoridate), parathion, methyl parathion, phthalic anhydride, diethylchlorophosphate and dimethyl chlorothiophosphate, by an initial rate method with an accuracy and precision of about 1.5%.

EXPERIMENTAL

Reagents

Substrates. Stock 1 mg/ml solutions were prepared of all compounds: benzoyl chloride (Eastman Organics), benzoyl bromide (Matheson, Coleman and Bell), parathion and methyl parathion (Monsanto), phthalic anhydride (J.T. Baker Chemical

Co.), diisopropylphosphorofluoridate (DFP), diethyl chlorophosphate (DECP), dimethyl chlorothiophosphate (DMCTP) and ethyl dichlorophosphate (EDCP) (Aldrich Chemical Co.). Reagent-grade acetone (J.T. Baker) was used in the preparation of all solutions.

Indole. A 10 mg/ml solution of indole (Calbiochem Co.) was prepared in acetone. Solutions are stable for about 5 days if refrigerated when not in use.

Homovanillic acid. A 1 mg/ml solution was prepared in water. The solution is stable indefinitely.

Sodium perborate ($NaBO_3 \cdot 4H_2O$ *or* $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, *J. T. Baker*). Stock 10 mg/ml solutions in water were prepared fresh daily.

Tris buffer. 0.2 *M*, pH 8.50, was prepared by dissolving tris-(hydroxymethyl) aminomethane (Sigma Chemical) in distilled water. The pH was adjusted to 8.50 with concentrated hydrochloric acid.

Apparatus

An Aminco fluoromicrophotometer, equipped with a Beckman linear recorder and a water bath for temperature control, was used in most studies. Alternatively, a Turner model 111 filter fluorimeter with a linear recorder was used. A Corning 7-60 primary filter was used in all studies. With indole a Kodak Wratten 3 and 48 combination secondary filter was employed; with HVA, a Kodak Wratten 2A and 47B filter combination was used.

A 0.01 μg/ml solution of quinine sulfate in 0.1 *N* sulfuric acid was used to standardize the fluorimeters daily in order to allow reproducible results.

Procedures

Determination of DECP and DMCTP. To 0.5 ml of indole add 0.5 ml of water, 1.0 ml of tris buffer and 1.0 ml of sodium perborate. Adjust the fluorescence of the solution to read zero. At zero time, add 2.0 ml of an acetone solution of DECP or DMCTP, and measure the inital rate of production of fluorescence per minute, ΔF/min. From a calibration plot of ΔF/min *vs.* concentration, determine the amount of substrate present.

Determination of DFP, parathion, methyl parathion, benzoyl chloride, phthalic anhydride and benzoyl bromide. Mix indole, water, sodium perborate and an acetone solution of the sample to be analyzed in the amounts given below, and measure the rate of production of fluorescence with time, ΔF/min, or the rate of decrease of fluorescence, $-\Delta F$/min. Determine the amount of these substances present from calibration plots as above.

Substrate (ml)		*ml indole*	*ml* H_2O	*ml* $NaBO_3$	*Method*
DFP	1.5	0.5	1.5	0.5	ΔF/min
Parathion	1.0	0.5	0	1.5	ΔF/min
Methyl parathion	1.5	0.5	1.0	1.0	ΔF/min
Benzoyl bromide	1.2	0.3	1.35	0.15	$-\Delta F$/min
Benzoyl chloride	2.0	0.5	2.0	0.5	$-\Delta F$/min
Phthalic anydride	1.0	0.5	1.25	0.25	$-\Delta F$/min

Determination of benzoyl chloride and bromide. HVA procedure. To 2 ml of HVA add 1 ml of sodium perborate and 2 ml of an acetone solution of the substance to be determined. Measure the rate of production of fluorescence with time, ΔF/min, and calculate the amount of benzoyl chloride or bromide present from calibration plots of ΔF/min *vs.* concentration.

RESULTS

Some typical results obtained in the determination of substances with indole by an initial rate method (ΔF/min) are indicated in Table I. Diethylchlorophosphate (DECP), diisopropyl phosphorofluoridate (DFP), and parathion were determined with relative errors of ± 0.67, 1.8 and 0.38%, respectively. The range of all substances determinable together with the accuracy and precision obtainable is indicated in

TABLE I

RESULTS OF THE DETERMINATION OF SUBSTRATES WITH INDOLE

Diethyl chlorophosphate (μg/ml)		*DFP (μg/ml)*		*Parathion (μg/ml)*	
Present	*Found*[a]	*Present*	*Found*[a]	*Present*	*Found*[a]
2.0	2.05	0.470	0.470	16.6	16.6
20.0	20.0	0.940	0.980	33.3	33.5
35.0	35.0	4.70	4.84	66.6	66.3
70.0	70.5	7.05	6.90	83.3	82.8
100.0	99.9	47.0	47.1	166.6	166.9

	Rel. error (%)		
	DECP	*DFP*	*Parathion*
	+2.5	0.0	0.0
	0.0	+4.0	+0.6
	0.0	+3.1	−0.5
	+0.7	−2.1	−0.6
	−0.1	+0.2	+0.18
Av. rel. error	±0.67	±1.8	±0.38

[a] Average of 3 or more determinations with a relative standard deviation of ± 1.5%.

TABLE II

RANGES OF SUBSTANCES DETERMINABLE WITH INDOLE AS INDICATOR

Substance	*Range (μg/ml)*	*Rel. error (%)*
Benzoyl chloride	0.02– 20	±1.8[a]
Benzoyl bromide	0.02– 20	±2.0[a]
Phthalic anhydride	0.08– 4.0	±1.32[a]
Diisopropyl phosphorofluoridate	0.4 – 50	±1.8[b]
Methyl parathion	2.5 – 25	±2.16[a]
(Ethyl) parathion	16 –167	±0.38[a]
Dimethyl chlorothiophosphate	2 – 80	±4.1[b]
Diethyl chlorophosphate	2 –100	±0.67[a]

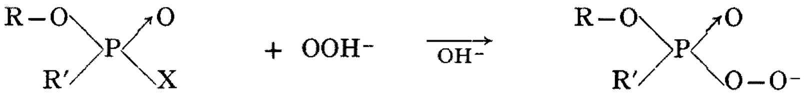
[a] Average of 3 or more determinations with precision of ± 1.5%.
[b] Average of 3 or more determinations with precision of ± 1.8%.

Table II. In general 0.02–100 μg/ml of the organic phosphorus and carbonyl compounds can be determined with precisions and accuracies better than ± 2%.

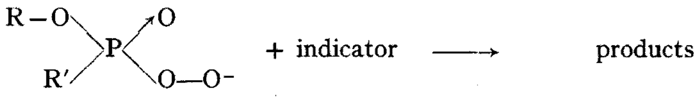
DISCUSSION

Effect of indicators

The Schoenemann reaction is based on the oxidation of a suitable reagent by an alkaline peroxide solution of an organophosphorus compound. In the initial step (eqn. (1)) a perphosphonate is formed from the phosphorus compound. This perphosphonate then oxidizes the reagent to give a colored, fluorescent or chemiluminescent material (eqn. (2)).



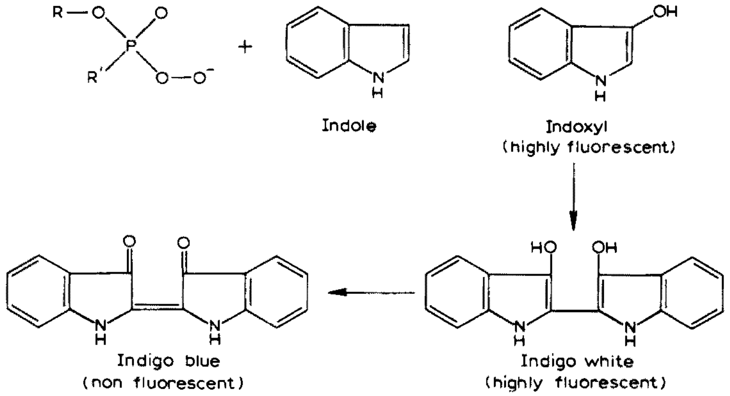
(1)



(2)

All pentavalent phosphorus compounds having a residual positive charge on the phosphorus atom, allowing nucleophilic displacement of a labile anionic group by perhydroxyl ion, should undergo this Schoenemann reaction[5].

Over 240 dyes have been tried in the Schoenemann reaction[3]. The most significant reagents have been *o*-dianisidine and triarylmethane compounds which yield colored products, luminol which yields a chemiluminescence, and indole which is oxidized to a fluorescent product[3]. The most sensitive reagent is indole; with this reagent as little as 0.05 μg of Sarin was reported detectable. Because of the high rate of oxidation of indigo white to the non-fluorescent indigo blue, good accuracies cannot be obtained from a measurement of the total fluorescence formed.



A search was made for other reagents which might yield a highly fluorescent species upon oxidation. Homovanillic acid[6], reduced resorufin[7], and diacetyl dichlorofluorescein[8] were tested, and compared to indole in stability to air oxidation, stability to oxidation by peroxide in the absence of organophosphorus compound, and ease of oxidation by the perphosphonate anion. The reduced forms of resorufin and diacetyl dichlorofluorescein are both easily air-oxidized and were not judged stable enough for routine laboratory use. In addition, they are both slowly oxidized by perphosphonate.

Homovanillic acid is extremely stable in aqueous solution, and solutions of this reagent could be used for up to a year with no appreciable oxidation observed. In contrast, indole is slowly oxidized by air, and solutions of this reagent must be discarded after about 5 days (Fig. 1). Both are stable to peroxide, and indole is oxidized by perphosphonate at about 10 times the rate of homovanillic acid. Some typical results obtained in the use of both indole and homovanillic acid are indicated in Table III. Indole allowed the determination of 0.01–25 μg/ml of benzoyl chloride, whereas only 10–500 μg/ml could be assayed with homovanillic acid. Thus, from the aspect of sensitivity, indole was judged to be the best indicator.

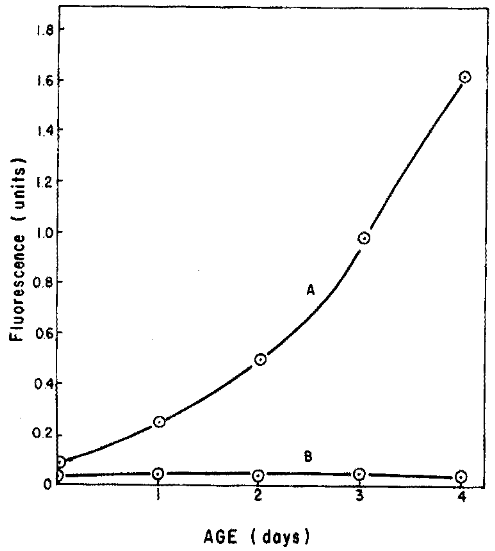


Fig. 1. Stability of indole (A) and homovanillic acid (B) in solution. The fluorescence of a stock solution of each reagent is plotted *vs.* the age of the solution in days.

TABLE III

COMPARISON OF RESULTS OBTAINED USING INDOLE AND HVA AS INDICATORS FOR THE DETERMINATION OF BENZOYL CHLORIDE

Indole method (μg/ml)			*HVA method (μg/ml)*		
Added	*Found*	*Rel. error (%)*	*Added*	*Found*	*Rel. error (%)*
0.0200	0.0210	+5.0	10.0	10.0	0.0
0.100	0.102	+2.0	20.0	18.8	−1.2
1.00	1.00	0.0	50.0	52.0	+4.0
10.0	10.08	+0.8	75.0	73.5	−2.0
20.0	20.2	+1.0	100.0	101.0	+1.0
Av. rel. error		±1.8			±1.6

A study was next made of the conditions for assay in order to improve the sensitivity, accuracy and precision of analyses.

A typical curve obtained in an analysis with indole is pictured in Fig. 2. Under assay conditions described in the experimental section, Curve A was obtained with 3.33 μg per ml of phthalic anhydride; Curve B, 2.50 μg per ml; Curve C, 1.66 μg per ml; Curve D, 0.833 μg per ml; Curve E, 0.166 μg per ml. These curves are representative of all compounds run with indole as indicator. An initial rate of increase of fluorescence with time is observed, owing to formation of indigo white. A peak fluorescence is reached. Then a rate of decay of fluorescence with time is obtained, owing to oxidation of indigo white to the non-fluorescent indigo blue. From these curves calibration plots of $+\Delta F$/min, peak fluorescence, or $-\Delta F$/min *vs.* concentration can be constructed and used for the determination of the organophosphorus or organocarboxyl compound. All three sections of this curve (the rate of formation of fluorescence, the time required to reach a peak fluorescence, and the rate of decay of fluorescence) will depend upon the nature of the organic compound, and the rate at which it forms a perphosphonate or percarbonyl anion. With compounds such as Sarin, benzoyl chloride, phthalic anhydride and benzoyl bromide, which rapidly form the peroxy anion,

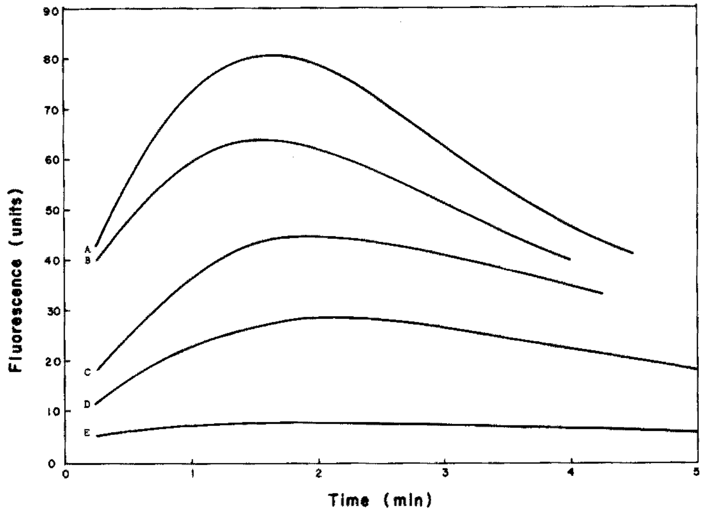
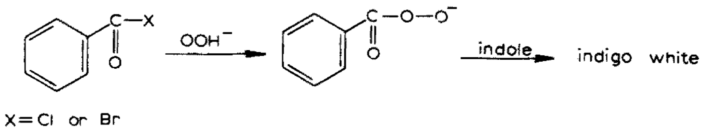


Fig. 2. Fluorescence *vs.* time curves obtained in an analysis of phthalic anhydride using indole as indicator. (A) 3.33 μg/ml, (B) 2.50 μg/ml, (C) 1.66 μg/ml, (D) 0.833 μg/ml, (E) 0.166 μg/ml.



very high rates of formation of fluorescence with time, ΔF/min, are observed, and the peak fluorescence is formed within 1–2 min. For best results in these systems the rate of decay of fluorescence with time, $-\Delta F$/min, is measured and equated to concentration. Attempts to measure ΔF/min and peak fluorescence result in high errors for these compounds (Table IV).

With other compounds that form perphosphonate or peroxy anions less readily such as DFP, ethyl parathion, methyl parathion, dimethyl chlorothiophosphate and diethyl chlorophosphate, the initial rate of production of fluorescence with time, ΔF/min, can be used as a measure of the concentration of these substances.

TABLE IV

COMPARISON OF RESULTS OBTAINED IN THE DETERMINATION OF PHTHALIC ANHYDRIDE BY THE INITIAL RATE, DECREASING RATE AND TOTAL FLUORESCENCE METHODS

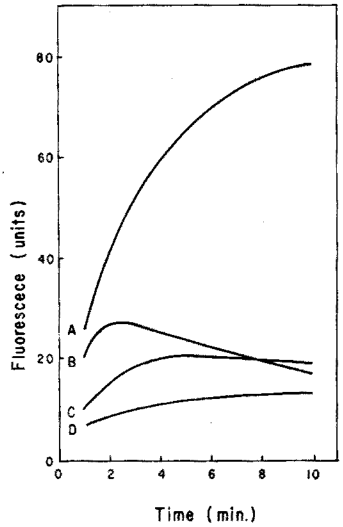
Added (µg/ml)	*Found (µg/ml)*			*Rel. error (%)*		
	ΔF/*min*	$-\Delta F$/*min*	*F(peak)*	ΔF/*min*	$-\Delta F$/*min*	*F(peak)*
0.0833	0.060	0.0833	0.833	−29.0	0.0	0.0
0.166	0.180	0.160	0.160	+ 8.0	−3.9	−4.0
0.833	0.937	0.820	0.850	+12.9	−1.6	+2.3
2.50	2.27	2.50	2.46	− 9.4	0.0	+1.8
3.33	3.23	3.36	3.33	− 3.0	+0.9	−1.5
Av. rel. error				±12.5	±1.3	±1.91

Effect of reagent concentrations

The optimum conditions for analysis vary from compound to compound. The rate of reaction, expressed as the rate of production of fluorescence with time, can be accelerated by making the solution more alkaline or by increasing the concentration of the sodium perborate (which supplies perhydroxyl ion as well as the proper alkalinization for the reaction), but the pH of the test solution must be kept below about 10. Below pH 8, development of fluorescence is negligible. As the pH is increased, both the rate of formation of fluorescence and the intensity of fluorescence increases. At high pH values, peroxide becomes a strong oxidizing agent and direct oxidation of indole by peroxide occurs, giving high blanks. Moreover, above pH 12, the rate of hydrolysis of the phosphorus and carbonyl compounds increases appreciably, and low results are obtained. For reproducible results, careful control of pH is essential.

By a control of the perborate concentration, the pH was adjusted to values between 8.5–10, the actual pH depending on the compound to be determined. Figure 3 shows some typical curves obtained in the analysis of diethyl chlorophosphate as a function of pH. The pH was adjusted with 0.1 M tris buffer to a value that resulted in a high initial rate, but one that was not too high to be measured. With DECP, DMCTP and EDCP this optimum pH is about 8.5. Because solutions of these three compounds are acidic, it was found that tris buffer was needed, in addition to sodium perborate, to maintain the pH at the desired level.

The effect of indole on the fluorescence *vs.* time curves is indicated in Fig. 4 for a typical compound, diethyl chlorophosphate. Increasing the indole concentration causes an increase in the rate of production of the fluorescent indigo white, but higher fluorescent blanks are also observed as the indole concentration is increased. An overall indole concentration of 1 mg/ml was judged to be optimum for analysis of most substances.



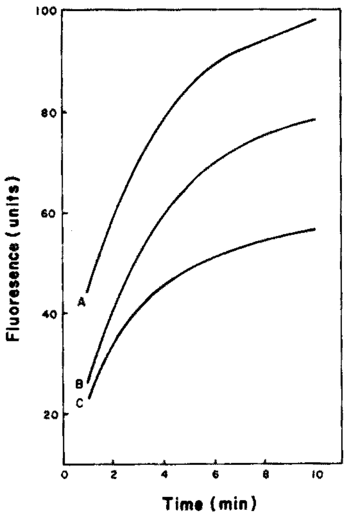


Fig. 3. pH dependence of fluorescence *vs.* time curves obtained in the analysis of diethyl chlorophosphate (DECP). [DECP] = 100 μg/ml; [$NaBO_3$] = 10 mg; [H_2O] = 2.5 ml; [acetone] = 2.5 ml; [tris buffer] = $2 \cdot 10^{-4}$ *M*. (A) pH 8.5, (B) pH 9.5, (C) pH 9.0, (D) pH 8.0.

Fig. 4. Effect of indole concentration on the fluorescence–time curves obtained in the analysis of diethyl chlorophosphate (DECP). Experimental conditions as described in the legend of Fig. 3, pH 8.50. (A) 2 mg/ml, (B) 1 mg/ml, (C) 0.5 mg/ml.

Effect of solvent

Because of the extremely rapid rate of hydrolysis of many of the organophosphorus and carbonyl compounds, the reaction must be carried out by the addition of the compound in a non-aqueous, non-alcoholic solvent, such as acetone, to a solution containing the alkaline peroxide and the indicator.

The sensitivity of the SCHOENEMANN reaction is increased by the presence of acetone, but the function of the acetone is not clearly understood[3]. KRAMER[9] postulated a complex formed by an interaction between the perhydroxy ion and the carbonyl group of acetone. This acetone-peroxide complex was considered capable of reacting with the organophosphorus and carbonyl compounds faster than with the peroxide alone. Only small quantities of acetone appear to be needed.

Interferences

Other pentavalent phosphorus compounds, such as phosphorus oxychloride and phosphorus pentachloride, will also give a SCHOENEMANN reaction, but trivalent phosphorus compounds do not interfere. Other organic compounds that react include aldehydes that form peracids, some esters, acid chlorides and arylsulfonyl halides.

Strong oxidizing agents give fluorescence in the SCHOENEMANN reaction by direct reaction with the indicator. Ozone, chlorine, etc., interfere in this manner. Other interferences include inorganic ions such as copper, iron and manganese which react with peroxide to form peracids. This latter interference can be eliminated by the use of a complexing agent such as Calgon.

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SUMMARY

A direct reaction rate method is proposed for the rapid, sensitive determination of organophosphorus and organocarbonyl compounds, based on a fluorimetric SCHOENEMANN reaction. From 0.02 to 100 μg/ml of benzoyl chloride, benzoyl bromide, phthalic anhydride, diisopropyl phosphorofluoridate, parathion, methyl parathion, diethyl chlorophosphate and dimethyl chlorothiophosphate can be determined with an accuracy and precision of about 1.5%.

RÉSUMÉ

Une méthode cinétique fluorimétrique est proposée pour le dosage rapide et sensible des composés organophosphorés et organocarbonyles, basée sur une réaction fluorimétrique de Schoenemann. On peut ainsi doser avec exactitude et une précision de 1.5% de 0.02 à 100 μg/ml de chlorure de benzoyle, de bromure de benzoyle, d'anyhdride phtalique, de diisopropylphosphofluoridate, de parathion, de méthyl-parathion, de diéthylchlorophosphate et de diméthylchlorothiophosphate.

ZUSAMMENFASSUNG

Eine kinetische Methode wird zur schnellen empfindlichen Bestimmung von Organophosphor- und Organocarbonyl-Verbindungen vorgeschlagen. Das Verfahren beruht auf der fluorimetrischen Reaktion nach Schoenemann. Folgende Verbindungen können im Bereich von 0.02 bis 100 μg/ml mit einer Reproduzierbarkeit und Richtigkeit von etwa 1.5 % bestimmt werden: Benzoylchlorid, Benzoylbromid, Phthalsäureanhydrid, Diisopropylphosphorofluoridat, Parathion, Methylparathion, Diaethylchlorophosphat und Dimethylchlorothiophosphat.

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THE DETERMINATION OF TRACES OF ANTIMONY, TIN AND ARSENIC IN CADMIUM BY PULSE POLAROGRAPHY

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Antimony, tin and arsenic are minor trace constituents in pure commercial cadmium products, their content usually being lower than 5–10 p.p.m.

Traces of antimony in cadmium have already been determined by emission spectrography[1,2], photometry[3,4] and polarography[5]. Emission spectrography[1,6] and the Gutzeit test[7] have been used for the determination of traces of arsenic impurities in cadmium. Tin has been determined almost exclusively by emission spectrography[1,2,6,8–10] which allows the detection of down to about 1 p.p.m., without previous separation. However, most of these determinations have been performed after a previous separation because of interference from the matrix element or other trace constituents often present in excess, or to lower the detection limit by a concentration enrichment.

This investigation deals with the determination of trace impurities of antimony, tin and arsenic in cadmium and its compounds by pulse polarography. This technique, already applied for the determination of bismuth, copper, lead[11] and thallium[12] in cadmium products, allows a much higher sensitivity and a better resolution than classical polarography.

The characteristics of the reduction of tin(IV) and antimony(III) at a dropping mercury electrode in various supporting electrolytes are well suited for the polarographic determination of these elements. The arsenic(III) reduction step is often reported to be ill defined and to show an anomalous behaviour.

In several base electrolytes, antimony(III), tin(IV) and arsenic(III) are reduced at potentials sufficiently more positive than cadmium(II) to allow their direct determination. However, elements that may interfere are often present in excess. Thus, mutual interference often occurs in the bismuth(III), copper(II), antimony(III) group, while lead(II), thallium(I), tin(II) and arsenic(III) are also frequently reduced at comparable potentials.

EXPERIMENTAL

Apparatus and reagents

Pulse polarograph Southern type A 1700 Mark II. The measurement of peak heights and working conditions were described previously[11]. The derivative method of operation was used.

Analytical grade sulphuric and hydrobromic acid were redistilled; very pure potassium thiocyanate was obtained by electrolysis for 24 h in separate electrode compartments of a 5 *M* solution in water, at a cathode potential of −1.5 V *vs.* S.C.E.

Water, mercury, nitrogen, hydrochloric and nitric acid were purified as previously described[11]. All other reagents were of analytical grade and were used without further purification.

The antimony, tin and arsenic stocks were prepared, respectively, from analytical-grade antimony(III) oxide, tin(II) chloride and arsenic(III) oxide, and standardised. Dilute solutions were freshly prepared by appropriate dilution.

Polarographic data

Antimony. In many conventional supporting electrolytes, the antimony(III)–cadmium(II) half-wave potential difference is amply sufficient to allow the direct determination of antimony in cadmium. However, bismuth(III), copper(II) and sometimes lead(II), (these last two being nearly always present in excess) are reduced at similar potentials. In hydrochloric acid, antimony(III) is almost reversibly reduced at −0.15 V *vs.* S.C.E., the wave preceding the copper(II) wave (second step) by 70 mV. However, in the presence of 1–2 *M* cadmium(II) chloride, antimony(III) was found to be reduced more irreversibly at a potential more negative than copper(II). The separation between the two peaks is better, when the hydrochloric acid concentration is decreased; in 1–2 *M* cadmium(II) chloride–0.1 *M* hydrochloric acid, the difference between the copper(II) and antimony(III) peak potentials is about 80 mV. This allows the determination of antimony in presence of a ten-fold molar excess of copper. This is insufficient for most commercially available cadmium samples as they exhibit more unfavourable copper–antimony molar concentration ratios.

The possibility of a direct determination was further examined after addition of a complexing agent to the cadmium solution. In a cadmium–EDTA mixture, the bismuth(III) and antimony(III) peaks could not be separated sufficiently. In 1 *M* cadmium(II)–0.1 *M* malonic acid, the difference between the antimony(III) and copper(II) peak potentials was about 180 mV, while bismuth and lead did not interfere. The pulse polarographic sensitivity of antimony(III) in this medium is limited to *ca.* $5 \cdot 10^{-7}$ *M*, corresponding to a detection limit of about 0.5 p.p.m. antimony in cadmium, because of the interference of the cadmium(II) reduction at high instrumental amplification. In view of this rather low sensitivity, this method was not further investigated.

Preference was given to a preliminary separation of antimony from copper and the bulk of the cadmium (which ensured a concentration enrichment) followed by the determination in a hydrochloric acid supporting electrolyte. Antimony can be determined if the bismuth–antimony molar concentration ratio is lower than about 25; a 7 mV pulse amplitude is used after the level of the base line has been recorded at the antimony(III) peak potential. The pulse polarographic sensitivity of antimony(III) amounts to $6 \cdot 10^{-9}$ *M* (±10 mm peak height at maximal instrumental amplification; drop time, ±4 sec). A calibration graph in the $3 \cdot 10^{-8}$–10^{-5} *M* range showed a linear relationship between peak height and concentration. Figure 1 shows a typical pulse polarogram of antimony(III) in hydrochloric acid.

Tin. In strong chloride or bromide supporting electrolytes, tin(IV) is reported to give two reduction steps, both well suited to the polarographic determination of this element[13-15]. In 6 M hydrochloric acid, the tin(IV) → (II) reduction peak was about five times lower than that of the tin(II) → (0) reduction, and it merged partially with the oxidation slope of the mercury of the dropping electrode. The enhanced sensitivity of the first reduction reported in the presence of tetraphenylarsonium chloride[16,17] could not be reproduced. No use was therefore made of the tin(IV) → (II) reduction and in view of the interference of the excess amount of lead[11], preference was given to a prior separation of tin.

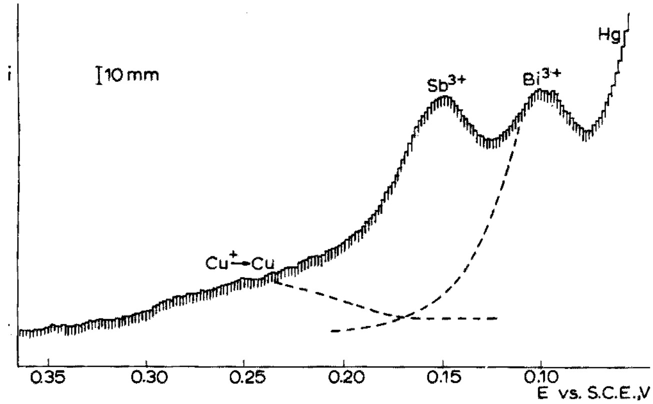

Fig. 1. Pulse polarogram of $1.24 \cdot 10^{-6}$ M Sb(III) in 2 M HCl+1% sodium hypophosphite, representing 0.195 p.p.m. Sb in very pure $Cd(NO_3)_2 \cdot 4\,H_2O$ (sample 5 from Table III, 7.74 g weight). Conditions: S 1/5, 7 mV, 9 int., 60 min/V, rec. 1 in/min.

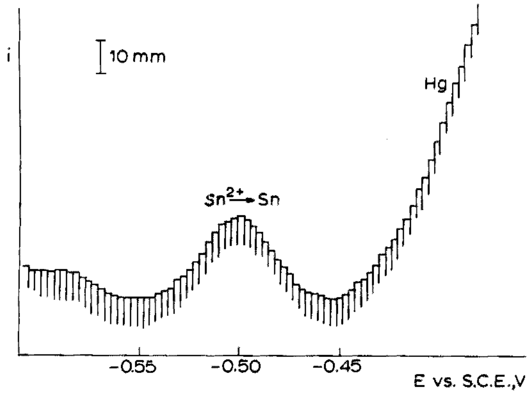

Fig. 2. Pulse polarogram of $2.45 \cdot 10^{-7}$ M Sn(IV) in 2 M HCl+2 M HBr, representing 0.050 p.p.m. Sn in analytical-grade cadmium (sample 3 from Table III, 5.82 g weight). Conditions: S 1/10, 35 mV, 3 int., 30 min/V, rec. 1 in/min.

The largest difference between the tin(IV) and lead(II) peak potentials (55 mV) was obtained in a 0.1 M potassium thiocyanate–0.01 M hydrochloric acid mixture. This allowed the determination of tin in the presence of an eight-fold excess of lead.

After the separation, tin was obtained in a hydrochloric–hydrobromic acid mixture. In a 2 M solution of both acids, tin(IV) gave a well-defined reversible reduction peak, so that the determination was possible down to 10^{-8} *M* (peak height ±11 mm at maximal instrumental amplification; drop time, ±4 sec). A typical pulse polarogram is shown in Fig. 2.

Arsenic. It is rather difficult to obtain satisfactory reduction waves of arsenic-(III) in conventional polarography, the reduction behaving anomalously in many supporting electrolytes, *e.g.*, in hydrochloric and sulphuric acid[18-21].

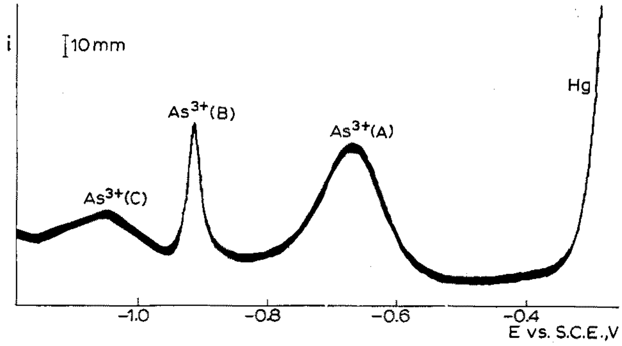

Fig. 3. Pulse polarogram of $2 \cdot 10^{-5}$ *M* As(III) in 1 *M* HCl. Conditions: S 1/80, 35 mV, 9 int. 15 min/V, rec. 1 in/min.

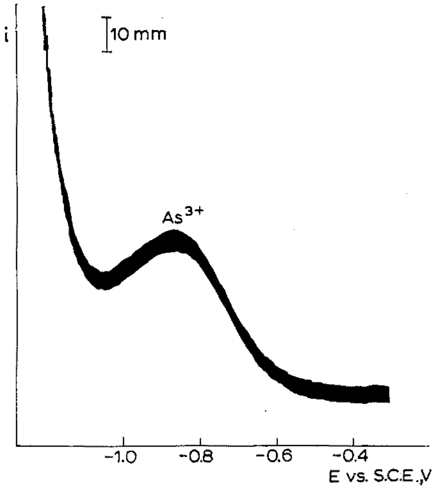

Fig. 4. Pulse polarogram of $4.82 \cdot 10^{-6}$ *M* As(III) in 0.8 *M* H_2SO_4 + 0.002% methylene blue, representing 0.822 p.p.m. As in pure cadmium (sample 2 from Table III, 4.39 g weight). Conditions: S 1/20, 35 mV, 9 int., 7.5 min/V, rec. 1 in/min.

For this reason pulse polarograms of arsenic(III) in some common base electrolytes were recorded. Figure 3 shows the pulse polarogram in 1 *M* hydrochloric acid. Three peaks are obtained with a peak potential difference of 240 mV between the first and the second, and 280 mV between the second and third peak. The peak half-width values (±43 mV for an ideal reversible 3-electron reduction at a pulse amplitude of 35 mV[22]) are, respectively, 110, 20 and 140 mV at a 35 mV pulse amplitude. The heights of the first and third peak are proportional to the concentration of arsenic(III) in the investigated 10^{-6}–$2 \cdot 10^{-5}$ M range. The sharp second peak is not present at concentrations lower than about $2.5 \cdot 10^{-6}$ M. Above this concentration, its height increases more than linearly. The lead(II) and cadmium(II) reduction peaks coincide respectively with the first and second peaks. With regard to its sharpness and nonlinear dependence on the concentration, the middle peak may correspond with a maximum. In classical polarography, arsenic(III) maxima can be suppressed by gelatine, methyl red and methylene blue[18–20] (of which methylene blue is best[20]) and by Triton-X-100[21]. After addition of 0.002% methylene blue, only one arsenic(III) reduction peak was observed, unfortunately coinciding with the cadmium(II) reduction peak. In 0.1 M hydrochloric and in sulphuric, nitric and perchloric acid the same three peaks were observed, but they were closer together than in 1 M hydrochloric acid.

With regard to the sensitivity and the interference of lead and cadmium, the best results were obtained in a sulphuric acid medium in the presence of 0.002% methylene blue (Fig. 4). Only one peak, twice as high as the first peak in the absence of the maximum suppressor, was observed. With methyl red or gelatine at the same concentration, the peaks did not merge completely or the maximum was not fully suppressed. Lead(II) and cadmium(II) were reduced at more positive potentials, the difference between peak potential values amounting to, respectively, 410 and 200 mV. No tin(IV) reduction was observed, and the thallium(I) reduction peak coincided with that of lead(II). At high amplifier gain, it was necessary to record a blank solution to determine the level of the base line at the peak potential, the arsenic(III) peak merging partially with the hydrogen ion reduction. As cadmium(II) was reduced at a potential 200 mV more positive, it could not be present in large amounts. The pulse polarographic sensitivity for arsenic(III) was found to be $4 \cdot 10^{-8}$ M (peak height *ca.* 10 mm at maximal instrumental amplification; drop time, *ca.* 4 sec).

Table I gives a calibration curve recorded in the 10^{-7}–$2.4 \cdot 10^{-4}$ M range. The

TABLE I

CALIBRATION CURVE OF ARSENIC(III) IN 0.1 M H_2SO_4 + 0.002% METHYLENE BLUE

As(III) (mole/l)	*Sensitivity*[a]	*Peak height (mm)*	*K (mm)*[b]
10^{-7}	1/2	12.6	10.1
$2.5 \cdot 10^{-7}$	1/5	13.9	11.1
$5 \cdot 10^{-7}$	1/5	29.7	11.9
10^{-6}	1/10	28.5	11.4
$2.5 \cdot 10^{-6}$	1/20	35.7	11.4
$5 \cdot 10^{-6}$	1/20	71.1	11.4
10^{-5}	1/40	72.2	11.6
$1.5 \cdot 10^{-5}$	1/40	108.6	11.6
$2 \cdot 10^{-5}$	1/40	146.4	11.7
$4 \cdot 10^{-5}$	1/80	136.9	11.0
$9 \cdot 10^{-5}$	1/160	143.4	10.2
$1.4 \cdot 10^{-4}$	1/320	104.5	9.6
$1.9 \cdot 10^{-4}$	1/320	130.8	8.8
$2.4 \cdot 10^{-4}$	1/320	168.0	9.0

[a] 35 mV, 9 int., 60 min/V.

[b] *K* represents the peak height converted for maximum sensitivity and a concentration of $4 \cdot 10^{-8}$ M.

peak heights varied linearly with the concentrations in the 10^{-7}–$2.5 \cdot 10^{-5}$ *M* range and decreased for higher values. From $1.24 \cdot 10^{-4}$ *M* a maximum appeared, which could not be fully suppressed by further addition of methylene blue.

Separation techniques

Originally, it was intended to separate the three elements from the cadmium matrix by fractional distillation[23]. Unfortunately, this technique was only suitable for arsenic which distils at the lowest temperature (111°), whereas the solubility of cadmium is much lower for the working conditions of the distillation of antimony and tin (>140°).

Antimony. Antimony can be separated from an excess of cadmium and copper by extraction[24–28], ion exchange[29], distillation[30], or coprecipitation[4,31–33]. Preference was given to the coprecipitation method. Preliminary experiments showed that antimony coprecipitated with iron(III) hydroxide at pH 4–5 and with manganese dioxide from nitric acid ($\leqslant 0.06$ *M*) in the presence of 0.25 *M* cadmium(II). The precipitation with aluminium(III) hydroxide at pH 4–5 was not quantitative. As manganese(II) does not interfere in the polarographic determination of antimony(III), while iron(III) has first to be reduced to the divalent form, and as the manganese dioxide precipitation can be performed at a lower pH, this method was further examined. It had already been used for the separation of thallium[12], hence both elements could be separated together if necessary.

Bismuth coprecipitates completely or partially with manganese dioxide, depending on the acidity of the solution[31–34]. When the method was applied to various concentrations of copper and bismuth in a 0.06 *M* nitric acid–0.25 *M* cadmium(II) solution, it was found that no coprecipitation of copper occurred, while about 50% of the bismuth and less than 0.1% of the cadmium accompanied the antimony in the precipitate.

The manganese dioxide precipitate was dissolved in a 1% sodium hypophosphite–2 *M* hydrochloric acid mixture.

Tin. Tin can also be precipitated with manganese dioxide, though lead will partially coprecipitate[31–34]. Preliminary experiments showed that from a 0.25 *M* cadmium(II)–0.5 *M* nitric acid solution, to which various amounts of lead were added, about 12% of the latter was coprecipitated. Increasing the acidity to 1.2 *M* had no marked effect. From a 0.5 *M* nitric acid solution, tin was precipitated quantitatively in the presence of 0.25 *M* cadmium(II) nitrate, chloride or sulphate.

In analyses of commercial cadmium products, a 12% lead content[11] may be considered too large a molar excess with respect to the tin content, to allow the determination in the thiocyanate–hydrochloric acid mixture; preference was therefore given to a further separation of tin from lead. This was performed by distillation in a special apparatus[35] from a sulphuric–hydrobromic–hydrochloric acid mixture at a temperature of 140–160°. After evaporation of the distillate to a small volume, the tin was determined directly; the use of the hydrochloric–hydrobromic acid mixture as the base electrolyte diminished the risk of lead contamination. Arsenic, if partially coprecipitated[36], will also co-distil, but does not interfere in this medium. The distillation of various amounts of tin was quantitative. Neither lead nor cadmium could be detected after distillation from a solution containing 4 mg of lead and 50 mg of cadmium.

To verify possible losses by evaporation of the distillate, 100-ml aliquots of $5 \cdot 10^{-8} - 5 \cdot 10^{-6} M$ tin(IV) solutions which were 3 *M* in both hydrochloric and hydrobromic acid were evaporated to *ca.* 3 ml. The tin recovery was complete when evaporation was done under an I.R. lamp (250 W) placed 20 cm above the solution surface.

Arsenic. On account of the volatility of arsenic(III) in hydrochloric acid solution compared to that of cadmium(II) and lead(II), separation of the arsenic by distillation was an obvious step. An all-glass apparatus[35] was used, supplied with an extra bulb to prevent the cadmium from being carried over with the arsenic. The distillation was performed in the presence of hydrazine sulphate to reduce arsenic(V) to the trivalent form, and of bromide, which is reported to promote the reduction[37]. The distillate was evaporated after addition of nitric and sulphuric acid to prevent losses of arsenic(III). To obtain complete reduction of arsenic(V) to (III) before the polarogram was recorded, it was necessary to heat with hydrazine sulphate in concentrated sulphuric acid solution.

As strong oxidizing agents such as nitric acid must be absent, cadmium nitrate has first to be converted into sulphate.

Procedures

Antimony. Dissolve a suitable sample weight of cadmium metal in a minimum amount of nitric acid (1+3). After complete decomposition of the metal, dilute to 250–600 ml to obtain a nitric acid concentration of *ca.* 0.06 *M*. Add 1 ml of 1% potassium permanganate solution and heat gently to boiling. Add two successive 1-ml portions of 1% manganese(II) nitrate solution and boil for 2 min after each addition. After cooling to 60–70°, filter through a fine sintered glass filter and wash with water. Dissolve the precipitate in a 2 *M* hydrochloric acid–1% sodium hypophosphite solution, transfer to a 10-ml volumetric flask and dilute to the mark. After de-aerating a part of the solution, record a pulse polarogram and determine the antimony by the standard addition method. For cadmium compounds, proceed in the same manner after dissolving the salt in water and adding nitric acid.

Tin. Dissolve a suitable sample weight of cadmium metal in nitric acid (1+3) to obtain an acid concentration of *ca.* 0.5 *M* after dilution to 200–600 ml. Heat to boiling and add 5 ml of 1% potassium permanganate solution followed by two 5-ml portions of a 1% manganese(II) nitrate solution, boiling for 2 min after each addition. Filter on a fine-porosity sintered-glass filter and wash with water. Dissolve the precipitate with 15 ml of 2 *M* hydrochloric acid–1% hydrazine sulphate solution and transfer to the distilling apparatus with 30 ml of sulphuric acid (1+1). Dip the end of the condenser into 30 ml of water in a small beaker. Pass a current of carbon dioxide through the apparatus at a rate of 2–3 bubbles/sec throughout the distillation. Increase the heat gradually until the temperature reaches 140–160°. Add 50 ml of a (3+1) mixture of hydrochloric and hydrobromic acid at a rate of 30–40 drops/min, maintaining the temperature between 140–160°. Evaporate the distillate to about 3 ml under an I.R. lamp (250 W) placed 20 cm above the surface of the solution. Transfer to a 10-ml volumetric flask with water and dilute to the mark. After de-aerating, record a pulse polarogram and determine the tin by the standard addition method.

For cadmium compounds proceed in the same way after dissolving the salt in water and adding nitric acid.

Arsenic. Transfer a suitable amount of cadmium as chloride or sulphate with 40 ml of hydrochloric acid (1+1), 0.3 g of hydrazine sulphate and 2 ml of hydrobromic acid to the distilling flask. Dip the end of the condenser into 50 ml of ice-cooled water in a small beaker. Pass a slow stream of carbon dioxide (2–3 bubbles/sec) through the solution. Raise the temperature to 109–111° and maintain it at this value while adding dropwise 40 ml of hydrochloric acid (1+1), which requires about 30 min. Add 10 ml of nitric acid and 0.25 ml of sulphuric acid to the distillate and evaporate to a small volume. Transfer the solution to a 10-ml beaker and heat until white fumes appear. Add 0.05 g of hydrazine sulphate and continue fuming for some minutes. Cool, transfer to a 10-ml volumetric flask with water and dilute to the mark. After adding 0.002% methylene blue, de-aerate and record a pulse polarogram. Determine the arsenic by the standard addition method.

RESULTS

As already mentioned, down to $6\cdot10^{-9}\,M$ antimony(III), $10^{-8}\,M$ tin(IV) and $4\cdot10^{-8}\,M$ arsenic(III) can be determined in the pure supporting electrolytes used.

When the antimony(III) peak is recorded, the remaining bismuth generally requires a high resolution capacity which excludes the use of the 35-mV pulse amplitude, so that a lower sensitivity of $3\cdot10^{-8}\,M$ is obtained.

In the determination of tin, the lead blank observed at the tin(IV) peak potential corresponded to $0.75\cdot10^{-8}\pm0.5\cdot10^{-8}\,M$ tin(IV). When $5\cdot10^{-8}\,M$ concentrations are determined, the possible error due to the variation of the lead blank can amount maximally to *ca.* 10%. This concentration represents a tin content of 0.006 p.p.m. in cadmium for a sample weight of 10 g and a final volume of 10 ml. Under the same conditions, down to about 0.003 p.p.m. arsenic and 0.004 p.p.m. antimony can be determined.

The methods were applied to a series of standard cadmium samples prepared by adding known amounts of antimony, tin and arsenic to cadmium solutions previously freed from arsenic by distillation and from antimony and tin by coprecipitation with manganese dioxide. The results are summarized in Table II.

Finally, some commercially available cadmium products were analysed to

TABLE II

DETERMINATION OF ANTIMONY, TIN AND ARSENIC IN CADMIUM
(5 g samples; final volume, 10 ml)

Antimony			*Tin*			*Arsenic*		
Added (μg)	*Found (μg)*	*Yield (%)*	*Added (μg)*	*Found (μg)*	*Yield (%)*	*Added (μg)*	*Found (μg)*	*Yield (%)*
60.87	60.41	99.2	11.80	11.44	96.9	187.30[a]	187.83	100.3
6.09	5.88	96.6	1.18	1.11	94.1	37.46[b]	37.91	101.2
1.22	1.20	98.4	0.590	0.593	100.5	7.49	7.59	101.3
0.608	0.585	96.2	0.236	0.252	106.8	1.87	2.00	107.0
0.122	0.113	92.6	0.118	0.110	93.2	0.935	1.01	108.0
			0.059	0.075	127.1	0.094	0.105	111.7

[a] Final volume, 250 ml.
[b] Final volume, 50 ml.

TABLE III

DETERMINATION OF ANTIMONY, TIN AND ARSENIC IN COMMERCIALLY AVAILABLE CADMIUM SAMPLES
(4–10 g samples; final volume, 10 ml)

Product	*Grade*	*Antimony (p.p.m.)*	*Tin (p.p.m.)*	*Arsenic (p.p.m.)*
Cadmium metal	pure	0.601	0.578	1.75
Cadmium metal	analytical	0.036	0.421	0.822
Cadmium metal	analytical	0.040	0.050	0.171
$Cd(NO_3)_2 \cdot 4\ H_2O$	very pure	0.144	0.173	[a]
$Cd(NO_3)_2 \cdot 4\ H_2O$	very pure	0.195	0.215	[a]
$CdCl_2 \cdot 2\frac{1}{2}\ H_2O$	analytical	0.012	0.032	0.091
$CdCl_2 \cdot 2\frac{1}{2}\ H_2O$	analytical	0.008	0.024	0.042
$3\ CdSO_4 \cdot 8\ H_2O$	analytical	[a]	0.342	0.084

[a] Not determined.

check the efficiency in practice. The results are given in Table III. For 10-g samples and final dilution to 10 ml, the contents of the three elements were well above the detection limit in nearly all cases. The bismuth–antimony molar concentration ratio, which was at a maximum of 20 in sample 3 after the coprecipitation (Table III), allowed the determination of antimony in all the samples analysed.

SUMMARY

Traces of antimony, tin and arsenic in cadmium products were determined by pulse polarography. Arsenic was distilled, while antimony and tin were precipitated as hydroxides with manganese dioxide as carrier; some lead was coprecipitated with tin, hence these elements were further separated by distillation. In all cases quantitative recoveries were obtained. Antimony(III) was determined in a hydrochloric acid–sodium hypophosphite mixture, tin(IV) in a hydrochloric–hydrobromic acid mixture and arsenic(III) in sulphuric acid as supporting electrolytes; for arsenic(III), methylene blue had to be added. A sample weight of 10 g and an end volume of 10 ml allowed the determination down to about 0.004 p.p.m. antimony, 0.006 p.p.m. tin and 0.003 p.p.m. arsenic in cadmium. Several synthetic samples and commercially available cadmium products were analysed.

RÉSUMÉ

On examine le dosage de traces d'antimoine, d'étain et d'arsenic dans un cadmium, par polarographie de pulsation. L'arsenic est distillé, tandis que l'antimoine et l'étain sont précipités comme hydroxydes en utilisant le dioxyde de manganèse comme entraîneur. Un peu de plomb peut coprécipiter avec l'étain; ces deux éléments sont ensuite séparés par distillation. L'antimoine(III) est dosé en milieu acide chlorhydrique-hypophosphite de sodium, l'étain(IV) en milieu acide chlorhydrique–acide bromhydrique et l'arsenic(III) en milieu acide sulfurique, comme électrolytes de base. Pour l'arsenic(III) on ajoute du bleu de méthylène. Une prise de 10 g avec un volume final de 10 ml permet le dosage de 0.004 p.p.m. d'antimoine, 0.006 p.p.m. d'étain et 0.03 p.p.m. d'arsenic dans le cadmium.

ZUSAMMENFASSUNG

Spuren von Antimon, Zinn und Arsen in Cadmium-Produkten wurden durch Puls-Polarographie bestimmt. Arsen wurde destilliert, während Antimon und Zinn als Hydroxid mit Mangandioxid als Träger gefällt wurden. Da etwas Blei mit dem Zinn mitgefällt wurde, wurden diese Elemente durch Destillation abgetrennt. In allen Fällen wurde eine quantitative Rückgewinnung erhalten. Antimon(III) wurde in einer Mischung aus Salzsäure und Natriumhypophosphit, Zinn(IV) in Salzsäure und Bromwasserstoffsäure und Arsen(III) in Schwefelsäure bestimmt; beim Arsen(III) wurde Methylenblau zugegeben. In einer Probe von 10 g und einem Endvolumen von 10 ml können bis hinab zu 0.004 p.p.m. Antimon, 0.006 p.p.m. Zinn und 0.003 p.p.m. Arsen bestimmt werden. Zahlreiche synthetische und kommerzielle Cadmiumprodukte wurden analysiert.

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POLAROGRAPHIC DETERMINATION OF ACIDS BY MEANS OF THE REDUCTION WAVE OF QUINONES IN METHYL CELLOSOLVE SOLUTION

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The influence of some additives on the polarographic behavior of quinones has been reported previously[1]. On addition of a small quantity of acid, methyl-*p*-benzoquinone gave a diffusion-controlled prewave preceding the reduction wave of the quinone itself in methyl cellosolve* solution containing sodium perchlorate. In the presence of an excess of quinone, the height of the prewave was proportional to the concentration of the acid added, and the half-wave potential became more positive as the acidity of the added species increased. The probable expression of the electrode reaction for the prewave caused by the presence of proton donor (which is denoted as HA) is,

$$Q + 2\,HA + 2\,e \rightleftarrows H_2Q + 2\,A^- \qquad (1)$$

The present paper deals with the application of the results obtained in the previous work to the determination of traces of acid impurities in commercial reagents. The application of the method to the simultaneous determination of mixed acids was also examined. The possibility of the polarographic determination of acid based on reaction (1) was suggested by ABBOTT AND COLLAT[2], but their data were restricted to aqueous media. The present work shows that the method can be extended to the determination of several kinds of inorganic and organic acids, especially those insoluble in water, and to the simultaneous determination of mixed acids.

EXPERIMENTAL

Methyl cellosolve[3,4] was found to be a satisfactory nonaqueous solvent for the present investigation. Guaranteed-reagent-grade methyl cellosolve was refluxed with anhydrous iron(II) sulfate for 1 h and distilled at atmospheric pressure, the distillate at 125.0 ± 0.5° being collected[4]. Methyl-*p*-benzoquinone (MQ) was purified by repeated sublimation (m.p. 67.7°). The supporting electrolytes used were 0.25 *M* lithium perchlorate or sodium perchlorate. The former was purified by repeated crystallization of the commercial reagent from *n*-butyl acetate, and the latter by recrystallizing the guaranteed reagent from ethanol and ether. Since a maximum was often found on the prewave in the presence of moderately high concentrations of acid, 0.001% methyl orange was added as a maximum suppressor.

D.C. polarograms were recorded on a Yanagimoto pen-recording polarograph

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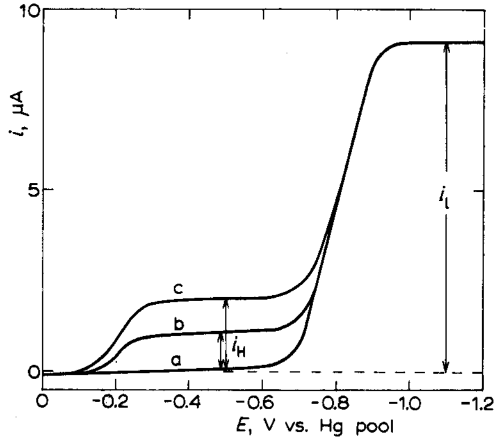
* 2-Methoxyethanol.

model PA-102. The dropping mercury electrode used had an m value of 1.24 mg/sec, and a drop time of 5.84 sec, which were measured in an air-free sodium perchlorate solution at open circuit and at 25°. A mercury pool electrode was used as an anode, care being taken to reduce the total electrical resistance of the circuit. The resistance between cathode and anode was about 300 Ω. All measurements were carried out at 25°.

RESULTS AND DISCUSSION

Polarograms of methyl-p-benzoquinone in the presence of acid

D.C. polarograms of a $1.9 \cdot 10^{-3}$ M solution of the quinone in the absence and presence of perchloric acid are shown in Fig. 1; a prewave appears in the presence of perchloric acid at a more positive potential than that of the reduction of the quinone.



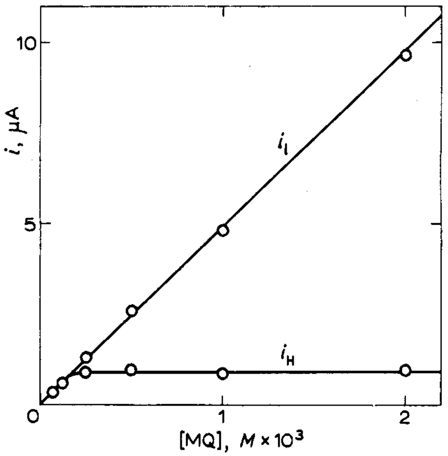


Fig. 1. Polarograms of $1.9 \cdot 10^{-3}$ M MQ in the presence of $HClO_4$. Concentration of $HClO_4$: (a) 0 M; (b) $4.79 \cdot 10^{-4}$ M; (c) $9.58 \cdot 10^{-4}$ M. Supporting electrolyte: 0.25 M $NaClO_4$.

Fig. 2. Relation between the values of i_l and i_H and the concentration of MQ obtained in solutions containing $4.60 \cdot 10^{-4}$ M $HClO_4$. Supporting electrolyte: 0.25 M $NaClO_4$.

As shown in Fig. 2, the limiting current (i_l) at −1.1 V was proportional to the concentration of the quinone, whereas the current of the prewave (i_H) at −0.5 V obtained at constant acid concentration remained unchanged irrespective of the quinone concentration provided that the quinone was present in excess. i_H was proportional to the concentration of perchloric acid and to the square root of the effective height of mercury reservoir, indicating that the current of the prewave is diffusion-controlled. A maximum was often found on the prewave in the presence of higher concentrations of acid.

The same type of prewave was also caused by the addition of other inorganic and organic monobasic acids, such as nitric acid, benzoic acid, acetic acid, phenols, etc.

Determination of free perchloric acid in commercial lithium perchlorate

The proportionality of the height of the prewave to the concentration of acid present can be utilized to determine traces of free perchloric acid in crude lithium perchlorate.

Two reduction waves were observed on the polarographic curve of methyl-*p*-benzoquinone in the methyl cellosolve media containing 0.25 M of the crude lithium perchlorate as a supporting electrolyte, whereas only one reduction wave corresponding to the second wave in the above solution was obtained in media containing purified 0.25 M lithium perchlorate. On addition of perchloric acid in the latter solution, a new reduction wave was found at the same potential as the first wave in the previous solution. This proves that the first wave is a prewave caused by free perchloric acid in the crude reagent used as supporting electrolyte.

A linear relation was obtained between the prewave height at -0.5 V and the concentration of perchloric acid over the range $0\text{–}2 \cdot 10^{-3}$ M, when the solution contained $2.0 \cdot 10^{-3}$ M methyl-*p*-benzoquinone and purified 0.25 M lithium perchlorate. Analyses of crude lithium perchlorate reagents are summarized in Table I.

TABLE I

DETERMINATION OF THE FREE PERCHLORIC ACID IN CRUDE LITHIUM PERCHLORATE

Commercial reagent	i_H[a] (μA)	*Content of free $HClO_4$ in crude $LiClO_4$*		
		In 0.25 M $LiClO_4$ soln.		*Wt. %*
		$M \cdot 10^4$	*g/l*	
Sample A	1.15	5.70	0.0573	0.216
Sample B	1.06	5.25	0.0528	0.199
Sample C	1.36	6.74	0.0677	0.255

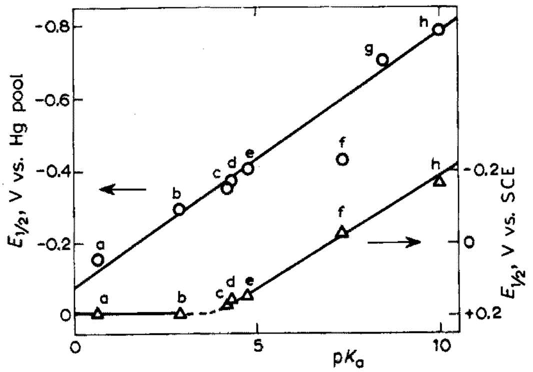
[a] The prewave heights measured in $2.0 \cdot 10^{-3}$ M MQ solution containing crude 0.25 M lithium perchlorate as supporting electrolyte.

Simultaneous determination of acids

As mentioned previously[1], the half-wave potentials of the prewave varied with the value of the dissociation constant (K_a) of the added acid. A decrease in the K_a value caused a negative shift of the half-wave potential, and a linear relationship was found between pK_a and the half-wave potential (see curve a in Fig. 3). In Fig. 3, the pK_a values obtained in aqueous solution are used, instead of those in methyl cellosolve, but this does not affect the linearity [1,5].

When two acids with widely different dissociation constants are present, two prewaves can be observed. When the half-wave potentials of these prewaves are sufficiently separated, the acid species can be determined simultaneously. The simultaneous determination was examined for the following 3 systems MQ–$HClO_4$–CH_3COOH, MQ–CCl_3COOH–CH_3COOH and MQ–$CHCl_2COOH$–CH_3COOH. Methyl orange was used as a maximum suppressor.

Figure 4 shows the polarographic curve of a methyl-*p*-benzoquinone solution containing traces of perchloric acid and acetic acid. Linear relationships are obtained between the prewave heights and the concentrations of perchloric acid or acetic acid (Fig. 5). Analyses of prepared sample solutions containing various concentrations of the two acids are shown in Table II; the acid concentrations were found from the prewave heights by means of the calibration curves shown in Fig. 5. The results are precise to within ± 2% for perchloric acid in the concentration range of 1–3 mM. The



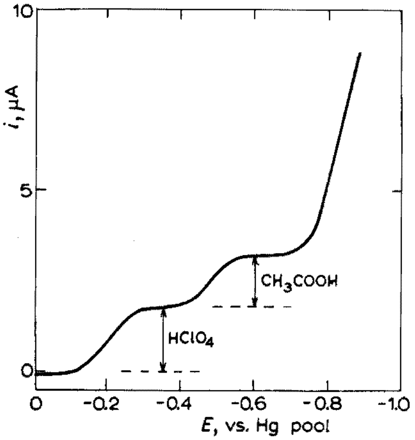


Fig. 3. Relation between pK_a and the half-wave potential of the prewave caused by addition of the following acids: (a) CCl_3COOH; (b) $CH_2ClCOOH$; (c) C_6H_5COOH; (d)$C_6H_5CH_2COOH$; (e) CH_3COOH; (f) 2,5–$Cl_2C_6H_3OH$; (g) o–ClC_6H_4OH; (h) C_6H_5OH. (○) methyl cellosolve solution; (△) aqueous solution. Half-wave potentials were measured in solutions containing $5–7 \cdot 10^{-4}$ M acids and no methyl orange.

Fig. 4. Polarographic curve of MQ–$HClO_4$–CH_3COOH system. [MQ] = $2.3 \cdot 10^{-3}$ M, [$HClO_4$] = $9.67 \cdot 10^{-4}$ M, [CH_3COOH] = $5.33 \cdot 10^{-4}$ M. Methyl orange (0.001%) was added as a maximum suppressor.

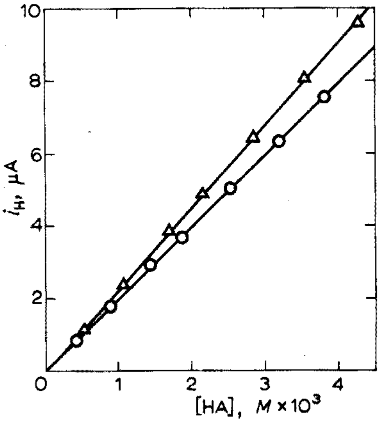


Fig. 5. Relation between the prewave height and the concentration of (○) $HClO_4$ and (△) CH_3COOH. The values of i_H were obtained in a $2.3 \cdot 10^{-3}$ M MQ solution containing 0.001% methyl orange at –0.35 V (for $HClO_4$) and –0.6 V (for CH_3COOH) *vs.* Hg pool.

results for acetic acid are less precise, because this waveheight was obtained by subtraction of the waveheight for perchloric acid from the total height.

Two prewaves were also observed in solutions containing methyl-*p*-benzoquinone and acetic acid with either trichloroacetic acid or dichloroacetic acid; the results of simultaneous determinations are summarized in Tables III and IV.

Three well-defined prewaves could not be observed in mixed solutions of methyl-*p*-benzoquinone and mono-, di- and trichloroacetic acid; only one elongated

TABLE II

THE DETERMINATION OF PERCHLORIC ACID (A) AND ACETIC ACID (B) FROM THE PREWAVE HEIGHTS OBTAINED IN THE MQ–$HClO_4$–CH_3COOH SYSTEM

[HA] added (M · 10³)		*i_H*[a] *(μA)*		*[HA] found (M · 10³)*		*Error (%)*	
A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
0.967	0.533	1.89	1.28	0.96	0.57	−0.72	+6.9
0.967	1.07	1.89	2.50	0.96	1.11	−0.72	+3.7
0.967	2.13	1.91	4.93	0.97	2.19	+0.31	+2.8
0.967	3.20	1.89	7.16	0.96	3.18	−0.72	−0.63
1.93	0.533	3.84	1.28	1.95	0.57	+1.0	+6.9
1.93	1.07	3.86	2.54	1.96	1.13	+1.6	+5.6
1.93	2.13	3.79	4.93	1.92	2.19	−0.52	+2.8
2.90	0.533	5.79	1.26	2.94	0.56	+1.4	+5.1
2.90	1.07	5.79	2.39	2.94	1.06	+1.4	−0.93

[a] Conditions as for Fig. 5.

TABLE III

THE DETERMINATION OF TRICHLOROACETIC ACID (C) AND ACETIC ACID (B) FROM THE PREWAVE HEIGHTS OBTAINED IN THE MQ–CCl_3COOH–CH_3COOH SYSTEM

[HA] added (M · 10³)		*i_H*[a] *(μA)*		*[HA] found (M · 10³)*		*Error (%)*	
C	*B*	*C*	*B*	*C*	*B*	*C*	*B*
0.89	0.53	1.76	1.28	0.90	0.57	+1.1	+7.0
0.89	1.07	1.80	2.48	0.92	1.10	+3.4	+2.7
0.89	2.13	1.80	4.88	0.92	2.17	+3.4	+1.8
1.79	0.80	3.37	1.91	1.72	0.85	−3.9	+6.3
1.79	1.07	3.39	2.57	1.73	1.14	−3.4	+6.5
1.79	2.13	3.45	4.90	1.76	2.18	−1.7	+2.3
2.68	0.53	5.15	1.28	2.63	0.57	−1.9	+7.0
2.68	1.07	5.11	2.57	2.61	1.14	−2.6	+6.5

[a] i_H values were obtained at −0.37 V (for CCl_3COOH) and −0.6 V (for CH_3COOH) *vs.* Hg pool. Other conditions as in Fig. 5.

TABLE IV

THE DETERMINATION OF DICHLOROACETIC ACID (D) AND ACETIC ACID (B) FROM THE PREWAVE HEIGHTS OBTAINED IN THE MQ–$CHCl_2COOH$–CH_3COOH SYSTEM

[HA] added (M · 10³)		*i_H*[a] *(μA)*		*[HA] found (M · 10³)*		*Error (%)*	
D	*B*	*D*	*B*	*D*	*B*	*D*	*B*
0.98	0.53	1.95	1.17	1.00	0.52	+2.0	−1.9
0.98	1.07	1.99	2.36	1.02	1.05	+4.1	−1.9
0.98	2.13	1.91	4.77	0.98	2.12	0	−0.47
0.98	3.20	1.89	6.97	0.97	3.10	−1.0	−3.1
1.97	1.07	3.78	2.57	1.94	1.14	−1.5	+6.5
1.97	2.13	3.86	4.79	1.98	2.13	+0.51	0
2.95	1.07	5.56	2.57	2.85	1.14	−3.4	+6.5

[a] i_H values were obtained at −0.37 V (for $CHCl_2COOH$) and −0.6 V (for CH_3COOH) *vs.* Hg pool. Other conditions as for Fig. 5.

prewave was obtained. To obtain clearly separated prewaves, the pK_a values of the acids must differ by more than 3.

A.C. polarography did not give satisfactory results for the simultaneous determination of the mixed acids; the peak height corresponding to the prewave was not reproducible, and the separation of the prewaves of different acids was not improved.

Advantages of the present method

The present work has extended the previous method of ABBOTT AND COLLAT[2] to the determination of several strong and weak acids. Methyl cellosolve as solvent gave satisfactory results, and dissolves various polar and non-polar materials, so that various organic acids which are insoluble in water, can be determined. Since the half-wave potentials of the prewaves vary with the acidity, mixed acids can be determined simultaneously. Higher prewaves are obtained in aqueous media than in methyl cellosolve media, but the organic medium allows a clear separation of half-wave potentials with acidity*.

Similar results were obtained with other quinones, such as *p*-benzoquinone, 1,4-naphthoquinone and their alkyl derivatives. *p*-Benzoquinone seems to be unstable, especially in non-aquesous solvents, and changes in the color of the solution and in the shape of the polarographic curves are often found with lapse of time. The use of alkyl-substituted quinones is recommended.

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SUMMARY

Methyl-*p*-benzoquinone (MQ) gives a single polarographic wave in methyl cellosolve media containing perchlorate as supporting electrolyte, but a prewave corresponding to the reaction $Q + 2\ HA + 2\ e \rightleftarrows H_2Q + 2\ A^-$, is found when an acid is added. The height of the prewave is proportional to the concentration of added acid. Traces (*ca.* 0.2%) of free perchloric acid can be determined in crude lithium perchlorate.

The half-wave potential of the prewave depends on the pK_a value of the acid; if the dissociation constants of acids differ sufficiently, two prewaves are found and each acid species can be determined simultaneously. This method was applied to the $MQ–HClO_4–CH_3COOH$, $MQ–CCl_3COOH–CH_3COOH$ and $MQ–CHCl_2COOH–CH_3COOH$ systems.

RÉSUMÉ

La méthyl-*p*-benzoquinone (MQ) donne une vague polarographique simple en milieu méthylcellosolve, renfermant du perchlorate comme électrolyte de base; cependant une vague préliminaire correspondant à la réaction $Q+2HA+2e \rightleftharpoons H_2Q+2A^-$ se produit lorsqu'on ajoute un acide. La hauteur de cette vague préliminaire est proportionnelle à la concentration de l'acide ajouté. Des traces (environ 0.2%) d'acide perchlorique libre peuvent être dosées dans du pérchlorate de lithium. Le potentiel de demi-vague de cette vague préliminaire dépend de la valeur pK_a de l'acide. Cette

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* The solvent effect on the prewave of quinone–acid system will be discussed elsewhere.

méthode peut s'appliquer aux systèmes MQ–$HClO_4$–CH_3COOH, MQ–CCl_3COOH–CH_3COOH et MQ–$CHCl_2COOH$–CH_3COOH.

ZUSAMMENFASSUNG

Methyl-*p*-benzochinon gibt in einer Lösung mit Perchlorat und 2-Methoxyäthanol nur eine polarographische Stufe. Bei Zugabe kleiner Mengen Säure tritt eine Vorstufe auf, die durch Reduktion nach folgender Gleichung

$$Q+2HA+2e \rightleftharpoons H_2O+2A^-$$

hervorgerufen wird. Die Höhe der Vorstufe ist proportional zur Konzentration der zugegebenen Säure. Auf diese Weise können Spuren freier Perchlorsäure in unreinem Lithiumperchlorat bestimmt werden. Das Halbwellenpotential der Vorstufe hängt vom pK_a-Wert der Säure ab. Falls die Dissoziationskonstanten der Säuren sich genügend unterscheiden, werden 2 Vorstufen gefunden, und die Säuren können gleichzeitig bestimmt werden. Diese Methode wurde auf die Systeme MQ–$HClO_4$–CH_3COOH, MQ–CCl_3COOH–CH_3COOH und MQ–$CHCl_2COOH$ angewandt.

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VOLTAMMETRIC BEHAVIOR OF NEPTUNIUM(VI) IN GLUTAMIC ACID MEDIA AT THE ROTATING GLASSY CARBON ELECTRODE*

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The investigation of the organic complexes of neptunium(VI) has been limited to the acetate[1] and malonate[2] complexes. KELLER AND EBERLE[3] attempted to prepare the neptunium(VI)–8-hydroxyquinoline complex, but the neptunium(VI) was rapidly reduced by the complexing ligand. The complexes of neptunium(V) have been more thoroughly investigated[3–8]. Glutamic acid, an α-amino acid, has not, however, been used as a complexing ligand for neptunium. The investigation of the glutamate complexes of the actinide elements has been limited to uranium(VI)[9,10]. This report is concerned with the voltammetry of the neptunium(VI) glutamate complex at the rotated glassy carbon electrode.

EXPERIMENTAL

Apparatus

All voltammograms were obtained at 25° with a calibrated Sargent Model XV recording polarograph. None of the measurements was damped. The electrolysis cell and the glassy carbon electrode (GCE) have been described[2,11]. The electrode was mounted in a Sargent synchronous rotator that had a rotation speed of 600 rev/min. The electrode was cleaned at the end of each measurement, by allowing the electrode to rotate for 15–30 sec in concentrated nitric acid.

The pH values of the solutions were measured with a Beckman Model H-2 pH meter and a glass electrode. The pH was adjusted with perchloric acid or sodium hydroxide.

The conductometric titrations were performed with a Model RC-16 (Industrial Instruments, USA) line operated conductivity bridge.

Reagents

The preparation and standardization of the neptunium(VI) and the neptunium(V) stock solutions have been described[2,11]. The disodium glutamate solution was prepared by dissolving sodium hydrogen glutamate monohydrate (Matheson, Coleman and Bell, USA) in a solution containing sufficient sodium hydroxide to neutralize the sodium hydrogen glutamate and make the final solution 0.1 *M* in sodium hydroxide. All other chemicals were reagent grade and prepared in the usual manner. Purified nitrogen was used to deaerate the test solutions.

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RESULTS AND DISCUSSION

Effect of pH

The effect of changes in acidity on the half-wave potential and on the limiting current of the neptunium(VI)–glutamate complex were investigated over the pH

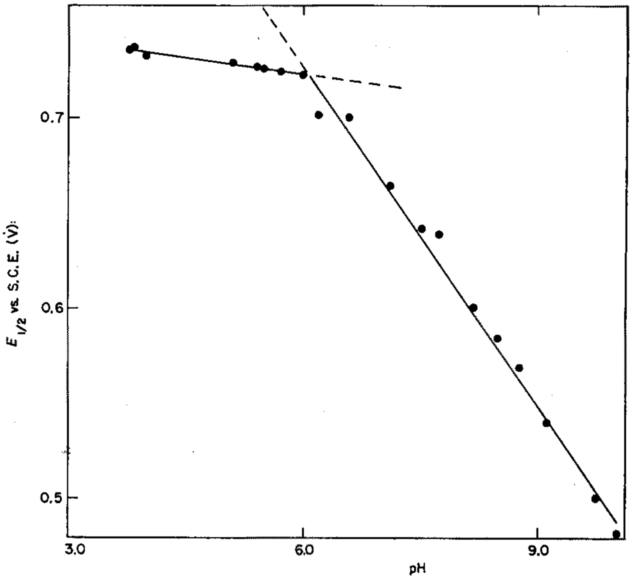

Fig. 1. Effect of pH on the half-wave potential. $7.83 \cdot 10^{-4}$ neptunium(VI), 0.5 *M* $NaClO_4$, 0.67 *M* $Na_2C_5H_7O_4N$.

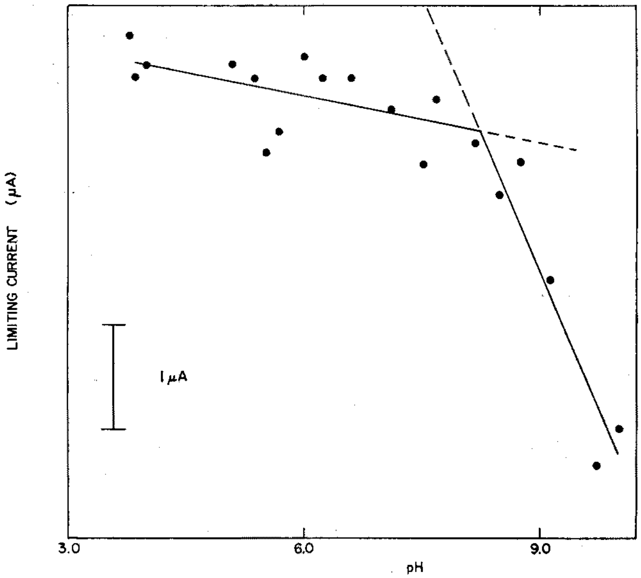

Fig. 2. Effect of pH on the limiting current. $7.83 \cdot 10^{-4}$ *M* neptunium(VI), 0.5 *M* $NaClO_4$, 0.67 *M* $Na_2C_5H_7O_4N$.

range 3.8–10.0 (Figs. 1 and 2). Below pH 3.8, glutamic acid began to precipitate, and above pH 10.0 neptunium precipitated. The test solutions were $7.83 \cdot 10^{-4}$ *M* in neptunium(VI), 0.67 *M* in disodium glutamate and 0.5 *M* in sodium perchlorate. The plot of pH *versus* half-wave potential (Fig. 1) can be divided into two straight-line portions, which correspond to the pH regions 3.8–6.1 and 6.1–10.0. In the pH range 3.8–6.1, the slope of the plot is essentially zero,which indicates that the half-wave potential is independent of the pH, and no hydrogen or hydroxyl ions are involved in the reduction of the neptunium(VI) ion. In the pH range 6.1–10.0, the half-wave potential is a function of the pH, and the relationship can be represented by the equation:

$$E_{\frac{1}{2}} = 1.089 - 0.060 \text{ pH}$$

This indicates that one hydrogen ion is involved in the reduction of each neptunium ion in this pH range.

The effect of pH on the limiting current is shown in Fig. 2. The limiting current is independent of the pH in the pH range 3.8–8.2 which indicates that a complex species with a constant composition exists in this range. As the pH is increased above pH 8.2, the limiting current decreases; this shows the competion between the hydroxyl ions and the glutamate ions for the neptunium.

Effect of glutamate concentration

The effect of changes in the glutamate concentration on the half-wave potential of the neptunium(VI)–glutamate complex was investigated in solutions which were $7.83 \cdot 10^{-4}$ *M* in neptunium(VI) and 0.5 *M* in sodium perchlorate, at pH 5.0 and 8.0. At pH 5.0 the plot of the logarithm of the glutamate concentration *versus* the half-wave potential (Fig. 3) showed that the half-wave potential is a function of the glutamate concentration. In the glutamate concentration range $2.0 \cdot 10^{-4}$–0.1 *M*, the slope of the

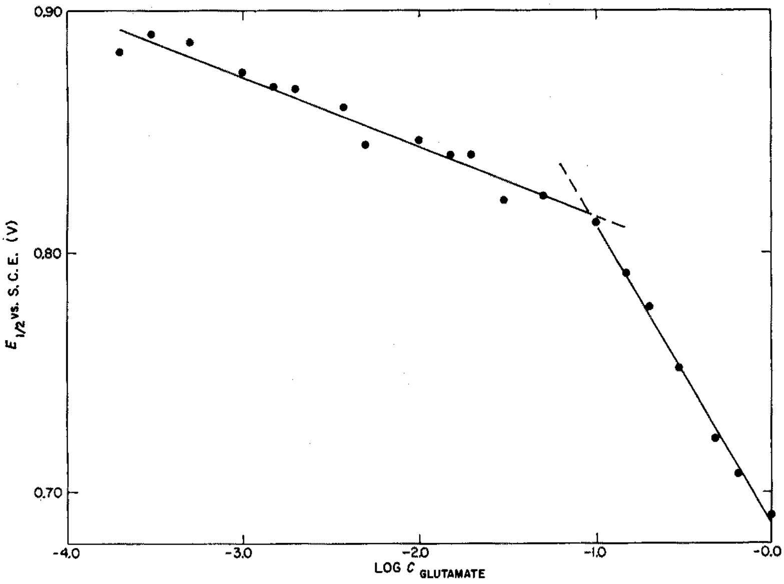

Fig. 3. Effect of glutamate concentration on the half-wave potential. $7.83 \cdot 10^{-4}$ *M* neptunium(VI) 0.5 *M* $NaClO_4$, pH 5.00±0.05.

plot is −0.029 V, whereas, in the glutamate concentration range 0.1–1.0 *M*, the slope of the plot is −0.125 V. Below a glutamate concentration of $2.0 \cdot 10^{-4}$ *M*, neptunium precipitated. The reversibility of the electrode reaction was determined by a log $i/(i_1-i)$ *versus* E_{RGC} plot. The slope of the plots for glutamate concentrations from $2.0 \cdot 10^{-4}$ to 0.1 *M* varied from 0.045 to 0.055 V, respectively. The values at glutamate concentrations less than 0.1 *M* were not in agreement with the theoretical value of 0.0591 V for a one-electron, reversible reaction. However, for the glutamate concentration range 0.1–1.0 *M*, the slope of the plots varied from 0.055 to 0.059 V; this agrees quite well with the theoretical value for a one-electron, reversible reaction. To confirm the irreversibility and reversibility of the electrode reaction, solutions were prepared which were $7.83 \cdot 10^{-4}$ *M* in neptunium(V) and 0.5 *M* in sodium perchlorate, with various concentrations of glutamate at pH 5.0 The neptunium(V) was oxidized, and the anodic half-wave potential was compared with the cathodic half-wave potential. These potentials did not agree when the glutamate concentration was less than 0.1 *M* (Table I). This indicates that the electrode reaction was irreversible. In the glutamate concentration range 0.1–1.0 *M*, the two potentials agreed quite well, which indicates reversibility in this glutamate range.

TABLE I

COMPARISON OF ANODIC AND CATHODIC HALF-WAVE POTENTIALS AT VARIOUS GLUTAMATE CONCENTRATIONS AT pH 5.00 AND 8.00

($7.83 \cdot 10^{-4}$ *M* neptunium, 0.5 *M* $NaClO_4$)

$Na_2C_5H_7O_4N$ (*moles/l*)	*pH 5.00*		*pH 8.00*	
	$(E_{\frac{1}{2}})_c$ *vs. S.C.E. (V)*	$(E_{\frac{1}{2}})_a$	$(E_{\frac{1}{2}})_c$ *vs. S.C.E. (V)*	$(E_{\frac{1}{2}})_a$
$2.0 \cdot 10^{-4}$	0.884	0.920		—[a]
$1.0 \cdot 10^{-3}$	0.875	0.922		—[a]
$5.0 \cdot 10^{-3}$	0.845	0.918		—[a]
$1.0 \cdot 10^{-2}$	0.847	0.902		—[a]
$5.0 \cdot 10^{-2}$	0.786	0.806		—[a]
0.1	0.785	0.784		—[a]
0.3	—	—	0.587	0.596
0.5	0.740	0.735	0.603	0.594
1.0	0.691	0.687	0.595	0.591

[a] Ill-defined waves.

Since the reduction of neptunium(VI) at glutamate concentrations less than 0.1 *M* in the pH range 3.8–6.1 was irreversible, no positive conclusions can be drawn from these data about the number of ligands attached to neptunium(VI) and neptunium(V). However, in this same pH range, but in the glutamate concentration range of 0.1–1.0 *M*, the neptunium(VI) reduction was reversible, and the above data indicate that neptunium(VI) has two more glutamate ligands bound to it than does neptunium(V).

At pH 8.00 the plot of the logarithm of the glutamate concentration *versus* the half-wave potential was a straight line in the glutamate concentration range 0.3–1.0 *M*; the slope was essentially zero. Below a glutamate concentration of 0.3 *M*, the voltammograms became ill-defined. Reversibility of the reduction of neptunium(VI) was demonstrated by the value of the slopes for the plots of log $i/(i_1-i)$ *versus* E_{RGC}.

The average value of these slopes in the glutamate concentration range 0.3–1.0 M was 0.057 V, which agrees well with the theoretical value for a one-electron, reversible reduction. The reversibility of the electrode reaction at pH 8.00 was confirmed in the same way as for pH 5.00 (Table I); at pH 8.00, the reaction was reversible only in the glutamate range 0.3–1.0 M. The above data indicate that the same number of glutamate ligands are bound to the neptunium(V) as are bound to the neptunium(VI).

Composition of neptunium(VI)-glutamate complex

To determine the composition of the metal–ligand ratio, a conductometric titration was performed; 5 ml of $1.958 \cdot 10^{-3}$ M neptunium(VI) solution diluted to 330 ml with water, was titrated with $4.89 \cdot 10^{-2}$ M disodium glutamate (Fig. 4). The titration curve indicates that when neptunium(VI) is in excess, the metal–ligand ratio is 1:1 and is 1:2 when the glutamate ion is in excess.

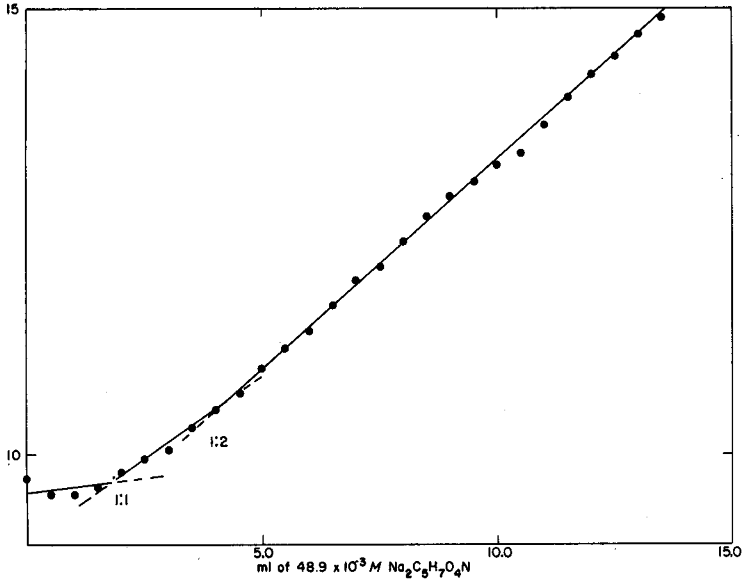

Fig. 4. Conductometric titration of neptunium(VI). 5 ml of $19.58 \cdot 10^{-3} M$ neptunium(VI), $48.9 \cdot 10^{-3} M$ $Na_2C_5H_7O_4N$, 325 ml of water.

Electrode reactions

Based on the foregoing data and discussion, the complex species and electrode reactions are postulated as follows when the disodium glutamate concentration is 0.67 M:

For pH < 6.1, and $q = p - 2$, $NpO_2A_2^{2-} + e^- \rightleftharpoons NpO_2^+ + 2A^{2-}$

For pH 6.1–8.2 and $q = p$, $NpO_2A_2^{2-} + 2H_2O + e^- \rightleftharpoons NpO_2(OH)A_2^{4-} + H_3O^+$

For pH > 8.2, and $q = p$, $NpO_2(OH)_2A_2^{4-} + e^- \rightleftharpoons Np(OH)A_2^{4-} + OH^-$

Diffusion coefficient

The diffusion coefficient of the neptunium(VI)–glutamate complex was determined at 25° in solutions which were $6.27 \cdot 10^{-4}\,M$ in neptunium(VI), $0.5\,M$ in sodium perchlorate and $0.67\,M$ in disodium glutamate, and at pH 4.5 and 9.4, by means of the equation[12]:

$$D^{\frac{2}{3}} = i_1 v^{\frac{1}{6}} / 1.500 \cdot 10^5 nACN^{\frac{1}{2}}$$

where i_1 = limiting current in μA, v = kinematic viscosity, n = number of Faradays, A = electrode area in cm², C = concentration in mmole/l, and N = revolutions per sec.

The value for the diffusion coefficient was determined as $0.35 \cdot 10^{-5}$ cm². sec⁻¹ at pH 4.5 and $0.30 \cdot 10^{-5}$ cm². sec⁻¹ at pH 9.4.

Neptunium(VI) concentration vs. limiting current

A calibration curve for neptunium was prepared by pipetting appropriate aliquots[7] of the standard neptunium stock solution into 25-ml volumetric flasks. To each flask were added 5 ml of $2.5\,M$ sodium perchlorate, 10 ml of $1.67\,M$ disodium glutamate, and sufficient perchloric acid to adjust the pH of the final solution to 5.0 The solution was diluted to volume with water. A portion was transferred to the electrolysis cell, and the solution was purged of oxygen by bubbling purified nitrogen through it for 5 min. Three voltammograms were recorded for each concentration.

The results (Table II) show that the limiting current is proportional to the neptunium concentration over the range $7.83 \cdot 10^{-5}$–$1.96 \cdot 10^{-3}\,M$. The relative standard deviation of the limiting current quotient, i_1/C, for the 21 voltammograms was 4.2%.

TABLE II

EFFECT OF NEPTUNIUM CONCENTRATION ON THE LIMITING CURRENT

(0.67 *M* Disodium glutamate, 0.5 *M* sodium perchlorate, pH 5.0)

NpO_2^{2+} *concn. (C) (moles/l)*	i_1 *(μA)*	i_1/C *(μA/mmole)*
$7.83 \cdot 10^{-5}$	1.95	24.9
$1.96 \cdot 10^{-4}$	4.56	23.3
$3.92 \cdot 10^{-4}$	9.25	23.6
$7.83 \cdot 10^{-4}$	18.6	23.8
$1.17 \cdot 10^{-3}$	28.4	24.3
$1.57 \cdot 10^{-3}$	36.0	22.9
$1.96 \cdot 10^{-3}$	44.8	22.9

SUMMARY

The voltammetry of neptunium(VI) glutamate was investigated over the pH range 3.8–10.0. A reversible, one-electron wave was obtained for glutamate concentrations above $0.1\,M$ in the pH range 3.8–6.1, or above $0.3\,M$ in the pH range 6.1–10.0. At pH 3.8–6.1, the half-wave potential was independent of pH, but at pH 6.1–10.0, it was a function of pH. The metal–ligand ratio was found to be 1:2 by conductometric titration. The limiting current was proportional to the concentration of the neptunium(VI) from $7.83 \cdot 10^{-5}$ to $1.96 \cdot 10^{-3}\,M$. The diffusion coefficient was $0.35 \cdot 10^{-5}$ cm² sec⁻¹ at pH 4.5 and $0.30 \cdot 10^{-5}$ cm² sec⁻¹ at pH 9.4.

RÉSUMÉ

On a effectué une étude de la voltammétrie du glutamate de neptunium(VI) à des pH allant de 3.8 à 10.0. Une onde à un électron réversible est obtenue pour des concentrations en glutamate supérieures à 0.1 *M*, à des pH compris entre 3.8, et 6.1 ou supérieures à 0.3 *M*, entre pH 6.1 et 10.0. Le rapport métal–ligand est de 1:2; il a été déterminé par titrage conductométrique. Le courant limite est proportionnel à la concentration du neptunium(VI) de 7.83×10^{-5} à 1.96×10^{-3} *M*. Le coefficient de diffusion est de 0.35×10^{-5} cm^2 sec^{-1} au pH 4.5 et 0.30×10^{-5} cm^2 sec^{-1} au pH 9.4.

ZUSAMMENFASSUNG

Das voltametrische Verhalten von Neptunium(VI)-Glutamat wurde im pH-Bereich von 3.8–10.0 untersucht. Für Glutamatkonzentrationen oberhalb 0.1 *M* im pH-Bereich von 3.8–6.1 und oberhalb 0.3 *M* im pH-Bereich 6.1–10.0 wurde eine reversible Einelektronen-Stufe erhalten. Beim pH 3.8–6.1 war dat Halbwellenpotential unabhängig vom pH; beim pH 6.1–10.0 war es eine Funktion des pH-Wertes. Durch konduktometrische Titration wurde ein Metall-Liganden-Verhältnis von 1:2 gefunden. Der Grenzstrom war proportional zur Konzentration von Neptunium(VI) von 7.83×10^{-5} bis 1.96×10^{-3} *M*. Der Diffusionskoeffizient beträgt 0.35×10^{-5} cm^2 sec^{-1} beim pH 4.5 und 0.30×10^{-5} cm^2 sec^{-1} beim pH 9.4.

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VOLTAMMETRIC STUDIES WITH SILICONE RUBBER-BASED GRAPHITE ELECTRODES

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Carbon electrodes are becoming increasingly important in voltammetry. Such electrodes are suitable for studying oxidation and reduction processes of both organic and inorganic compounds but are primarily employed for the investigation of electrochemical oxidation processes, because of their wide anodic polarisation range and low residual current within this range; carbon electrodes in the positive potential range have several advantages over mercury electrodes. They also offer special advantages over noble metal electrodes; the latter form surface films of oxide during use so that large residual currents are obtained and the electrode reactions are affected. These errors do not occur with carbon electrodes.

The first graphite electrodes used in voltammetry[1,2] were unsatisfactory for analytical purposes because of poor reproducibility, caused by large residual currents resulting from impurities. Later, impregnated graphite electrodes were used[3,4]. Various waxes and silicone polymers were tested as the impregnating material. Wax-impregnated graphite electrodes proved to be the most satisfactory and were used in studies of many organic and inorganic salts. These electrodes with slight modifications are still widely used, particularly in studies of the oxidation processes of organic compounds[5,6].

The so-called "carbon-paste electrode"[7], which is made from spectral-grade graphite and organic solvents immiscible with water, has the advantages that it can be made quickly and that its residual current is lower than that of the wax-impregnated carbon electrodes. The voltammetric behaviour of many compounds has been studied with this electrode[8]. A paste electrode made from spectral graphite powder and silicone oil has also proved to be very good for analytical purposes[9]. Carbon-paste electrodes could initially be used only in aqueous media; the reason for this, according to various authors, is that in certain cases the organic solvent moistens the carbon more than the impregnating liquid. However, electrodes have been made recently for use even in non-aqueous media[10,11].

Both wax-impregnated graphite and carbon-paste electrodes contain an impregnating material which in certain cases may influence the electrode reactions or the behaviour of the electrodes. These effects can be eliminated by the use of pyrolytic graphite electrodes. Pyrolytic graphite is a hard, non-porous, black porcelain-like material[12] which can be used without impregnation as an electrode material. LAITINEN AND RHODES[13] first prepared electrodes from pyrolytic graphite. Such electrodes were later used as indicator electrodes in aqueous media[14,15]. ZITTEL AND MILLER[16] made electrodes from a new type of carbon — glassy carbon — which, like pyrolytic graphite, is an impermeable, electrically conductive material resistant to chemical effects, and can be used directly as an electrode.

Other modifications of carbon electrodes include a wax-impregnated graphite electrode with a mercury layer electrolysed on to the measuring surface which was used for the examination of both reversible and irreversible systems[17]; and rotating disc electrodes made by suspending graphite in an epoxy resin, which were used to study hexacyanoferrate[18] systems.

In this paper a new type of graphite electrode formed with silicone rubber is described[19]. It was necessary to establish whether this type of electrode was suitable for analytical purposes or not. Accordingly, studies were made of the polarisation range of the electrode, the magnitude of the residual current within this range, the pretreatment procedure, the cleaning and storage of the electrodes and the reproducibility of the voltammetric curves recorded. Furthermore, the dependence of the peak-height of the voltammetric curves on the concentrations of the electroactive components was also investigated. Experiments were carried out to establish the oxidisability and reducibility of various organic and inorganic compounds on these electrodes.

EXPERIMENTAL

Preparation of electrodes. The electrodes were prepared by homogenising powdered spectral graphite in polysiloxanediol. Plates or rods were formed from the homogenized mass and were then cold-vulcanized. Discs were cut from the plates and sealed on the end of a glass tube; a few drops of mercury were put into the tube to ensure electrical contact. In the case of rod electrodes, one end of the graphite rod was inserted into a glass tube and the part protruding (except for the measuring surface in contact with the solution) was covered with silicone rubber to act as an insulator; the surfaces of the electrodes could be renewed by cutting off a thin layer. Electrical contact was again ensured by mercury. The surface of the plate electrodes was 0.25 cm^2 and that of the rod electrodes, 0.4 cm^2.

Methods

The measurements were carried out with a Radelkis type OH-102 polarograph with an H-cell. A saturated calomel electrode was used as a reference electrode and was connected to the measuring electrode system by means of an agar salt bridge in an H-cell. The total resistance of the cell and the electrode was not greater than 300 Ω.

The voltammetric curves were recorded in unstirred solutions with a linearly increasing potential. In all experiments, a polarisation rate of 1.5 V/min was used. To ensure identical experimental conditions, the solution was stirred for 30 sec between each recording or, in some cases, reversed polarisation was employed. Chemicals used were of analytical-reagent grade.

RESULTS

Examination of the residual current

Both the anodic and cathodic ranges of the electrode were studied; because the great advantage of graphite electrodes is that they can be used in the anodic range, this region was studied in greater detail.

To examine the anodic polarisation range of the electrode, current–potential curves were recorded in various supporting electrolytes. The residual currents did not exceed 0.2 μA even at +1.0 V in most of these supporting electrolytes. The results are summarised in Table I, where the limit of the anodic polarisation range is given by the potential corresponding to a residual current of 1 μA. From these measurements, it can be concluded that the residual current is very low; generally at +0.7 V a residual current of a few hundredths of a microampere appears and increases slowly towards more positive potentials.

TABLE I

EXAMINATION OF THE ANODIC POLARISATION RANGE

Supporting electrolyte	*Polarisation range vs. S.C.E. (V) (i = 1 μA)*
0.1 *M* KCl	+1.35
1.0 *M* KCl	1.32
0.1 *M* Na_2SO_4	1.25
1.0 *M* NH_4NO_3	1.30
0.2 *M* CH_3COOH	1.40
0.1 *M* HCl	1.30
0.1 *M* H_2SO_4	1.40
0.1 *M* $NaNO_3$	0.65
0.1 *M* NaOH	0.70
Britton–Robinson buffer pH 8.1	1.20
Britton–Robinson buffer pH 4.5	1.20
Michaelis phosphate buffer pH 7.0	1.25

In the cathodic polarisation range, no residual current appears at potentials more positive than −0.3–0.4 V; at more negative potential values a residual current greater than 2 μA is present even in de-oxygenated solutions and this decreases the sensitivity of the measurements.

Cleaning and storage of the electrodes

An advantage of the silicone rubber-based graphite electrode is that it requires no pretreatment before use. After use, the electrodes can be cleaned simply by washing with distilled water, except in cases where a film is formed on the surface of the electrode during the electrochemical process, which alters the surface of the electrode (*e.g.*, when phenols are used). In such case, the surface of the electrode must, of course, be renewed to obtain reproducible results. This problem can be solved when rod electrodes are used, by cutting off the old surface before each measurement. The electrodes are stored either dry or in distilled water.

Reproducibility of the voltammetric curves

The reproducibility of the voltammetric curves is very important, for a measurement is reliable only if the deviation of the values measured under the same conditions is known to be satisfactory for practical purposes.

The reproducibilities of the two characteristics of the voltammetric curves

— the peak current (i_p) and the half-peak potential ($E_{p/2}$) — were examined for many electroactive compounds. This was done by repeated recording of the curve with the same electrode surface in a given solution. Between measurements the solution was stirred for 30 sec in order to attain the same experimental conditions. The reproducibility of the electrode in the examined systems was very satisfactory. This is illustrated in Fig. 1, in which the oxidation curves of iodide are presented. The five curves were recorded on top of each other and are almost identical.

A similarly good reproducibility was observed in solutions of potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), hydroquinone, quinone, *p*-phenylenediamine, *p*-toluidine, etc. The reproducibility of the peak current of all the compounds mentioned given as the relative standard deviation was less than 0.2%.

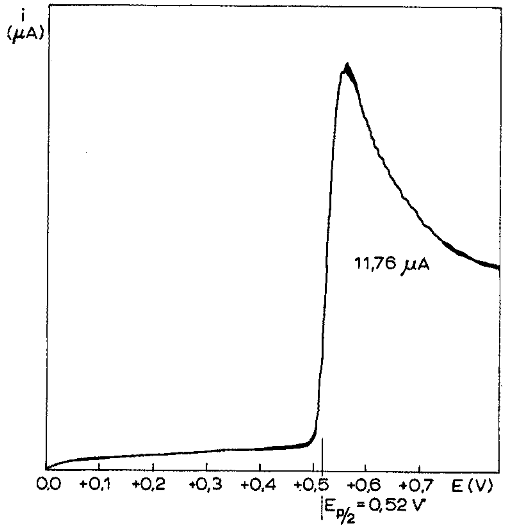

Fig. 1. Oxidation curve of iodide ions (5 recordings). KI concn.: $5 \cdot 10^{-4}$ *M*; supporting electrolyte: 0.1 *M* KCl; scan rate: 1.5 V/min.

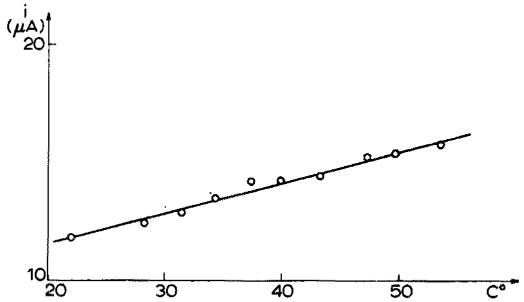

Fig. 2. Dependence of peak current on temp. $K_4[Fe(CN)_6]$ concn.: 10^{-3} *M*; supporting electrolyte: 1 *M* KCl.

The effect of temperature

The temperature-dependence of the limiting current of 10^{-3} *M* potassium hexacyanoferrate(II) was examined in 1 *M* potassium chloride as supporting electrolyte. The peak current changed linearly with temperature as shown in Fig. 2. The temperature coefficient of the hexacyanoferrate(II) oxidation peak was 1.1%/°C.

The dependence of the peak current on the concentration of the electroactive components examined

For analytical purposes, the variation of the peak current with the concentration of the required substance is important, hence this factor was studied for many systems. The peak height of various inorganic and organic compounds was found to vary linearly with the concentration of the investigated species between concentrations of 10^{-4} and 10^{-2} M[19], within the error of the reproducibility, *i.e.*, 0.2% relative error. A detailed comparison of the parameters valid in the reduction or oxidation of some inorganic and organic compounds at a silicone rubber-based graphite electrode is shown in Table II.

DISCUSSION

From the above results, it appears probable that many compounds can be analysed voltammetrically with the silicone rubber-based graphite electrode. Because of the relatively large surface area and the reproducibly small residual current values of the electrodes, the electroactive compounds give an easily measurable current even at low concentrations. Experiments carried out on numerous compounds showed that the height of the peak current is proportional to the concentration.

The reproducibility of the current–potential curves on the same electrode surface was found to be very satisfactory (relative standard deviation, 0.2%), except for those organic compounds which required a fresh electrode surface to yield reproducible results (phenol, resorcinol, naphthylamine).

The advantage of the electrode is that no pretreatment is required before use and the electrode surface in the course of repeated recordings can be restored to its original condition by stirring or reversed polarisation (the latter method was generally used for the examination of metals). After use, the electrodes can be cleaned by rinsing them with distilled water except for the cases mentioned above.

SUMMARY

The behaviour of a new type of graphite electrode prepared by mixing spectral graphite with silicone rubber before cold vulcanisation, is described. Electrodes can be prepared as plates or rods. The residual current is reproducibly small or negligible in the potential range −0.3 V to +0.7 V. The height of the peak current is proportional to the concentration for a wide range of substances. The reproducibility of i–E curves at the same electrode surface is excellent. The electrode requires no preliminary treatment and the surface can be easily cleaned or renewed. The temperature coefficient measured for hexacyanoferrate(II) was 1.1%/°C.

RÉSUMÉ

On examine le comportement d'un nouveau type d'électrode en graphite, préparée en mélangeant du graphite spectral avec du caoutchouc de silicone, avant

TABLE II

THE OXIDATION OR REDUCTION OF SOME ORGANIC AND INORGANIC COMPOUNDS AT A SILICONE RUBBER-BASED GRAPHITE ELECTRODE

Compound	*Data for proposed electrode (scan rate 1.5 V/min)*		*Literature data*			
	Supporting electrolyte	*$E_{p/2}$ (V vs. S.C.E.)*	*Supporting electrolyte*	*$E_{p/2}$ (V vs. S.C.E.)*	*Electrode*[a]	*Ref.*
Oxidation of organic compounds						
Hydroquinone	pH 7.0[b]	+0.23	pH 7.0	+0.018	W.I.G.E.	20
			pH 4.4	+0.21	,,	
p-Phenylenediamine	0.1 *M* HCl	+0.505	pH 4.5[c]	+0.540 *vs.* Ag/AgCl	,,	4
p-Toluidine	0.1 *M* HCl	+0.83				
Phenol	pH 7.0[b]	+0.62	pH 7.0	+0.537	,,	20
Pyrocatechol	pH 7.0[b]	+0.18	pH 4.5[c]	+0.32 *vs.* Ag/AgCl	,,	4
Resorcinol	pH 7.0[b]	+0.39	pH 7.0[c]	+0.49	,,	20
			pH 4.5[c]	+0.697 *vs.* Ag/AgCl	,,	4
p-Phenetidine	pH 7.0[b]	+0.29				
α-Naphthylamine	0.1 *M* KCl	+0.26	pH 5.1[d]	+0.53	CE-BnP	8
Oxytetracycline	0.1 *M* KCl	+0.45				
Ascorbic acid	pH 4.0[d]	+0.41	pH 3.6[d]	+0.279	W.I.G.E.	20
			pH 3.6[d]	+0.30[e]	,,	5
				+0.276[e]	,,	
Pyrogallol	pH 7.0[d]	+0.06				
Adrenaline	pH 3.61[d]	+0.64				
Gallic acid	pH 3.61[d]	+0.40				
Reduction of organic compounds						
p-Quinone	pH 7.0[b]	−0.09	pH 4.4	+0.14	W.I.G.E.	20
			pH 7.0[b]	+0.09	,,	5
			pH 5.45[c]	+0.03	,,	4
Methylene blue	pH 2.92[d]	−0.025				
Oxidation of some inorganic compounds						
$Fe(CN)_6^{4-}$	1 *M* KCl	+0.23	0.5 *M* KCl	+0.19 +0.20	Boron carbide	21
			0.5 *M* KCl	+0.203	W.I.G.E.	22
			0.5 *M* KCl	+0.21	W.I.G.E.	5
			1.0 *M* KCl	+0.211	C.P.E.	23
			0.5 *M* KCl	+0.226	P.G.E.	20
				+0.205	W.I.G.E.	20
Tl^+	0.1 *M* NaOH	+0.20	1.0 *M* NaOH	+0.32	CE-NjP	8
CN^-	pH 9.35[d]	+0.95				
Br^-	0.1 *M* Na_2SO_4	+1.25	0.1 *M* Na_2SO_4	+1.10	CE-NjP	24
			pH 2.4[d]	+1.10	CE-NjP	24
			0.5 *M* K_2SO_4–0.5 *M* H_2SO_4	+1.009	rotating P.G.E.	25
I^-	0.1 *M* KCl	+0.53	0.5 *M* K_2SO_4–0.5 *M* H_2SO_4	+0.50 +0.56	rotating P.G.E.	25
			1.0 *M* $NaClO_4$	+0.53	P.G.E.	26
			1.0 *M* H_2SO_4	+0.461	CE-CCl_4 paste	7
			pH 2.4[d]	+0.49	CE-NjP	8
			1.0 *N* H_2SO_4	+0.44	CE-NjP	8
			0.1 *M* KCl	+0.65	C.P.E.	9

TABLE II (continued)

Compound	*Data for proposed electrode (scan rate 1.5 V/min)*		*Literature data*			
	Supporting electrolyte	$E_{p/2}$ *(V vs. S.C.E.)*	*Supporting electrolyte*	$E_{p/2}$ *(V vs. S.C.E.)*	*Electrode*[a]	*Ref.*
Reduction of some inorganic compounds						
Ag^+	0.1 *M* KNO_3	+0.05	0.1 *M* KNO_3	+0.296	W.I.G.E.	20
			0.1 *M* KNO_3– 0.1 *M* HNO_3	+0.24	P.G.E.	20
			0.1 *M* $NaNO_3$	+0.057[e] +0.061[e]	C.P.E.	23
			0.1 *M* KCl	+0.13	W.I.G.E.	3
$Fe(CN)_6{}^{3-}$	1.0 *M* KCl	+0.28	0.5 *M* KCl	+0.222	,,	22
			0.5 *M* KCl	+0.16	,,	5
			1.0 *M* KCl	+0.273	C.P.E.	27
			pH 2.4[d]	+0.21	CE-BnP	8
Hg^{2+}	0.1 *M* KNO_3	−0.070	0.1 *M* KNO_3– 0.001 *M* HNO_3	−0.13	W.I.G.E.	4
			0.1 *M* HNO_3	+0.16	P.G.E.	20
Cu^{2+}	0.1 *M* KNO_3 0.1 *M* KCl	−0.020 −0.20	1.0 *M* KCl– 0.1 *M* HCl	+0.17	P.G.E.	20
			0.1 *M* K_2SO_4	−0.060	W.I.G.E.	20
			0.1 *M* KCl	+0.220	,,	20
			0.1 *M* KNO_3	−0.020	,,	22
			0.5 *M* KNO_3	−0.030	,,	22
			1.0 *M* $HClO_4$	−0.23	CE-NjP	8
			1.0 *M* KCl	−0.20	CE-NjP	8
Cl_2	0.1 *M* H_2SO_4	+0.36				

[a] CE-BnP = Carbon electrode–bromonaphthalene paste.
CE-NjP = Carbon electrode–nujol paste.
CE-CCl_4 paste = Carbon electrode–CCl_4 paste.
C.P.E. = Carbon paste electrode.
P.G.E. = Pyrolytic graphite electrode.
W.I.G.E. = Wax-impregnated graphite electrode.

[b] Phosphate buffer.

[c] Acetate buffer.

[d] Britton–Robinson buffer.

[e] Value depends on concentration.

vulcanisation à froid. On peut fabriquer ainsi soit des plaques, soit des barres. Le courant résiduel est faible ou négligeable entre −0.3 V et +0.7 V. La hauteur du pic de courant est proportionnelle à la concentration pour une grande variété de substances. La reproductibilité des courbes intensité/potentiel sur une même surface d'électrode est excellente. L'électrode ne demande aucun traitement préliminaire; sa surface peut facilement être nettoyée et régénérée. Le coefficient de température pour l'hexacyanoferrate(II) est de 1.1% par °C.

ZUSAMMENFASSUNG

Das Verhalten eines neuen Typs einer Graphitelektrode, die durch Mischen von Spektralgraphit mit Siliconkautschuk vor der kalten Vulkanisation hergestellt wurde, wird beschrieben. Die Elektroden können als Platten oder Stäbe hergestellt werden. Der Reststrom ist reproduzierbar klein oder vernachlässigbar im Potentialbereich von −0.3 V bis 0.7 V. Die Höhe des Peak-Stroms ist proportional zur Konzen-

tration bei einer grossen Anzahl von Substanzen. Die Reproduzierbarkeit von i–E Kurven mit derselben Elektrodenoberfläche ist ausgezeichnet. Die Elektrode erfordert keine vorhergehende Behandlung, die Oberfläche kann leicht gereinigt oder erneuert werden. Der Temperaturkoeffizient betrug beim Hexacyanoferrat(II) 1.1%/°C.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) WITH 2-THENOYLTRIFLUOROACETONE AND THE SYNERGETIC EFFECT OF PYRIDINE

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2-Thenoyltrifluoroacetone (TTA) has already been employed as the chelating agent in the determination of trace amounts of iron(III)[1,2]. However, the extraction behavior of the TTA chelate of iron(II) has not been clarified probably because iron(II)–TTA can readily be destroyed by atmospheric oxidation. Although a similar situation has been observed in the extraction of mangenese(II) dithizonate and the resulting chelate has no analytical use[3], it has been shown[4] that manganese(II) dithizonate can be extracted quantitatively into an organic phase by using the synergetic effect of pyridine.

In the same manner, an increase in extractability may be expected for the TTA extraction of iron(II) if the chelate has residual coordinating sites and forms an adduct with a neutral base containing an electron donor. In fact, so-called synergetic effects have been reported for the extraction of some divalent metal ions of the first transition series with TTA[5]. In the work described below, it was found that the extractability of the iron(II)–TTA complex into the organic phase can be increased by the addition of pyridine and that the extracted complex is stable enough for analytical purpose.

EXPERIMENTAL

Apparatus

Visible absorption spectra were measured with a Hitachi EPS-2U type recording spectrophotometer. The optimal conditions for determining iron(II) were established by measurements with a Shimazu Spectronic 20 type photoelectric photometer and 1.17-cm glass cells. The pH value of the aqueous phase was measured after extraction with a Hitachi-Horiba F-5 type pH-meter and a glass electrode.

Reagents

TTA and benzene (Wako Pure Chemical Inc.) were used without further purification. Pyridine and all other materials used in this work were of guaranteed grade. Deionized water was used throughout.

Extracting solution. A 0.2 M pyridine solution was prepared by dissolving a weighed amount of the reagent in benzene. Equal volumes of the base solution and of a 0.02 M TTA solution in benzene were mixed before the extraction experiments.

Standard iron solution. Iron(II) solution (100 mg/l) was prepared by dissolving Mohr's salt in 0.01 N hydrochloric acid.

General procedure

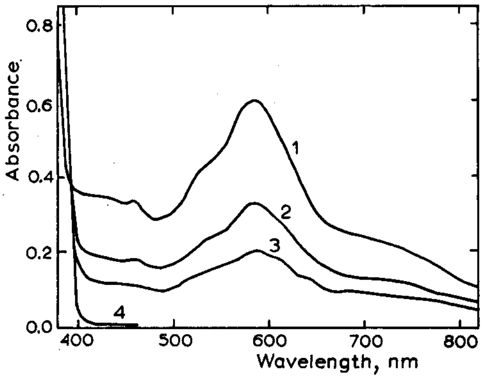
Transfer the sample solution containing 7–100 μg of iron to a separatory funnel. Add 2 ml of aqueous 10% hydroxylamine hydrochloride solution and adjust the pH of the solution to about 5 by adding 1 M sodium acetate – 0.5 M acetic acid buffer solution. Then extract with 10 ml of extracting solution by shaking for 3 min. Allow the phases to separate and measure the absorbance of the organic phase against benzene at 580 nm.

RESULT AND DISCUSSION

Erratic results were obtained when extractions were done in the absence of either pyridine or hydroxylamine hydrochloride. In order to obtain sufficiently reproducible absorbance measurements, both pyridine and hydroxylamine hydrochloride should be added before the extraction. The addition of hydroxylamine hydrochloride ensures the presence of iron(II) and prevents atmospheric oxidation of the resulting chelate. Although the extraction rate of iron(II) with TTA in the absence of pyridine could not be established, its extraction in the presence of the base was very rapid and the extraction equilibrium could be obtained by shaking only for 30 sec. In the present work the mixture was shaken for 3 min in order to ensure complete extraction.

Absorption spectrum of the extracted complex

The visible absorption spectra of TTA and of its complex of iron(II) in benzene are shown in Fig. 1. The spectrum of the extracted complex has a maximum absorbance at around 580 nm, and the intensity is stable for at least 3 h in a separatory funnel. The complex decomposes within a few days and a red colored species is formed,



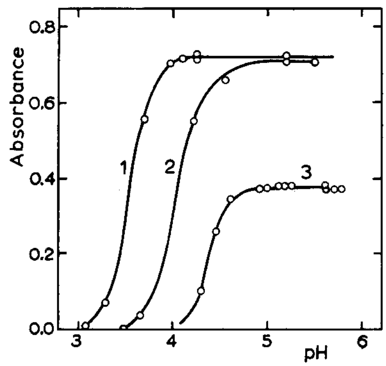


Fig. 1. Absorption spectra. 0.01 M TTA, 0.1 M pyridine. Fe(II): (1) 100 μg, (2) 50 μg, (3) 30 μg, (4) none (blank).

Fig. 2. Extraction curves. (1) 100 μg Fe(II), 0.01 M TTA, 0.1 M pyridine. (2) 100 μg Fe(II), 0.01 M TTA, 0.01 M pyridine. (3) 50 μg Fe(II), 0.001 M TTA, 0.1 M pyridine.

the visible absorption spectrum of which is similar to that of the iron(III)–TTA complex.

Effect of pH on the extraction of iron(II)

In previous work[6], the following reaction was suggested for the extraction of iron(II).

$$Fe^{2+} + 2\ HTTA + 2\ Base = Fe(TTA)_2(Base)_2 + 2\ H^+$$

This mechanism indicates that the extractability of iron (II) may be affected by the pH of the solution, and by the concentrations of TTA and pyridine.

As shown in Fig. 2, an increase in pH leads to an increase in the extractability of iron(II), and above pH 5 the absorbance becomes constant. The extractability also increases with an increase in the concentration of TTA or pyridine, as expected.

Since the ratio of the volume of the aqueous phase to that of the organic phase may affect the concentration of the extractants, the effect of the volume of sample solution on the absorbance was studied. The results (Table I) show that the absorbance is only slightly affected by changes in the volume of sample solution from 5 to 100 ml.

The proposed method has advantages over the extraction of the iron(III)–TTA complex: the optimum pH range for the extraction of iron(III) is narrow and the extraction rate is relatively low. In contrast, the pH of the sample solution for the extraction of iron(II) can easily be adjusted because of the broad optimum pH range, and the extraction of iron(II) is quite rapid.

TABLE I

EFFECT OF VOLUME OF SAMPLE SOLUTION ON THE ABSORBANCE[a]

Sample solution (ml)	5	10	30	50	100
Absorbance	0.69	0.69	0.70	0.70	0.71

[a] 100 μg of iron(II) extracted with 10 ml of benzene solution.

Calibration curve

Calibration curves obtained by the above-mentioned procedure are linear for 0–10 p.p.m. of iron(II) in the organic phase and pass through the origin. The reproducibility of absorbance measurements was better than 1%, the sensitivity being 0.012 μg/cm² at 580 nm. Although the sensitivity of the proposed method is slightly lower than those of the 2,2-bipyridyl, 1,10-phenanthroline or thiocyanate methods[7], it is quite high compared with the sensitivities of TTA extractions of other divalent metals[8].

Diverse ions

The TTA extraction of many metal ions has been extensively investigated and their extraction behaviors have also been reported by several workers[9]. Metals reacting with TTA at about pH 5 may interfere with the determination of iron(II); of these metals, 1000 μg of cobalt(II), nickel(II) or zinc(II) interfered to some extent. However, many cations and anions (except fluoride and citrate) could be tolerated (Table II).

TABLE II

EFFECT OF DIVERSE IONS

(Iron(II) = 50.0 μg)

Diverse ion	*Added as*	*Diverse ion added (mg)*	*Fe found (μg)*	*Difference (μg)*
Ca^{2+}	$Ca(NO_3)_2 \cdot 6H_2O$	1.00	50.0	0.0
Mg^{2+}	$MgSO_4 \cdot 7H_2O$	1.00	50.4	+0.4
Sr^{2+}	$SrCO_3$(dissolved in HCl)	1.00	50.0	0.0
Th^{4+}	$Th(NO_3)_4 \cdot 4H_2O$	1.00	50.0	0.0
Cr^{3+}	$K_2Cr_2(SO_4)_4 \cdot 24H_2O$	1.00	50.1	+0.1
Mn^{2+}	$MnSO_4 \cdot 4H_2O$	1.00	51.0	+1.0
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	1.00	57.5	+7.5
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	1.00	55.0	+5.0
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	1.00	50.1	+0.1
Zn^{2+}	Metal(dissolved in HCl)	1.00	51.4	+1.4
Cl^-	NaCl	500	51.5	+1.5
F^-	NaF	500	5.3	−44.7
SO_4^{2-}	K_2SO_4	500	50.0	0.0
$S_2O_3^{2-}$	$Na_2S_2O_3$	500	50.5	+0.5
PO_4^{3-}	$NH_4H_2PO_4$	500	48.7	−1.3
BO_3^{3-}	H_3BO_3	500	50.5	+0.5
tart^{2-}	Rochelle salt	500	48.7	−1.3
cit^{3-}	Ammonium citrate	500	31.6	−18.4

TABLE III

ANALYSIS OF WATERS

Sample no.	*Fe present*[a] *(μg/ml)*	*Fe added (μg/ml)*	*Fe found*[a] *(μg/ml)*
1[b]	2.31 ± 0.20	1.00	3.11 ± 0.23
2[b]	0.54 ± 0.08	0.40	0.90 ± 0.02
3[b]	0.060 ± 0.005	0.050	0.11 ± 0.005
4[c]	0.013 ± 0.001	0.010	0.026 ± 0.002
5[c]	0.14 ± 0.009	0.080	0.21 ± 0.008
6[c]	0.056 ± 0.003	0.20	0.25 ± 0.005

[a] Average value of 5 determinations and 95% confidence limit.
[b] Samples taken from the Agatsuma river.
[c] Samples taken from the Watarase river.

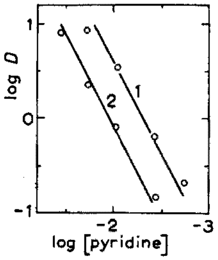


Fig. 3. Effect of pyridine concentration on the distribution ratio of iron(II). $1.0 \cdot 10^{-2}$ *M* TTA; pH: (1) 4.2, (2) 4.0.

Determination of iron in natural waters

The results obtained by the suggested procedure for samples of natural water after evaporation to less than 100 ml indicate satisfactory reproducibility (Table III).

Composition of the extracted complex

The mole ratio of iron(II) to TTA in the extracted complex was shown to be 1:2 by Job's method of continuous variation[6]. Similar experiments for determining the mole ratio of pyridine to $Fe(TTA)_2$ failed, mainly because of the atmospheric oxidation of the resulting chelate and the poor reproducibility of absorbance measurements for low pyridine concentrations. However, a logarithmic plot of the distribution ratio of iron(II) against the concentration of pyridine gave a straight line with a slope of 2 (Fig. 3). This indicates that the extracted complex may be $Fe(TTA)_2(pyridine)_2$ and that the synergetic effect in the extraction is attributable to the formation of the pyridine adduct.

SUMMARY

Pyridine has a synergetic effect on the extraction of iron(II) with TTA. The spectrophotometric determination of iron (7–100 μg) based on this reaction is rapid, highly reproducible and reasonably selective. The optimal pH range is wide and the sensitivity is 0.012 μg/cm² at 580 nm. The method can be applied to the analysis of natural waters.

RÉSUMÉ

La pyridine a un effet synergétique sur l'extraction du fer(II) à l'aide de 2-thénoyltrifluoroacétone. Le dosage spectrophotométrique du fer (7–100 μg) basé sur cette réaction est rapide, très reproductible et sélectif. Le domaine de pH optimal est étendu; la sensibilité est de 0.012 μg/cm² à 580 nm. Ce procédé peut s'appliquer à l'analyse des eaux naturelles.

ZUSAMMENFASSUNG

Pyridin zeigt einen synenergetischen Effekt bei der Extraktion von Eisen(II) mit TTA. Die auf dieser Redaktion beruhende spektralphotometrische Bestimmung von Eisen (7–100 μg) ist schnell, sehr gut reproduzierbar und weitgehend selektiv. Der optimale pH-Bereich is gross. Die Empfindlichkeit beträgt 0.012 μg/cm² bei 580 nm. Die Methode kann bei der Analyse natürlicher Wässer angewandt werden.

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THE EXTRACTION OF THORIUM FROM NITRIC ACID SOLUTIONS BY LONG-CHAIN ALIPHATIC AMINES

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(Received April 25th, 1968)

The extraction of thorium(IV) from nitric acid solutions by high-molecular-weight amines has been studied by several investigators[1,2], but observations on the extraction mechanism and on the composition of the extracted complex are few. The extraction of uranium(VI) from nitric acid solutions by long-chain aliphatic amines has already been studied[3]. The present paper contains a more detailed study on the extraction of thorium by such amines.

EXPERIMENTAL

Reagents

The amines used were as follows: di-*n*-octylamine (DOA), tri-*n*-octylamine (TOA), tri-*n*-dodecylamine (TDA) and tris-(2-ethylhexyl)amine (TEHA) (all from Kao Soap Co. Ltd. except for TEHA from Yoshitomi Pharmaceutical Industries Ltd.). They were diluted with various organic solvents, and were not preequilibrated with nitric acid solutions. The thorium nitrate solution was prepared by dissolving the tetrahydrate (Yokozawa Chemical Co. Ltd.) in nitric acid solution of the required concentration. The amines and the thorium nitrate tetrahydrate were of a high purity and were used without further purification. The other chemicals were analytical-reagent grade.

Extraction and analytical procedures

The amine solution in the organic solvent (20 ml) and thorium nitrate solution (20 ml) containing nitric acid were shaken for 10 min in 50-ml stoppered conical flasks in a water-bath thermostatted at the required temperature. Preliminary experiments showed that equilibration was complete in 10 min. The mixture was centrifuged and separated, and thorium was stripped from the organic phase with 1 *N* hydrochloric acid. Then the partition coefficient (the ratio of the equilibrium concentration of thorium in the organic phase to that in the aqueous phase) was obtained.

Thorium(IV) was determined by titration with EDTA with xylenol orange as indicator[4]. The acidity of the organic phase was determined by adding 2 ml to 25 ml of 75% ethanol and titrating with 0.01 *N* sodium hydroxide solution (pH meter). The water content of the organic solution was determined by the Karl Fischer method.

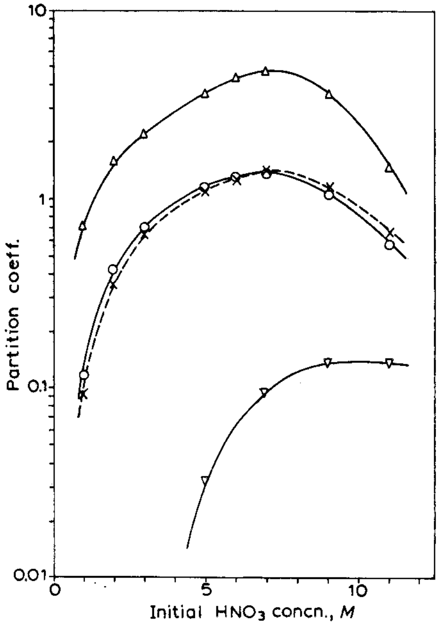
Infrared spectral measurement

The infrared spectra were measured with a Shimazu Model IR-27C recording spectrophotometer equipped with sodium chloride prisms. The spectra of organic extracts were determined with benzene as reference liquid, matched 0.1-mm cells, and a thallium halide window.

RESULTS AND DISCUSSION

Extraction efficiency of various systems

The extraction of thorium nitrate solution (5 g/l) containing various concentrations of nitric acid, with 0.2 *M* solutions of amines in benzene at 20° gave the results shown in Fig. 1. The order of the extraction efficiency for thorium is: TEHA > TDA ≈ TOA > DOA. Thus the tertiary amines are more efficient extractants than the secondary amines, and the efficiency is enhanced when the alkyl chain is branched.



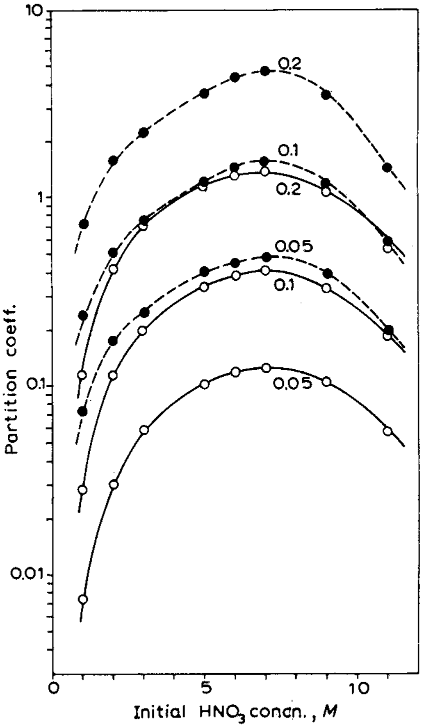


Fig. 1. Extraction of thorium from nitric acid solutions with 0.2 *M* solutions of various amines in benzene (▽ DOA, ○ TOA, × TDA, △ TEHA).

Fig. 2. Extraction of thorium from nitric acid solutions with solutions of TOA and TEHA (○ TOA, ● TEHA; numbers on curves are amine concentrations, *M*).

These results are essentially in agreement with those obtained in the extraction of thorium[2] or uranium(VI)[5] by cyclohexyl alkylamines and benzylalkylamines, and of uranium(VI) by long-chain aliphatic amines[3]. The shape of the extraction curve in benzene resembles the form of the curve for uranium(VI)[3]: the partition coefficient rises rapidly to a maximum which occurs at initial nitric acid concentrations of about

7 *M* for TOA, TDA and TEHA, and of 9 *M* for DOA. The optimal initial acidities of the aqueous layer are virtually unrelated to the amine concentration, as indicated in Fig. 2 for TOA and TEHA in benzene. These curves may be interpreted as follows: the increase in the partition coefficient at low acidities is attributed to salting-out by nitric acid or to the formation of a thorium nitrate – nitric acid complex; the decrease at higher acidities arises either from competition between thorium and nitric acid for association with the amine or from the formation of less readily extractable complexes.

Table I shows some representative results for various TOA–organic solvent systems used in the extraction of thorium nitrate solutions (5 g/l) containing 6 *M* nitric acid at 20°. Clearly the extraction efficiency of TOA for thorium is higher with hydrocarbons such as alkane or cycloalkane (although a third phase is formed by them) than with aromatic hydrocarbons; chloro-substituted solvents are very poor extraction media.

TABLE I

EXTRACTION OF THORIUM FROM 6 *M* NITRIC ACID SOLUTION WITH 0.1 *M* TOA IN VARIOUS ORGANIC SOLVENTS

Diluent	*Partition coefficient*	*Diluent*	*Partition coefficient*
Kerosene	4.59[a]	Chloroform	0.028
Benzene	0.385	Chlorobenzene	0.198
Cyclohexane	4.82[a]	1,2-Dichloroethane	0.073
Carbon tetrachloride	1.01	*o*-Dichlorobenzene	0.215
n-Hexane	3.70[a]	Nitrobenzene	0.596
Toluene	0.473		

[a] Since a third phase was formed in this extraction system, the thorium concentration of the organic phase was calculated by deducting the equilibrium concentration of thorium in the aqueous phase from the initial thorium concentration.

Extraction in presence of sodium nitrate

The extraction of thorium nitrate solutions (5 g/l) containing 0.1 *M* nitric acid and various concentrations of sodium nitrate, by 0.1 *M* TOA in benzene at 20° is shown in Fig. 3; data for similar extractions from nitric acid solutions alone are also given. The partition coefficient reaches a maximum when the initial concentration of nitric acid in the aqueous phase is about 7 *M*, but when part of the nitric acid is replaced by sodium nitrate, the partition coefficient increases with the total nitrate ion concentration. This can probably be explained in the same way as for other cases[2,3,5], *viz.*, a reduction in nitric acid competition for association with the amine. In the partition of nitric acid between mixed 0.1 *M* nitric acid–sodium nitrate solutions (in the absence of thorium) and 0.1 *M* TOA solutions in benzene, the acidity of the organic phase is not influenced by the presence of sodium nitrate (Fig. 4). Thus the sodium nitrate itself appears to be virtually non-extractable and to be effective as a salting-out agent. Figure 4 also shows that the acidity of the organic phase in the extraction of thorium increases as the concentration of sodium nitrate increases; this increase corresponds roughly to 4 times the thorium concentration in the organic phase, based on the extraction of thorium nitrate.

Dependence on concentrations of solvent and thorium

The variation in the partition coefficient with different concentrations of TOA in benzene for the extraction of thorium nitrate solutions (5 g/l) containing nitric acid at 20° is shown in Fig. 5. A log–log plot of the partition coefficient *vs.* the initial TOA concentration gave straight lines whose slopes are 1.95 in 1 M HNO_3, 1.85 in 3 M HNO_3, 1.75 in 6 M HNO_3, 1.70 in 9 M HNO_3, 1.65 in 11 M HNO_3 and 2.0 in 0.1 M $HNO_3 + 6 M NaNO_3$. Similar results were also obtained for the extraction with TEHA in benzene (Table II). Accordingly, it is postulated that the partition coefficient is a second-order function of the amine concentration.

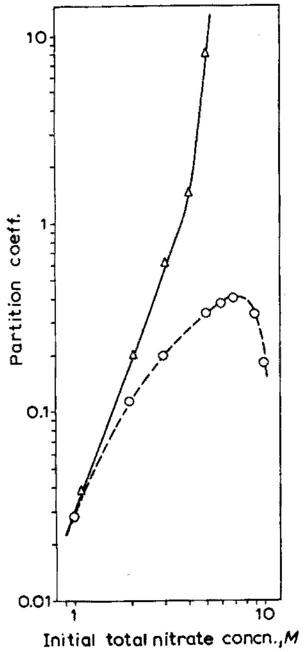


Fig. 3. Salting-out effect of nitric acid and sodium nitrate on the extraction of thorium with 0.1 M TOA in benzene (△ in the presence of 0.1 M nitric acid and sodium nitrate, ○ in the presence of nitric acid only).

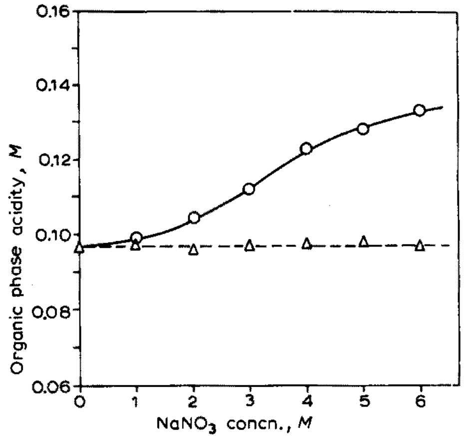


Fig. 4. Change in acidity of organic phase on the extraction of thorium from 0.1 M nitric acid plus various concentrations of sodium nitrate with 0.1 M TOA in benzene (○ in the presence of thorium, △ in the absence of thorium).

TABLE II

SLOPES OF LOG–LOG PLOTS OF THE PARTITION COEFFICIENT *VS.* THE INITIAL TEHA CONCENTRATION AT DIFFERENT AQUEOUS NITRIC ACID CONCENTRATIONS

HNO_3 concn. (M)	1	2	3–6	7	9	11
Slope	1.65	1.61	1.60	1.70	1.60	1.50

Various concentrations of thorium nitrate solutions containing 6 M nitric acid, or 0.1 M nitric acid and 6 M sodium nitrate, were extracted with 0.1 M TOA in benzene at 20°, and the variation in the thorium concentration of the organic phase was determ-

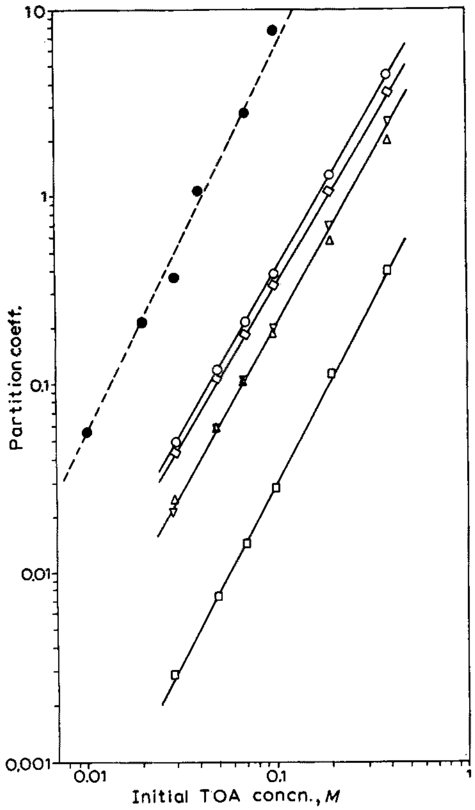


Fig. 5. Solvent dependence of the partition coefficient for the extraction of thorium from nitric acid solutions by TOA in benzene (□, ▽, ○, ◇, △ 1, 3, 6, 9 and 11 M HNO_3 respectively; ● 0.1 M HNO_3+6 M $NaNO_3$).

ined (Fig. 6). However, the organic phase was never saturated with thorium in the range of initial thorium concentrations studied, hence the solvation ratio of TOA to thorium could not be determined.

The results above indicate that the mechanism of this extraction is similar to that for tertiary cyclohexyl- and benzyl-alkylamines[2]:

$$Th(NO_3)_4\,(aq) + 2\,R_3NHNO_3\,(org) \rightleftarrows (R_3NH)_2Th(NO_3)_6\,(org) \qquad (1)$$

Infrared study

The organic phase obtained from the extraction of thorium nitrate solutions (5 and 100 g/l) containing 0.1 M nitric acid and 6 M sodium nitrate, with 0.1 M TOA in benzene at 20° was examined by infrared spectroscopy. The spectra are given in Fig. 7, compared with that from the extraction of 0.1 M nitric acid alone. The spectrum for the extraction of 0.1 M nitric acid solution shows the following absorptions: the intense peaks at 1415 and 1285 cm^{-1}, assigned to the NO_2 asymmetric and symmetric stretching respectively; the band at 1020 cm^{-1}, assigned to the N–O stretching (usually inactive in the infrared for the nitrate ion)[3,6,-9]; the vibration at 820 cm^{-1}, assigned

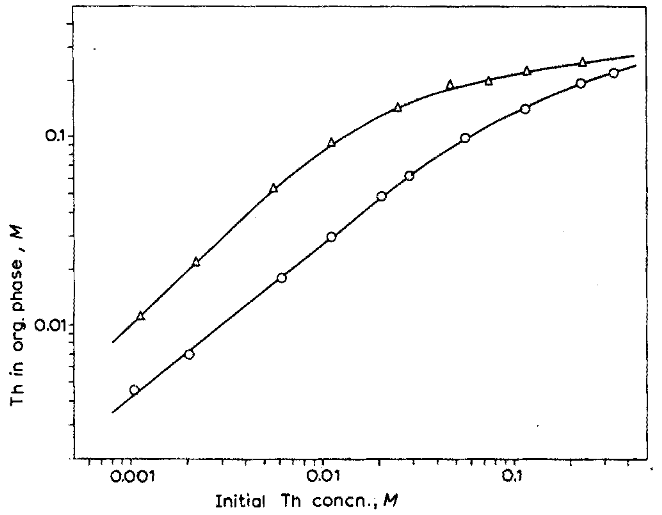
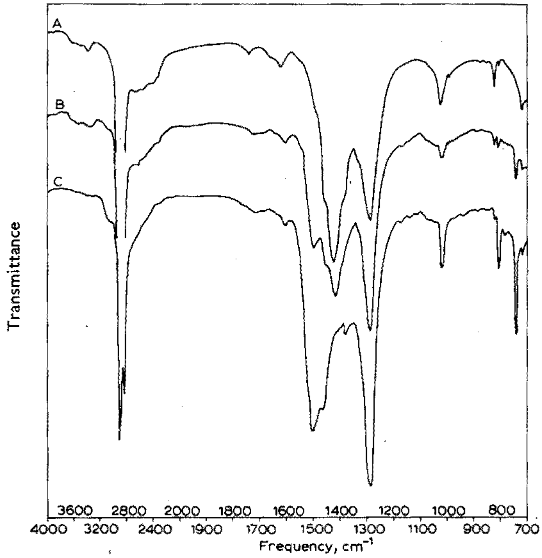


Fig. 6. Variation in thorium concentration in the organic phase with initial thorium concentrations, for extractions from nitric acid solutions with 0.1 *M* TOA in benzene (○ 6 *M* HNO_3, △ 0.1 *M* NHO_3 + 6 *M* $NaNO_3$).



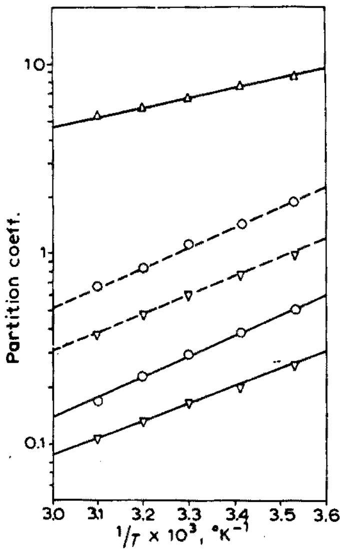


Fig. 7. Infrared spectra of the organic phases obtained from the extraction of thorium nitrate solutions containing 0.1 *M* nitric acid and 6 *M* sodium nitrate with 0.1 *M* TOA in benzene. (A) 0.1 *M* nitric acid solutions without thorium; (B) thorium nitrate solution (5 g/l); (C) thorium nitrate solution (100 g/l).

Fig. 8. Temperature dependence of partition coefficient for the extraction of thorium from nitric acid solutions with 0.1 *M* TOA and TEHA in benzene (▽ 3 *M* HNO_3, ○ 6 *M* HNO_3, △ 0.1 *M* HNO_3 + 6 *M* $NaNO_3$; continuous and broken lines represent TOA and TEHA, respectively).

to the non-planar rocking frequency; the NH^+ stretching vibration[10,11], which indicates the presence of strong hydrogen bonding, is observed in the weak broad band centered at 2650–2410 cm^{-1}. The spectrum of organic phase from the extraction of 0.1 M HNO_3 + 6 M $NaNO_3$ closely resembled that for 0.1 M nitric acid solution alone, which confirmed that sodium nitrate was not extracted.

The spectrum of the organic solution obtained from the extraction of thorium nitrate solution (5 g/l) containing 0.1 M nitric acid and 6 M sodium nitrate shows the bands at 1495, 1280, 1018, 805 and 739 cm^{-1}, whereas those of the amine nitrate become weaker. They are assigned to the vibrational frequencies of the nitrato group [7,12], indicating a lower symmetry (point group C_{2v} symmetry) than the nitrate ion[13] (point group D_{3h} symmetry), co-ordinated to the thorium ion; the bands at 1415, 1280, 1080 and 805 cm^{-1} are assigned as above, with slight shifts, the band at 739 cm^{-1} being assigned to NO_2 symmetric bending. In addition to these, there is absorption at 3060 cm^{-1} from the NH^+ stretching vibration which arises from the formation of the complex. In the organic phase from the extraction of an aqueous solution containing 100 g Th/l, the intensities of the bands caused by the amine nitrate decrease and the absorption bands due to the nitrato complex of thorium intensify; the bands at 1465 and 1375 cm^{-1}, assigned to the CH_3 degenerate (and CH_2 scissoring) and symmetrical bending modes of TOA, are observed more clearly from the reduction in the absorptions at 1415 and 1285 cm^{-1} due to the amine nitrate. Furthermore, the intensities of the bands due to the OH stretching and bending bands almost disappear. This accords with the fact that the water content of the organic phase, determined by the Karl Fischer titration, decreases with increasing thorium concentration.

It is therefore concluded that the amine–thorium nitrato complex possesses the stoichiometry $(R_3NH)_2Th(NO_3)_6$, as indicated in eqn. (1).

Effect of temperature

Thorium nitrate solutions (5 g/l) containing 3 and 6 M nitric acid, or 0.1 M nitric acid plus 6 M sodium nitrate, were extracted with 0.1 M TOA and TEHA in benzene at between 10 and 50°. Figure 8 shows that the partition coefficient decreases with rising temperature, and the heat of reaction (change in enthalpy) (in kcal/mole) in eqn. (1) is estimated as follows: for TOA, 4.1 in 3 M HNO_3, 5.4 in 6 M HNO_3 and 2.3 in 0.1 M HNO_3+6 M $NaNO_3$; for TEHA, 5.0 in 3 M HNO_3 and 5.4 in 6 M HNO_3. As these values are close to those for the energy of hydrogen bonds[14], it is assumed that the nature of the bonding in the organic phase is similar to that for hydrogen bonds.

The author wishes to thank Mr. S. HENMI for assistance with experimental work, and the Kao Soap Co. Ltd. and the Yoshitomi Pharmaceutical Industries Ltd. for samples of various amines.

SUMMARY

The partition of thorium between nitric acid solutions and solutions of long-chain aliphatic amines in benzene is described. The organic phase was examined by infrared spectroscopy. Tertiary amines are more efficient extractants for thorium than are secondary amines; the efficiency is enhanced when the alkyl chain is branched and is strongly influenced by the organic solvent used as diluent.

RÉSUMÉ

On décrit le partage du thorium, entre des solutions acide nitrique et des solutions d'amines aliphatiques à longue chaîne, dans le benzène. La phase organique est examinée par spectroscopie infra-rouge. Pour le thorium, le pouvoir d'extraction des amines tertiaires est supérieur à celui des amines secondaires; il augmente lorsqu'une chaîne alcoyle est introduite et il varie beaucoup avec la nature du solvant organique utilisé comme diluant.

ZUSAMMENFASSUNG

Es wird die Extraktion von Thorium mit langkettigen aliphatischen Aminen aus salpetersauren Lösungen beschrieben. Tertiäre Amine sind wirksamere Extraktionsmittel als sekundäre Amine. Die Wirksamkeit wird gesteigert, wenn die Alkylkette verzweigt ist. Sie wird ferner stark durch das organische Lösungsmittel beeinflusst.

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REGULARITIES IN THE DISTRIBUTION OF TTA AND ITS SCANDIUM CHELATE INTO A SERIES OF ESTER SOLVENTS

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(Received March 18th, 1968)

Solvent extraction is one of the most widely used separation methods, but the factors that affect the magnitude of the distribution coefficient are not completely understood; nearly always, solvents are selected empirically. Some systematic studies on the role of the solvent itself in so-called inert solvent systems[1-3] and alcohol systems[4,5] have been carried out. Recently, MOTTOLA AND FREISER[6] have studied comprehensively the distribution of certain 8-quinolinols and their copper chelates into various organic solvents[6]. In chelate extraction systems, inert solvents are mainly used. In the present work, the relationship between the distribution coefficient of a species and the physico-chemical properties of oxygen-containing solvents was studied. This was considered to be of interest because of the synergetic effects possible with such solvents.

Since esters, ethers and ketones are polar solvents, application of the same treatment as for inert solvent systems, may seem dubious; however, in all these solvents, dispersion forces predominate in the cohesive energies among liquid molecules[7,8], hence the same treatment should be permissible.

In this work, 2-thenoyltrifluoroacetone (TTA) was chosen as a typical chelating agent, and the distribution coefficient of TTA into various esters, including ethyl acetate, was determined. When a regularity in the distribution of TTA is observed in relation to the solubility parameter, a correlation between the distribution coefficient of TTA and that of a metal chelate with TTA may be expected.

EXPERIMENTAL

Reagents and apparatus

TTA (Dojindo Co. Ltd.) was purified by sublimation under reduced pressure and dried over phosphorus pentoxide.

The purest solvents commercially available were washed successively with saturated solutions of potassium carbonate and of calcium chloride, and then with distilled water; the solvent was dried over potassium carbonate and then distilled.

Scandium-46 was obtained as a scandium chloride solution in hydrochloric acid (New England Nuclear Corp., U.S.A.); this solution was treated as described previously[5].

The equipment for UV, NMR, pH and radioactivity measurements was the same as described previously[4,5].

Procedures

Distribution ratio of TTA (D_{HA}). An ester solution of TTA was shaken with an aqueous perchloric acid solution of ionic strength 0.1 (by adding sodium perchlorate) for a fixed time in an air thermostat at 25°. The amount of TTA in the aqueous phase was determined by measuring the absorbance at 290 nm. For some solvents, the solvent itself absorbed at about 290 nm; this interference was avoided by using an aqueous solution equilibrated with the same solvent free from TTA as blank.

Aqueous solutions and solvents were pre-equilibrated with each other before the distribution experiments. After shaking for 8 h, no significant differences in the distribution coefficients were observed for any solvent; shaking for 16 h was chosen as a standard procedure, for convenience.

UV spectrum. To avoid any dilution effect on the absorption spectra, the relevant pre-equilibrated organic solvent was used for dilution and the spectra were measured immediately.

Measurement of enol ratio. TTA solution (0.5 *M*) in an ester solvent and the aqueous solution of pH 2 were equilibrated, the organic phase was separated and the NMR spectrum was measured. The apparent enol ratio was obtained by measurement of the vinyl proton signal.

Distribution ratio of scandium (D_M). An aliquot of a perchloric acid–sodium perchlorate solution of ionic strength 0.1 containing ^{46}Sc tracer, and an equal volume of TTA solution in an ester solvent were shaken in an air thermostat at 25°. After the phases had been separated, the pH of the aqueous phase and the radioactivities of both phases were measured. Equilibration was attained after shaking for 10 h, and a shaking time of 20 h was chosen.

RESULTS AND DISCUSSION

Distribution coefficient of TTA

Before these distribution coefficients were determined, it was necessary to confirm that the measured distribution coefficient was related to the distribution coefficient of a fixed TTA species. In an ester phase, as in an alcohol phase[4], considerable amounts of the keto form will exist, the keto–enol equilibrium depending on the experimental conditions. Typical UV spectra of TTA in equilibrated ester phases are shown in Fig. 1, a and b. The peaks observed at 265 nm and 290 nm correspond to the keto form and/or hydrated keto form, and the peak at 320∼340 nm corresponds to the enol form and/or enolate form. The peak of the keto form shows no obvious shift with different solvents, but the enol peak shifts depending on the solvent as well as on the pH-value of the aqueous phase. This suggests that the enol form consists of *cis*-enol and *trans*-enol[9], but their differentiation is difficult, hence only total enol is used in this paper.

The keto–enol equilibrium of TTA depends not only on the organic solvent but also on the conditions in the aqueous phase; Fig. 1 shows that the keto form decreases and the enol form increases as the pH of the aqueous phase increases. In the case of these ester solvents, except ethyl acetate, the keto–enol equilibrium is much less dependent on pH than in the case of alcohol solvents. When the ester solvents were equilibrated with the aqueous solution below pH 5, almost the same spectra were obtained in all ester solvents. Accordingly, the distribution ratio of

TTA determined below pH 5 can be regarded as reliable at a fixed keto–enol equilibrium.

It is difficult to determine the enol ratio from UV spectra, because the mechanism of keto–enol equilibrium has not yet been elucidated and the molar ab-

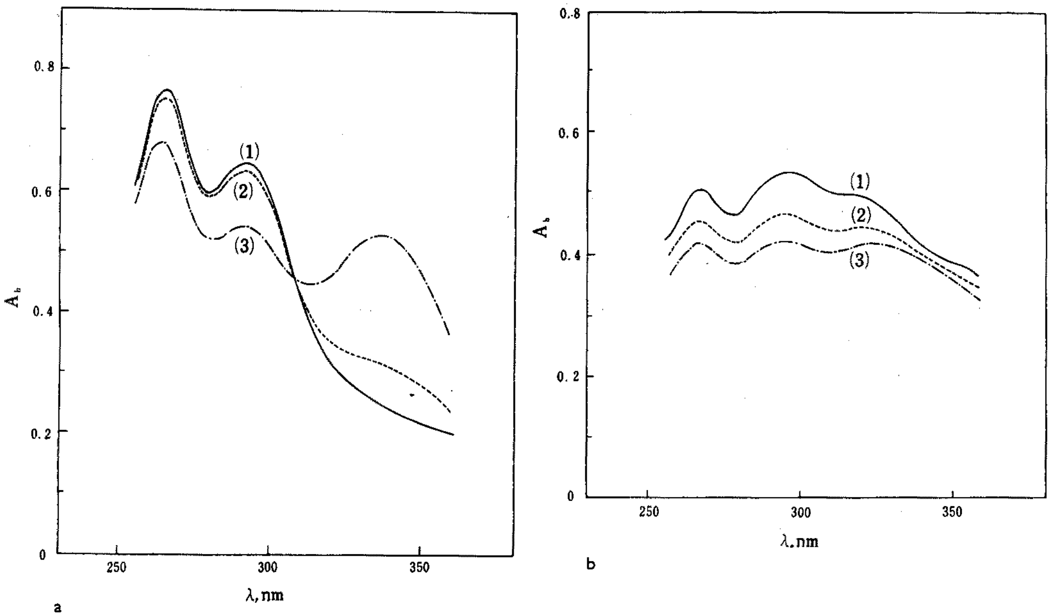

Fig. 1. Absorption spectra of TTA in ester equilibrated with aqueous phase. (a) In ethyl acetate. $[HA]_{org,init} = 1.41 \cdot 10^{-2}$ *M*; pH: (1) 2.3∼5.2; (2) 6.8; (3) 7.7. Organic phase diluted 121-fold; light path length = 0.6 cm. (b) In butyl butyrate. $[HA]_{org,init} = 8.02 \cdot 10^{-3}$ *M*; pH: (1) 1.04∼4.8; (2) 7.60; (3) 8.15. Organic phase diluted 121-fold; light path length = 1.0 cm.

TABLE I

DISTRIBUTION COEFFICIENTS OF TTA AND ITS SCANDIUM CHELATE
(Ionic strength, 0.10 (H,Na)ClO$_4$; 25°)

No.	*Solvent*	δ_{org}[a]	*log* P_{HA}	*Enol ratio*[c]	*log* D_M ($pA = 8.0$)
1	Ethyl acetate	9.1	2.27	0.35	0.20
2	*n*-Propyl acetate	8.8	2.30	0.42	0.43
3	Isopropyl acetate	8.4	2.29	0.46	0.49
4	*n*-Butyl acetate	8.5	2.22	0.46	0.22
5	Isobutyl acetate	8.3	2.18	0.42	0.20
6	2-Butyl acetate	8.2	2.19	0.51	0.13
7	*n*-Amyl acetate	8.5	2.11	0.55	0.06
8	Isoamyl acetate	8.1[b]	2.26	0.51	0.53
9	*n*-Octyl acetate	8.0[b]	1.81	0.54	−0.62
10	2-Ethylhexyl acetate	7.8[b]	1.84	0.54	−0.50
11	Benzyl acetate	9.5[b]	2.02		−0.37
12	Ethyl propionate	8.4	2.24	0.53	0.23
13	Butyl propionate	8.8	2.03	0.51	−0.08
14	Butyl butyrate	8.1	1.94	0.54	−0.32
15	Ethyl benzoate	9.4	2.00		−0.18

[a] Quoted from ref. 12.
[b] Estimated from eqn. (5).
[c] Defined as [apparent enol form of TTA]/[total TTA].

sorptivity of related chemical species in the ester solvent cannot be estimated correctly. In this work, an apparent enol ratio was obtained by measuring the vinyl proton signal in the NMR spectrum. The enol ratios of TTA thus obtained are shown in the fifth column of Table I.

The enol ratio is relatively small for ethyl acetate media, but the enol ratio in ester solvents is generally larger than that in alcohol solvents; there is little difference in the values among other ester solvents. In general, the greater the dielectric constant of the solvent, the smaller the enol ratio; the dielectric constants of esters are smaller than those of alcohols and the differences in the dielectric constants among the ester solvents are small.

In the cases of benzyl acetate and ethyl benzoate, no enol ratio could be estimated by either NMR or UV spectra because the solvent interfered; however, since the dielectric constants of these solvents are similar to those of the other solvents, the enol ratios are probably also similar.

The distribution coefficient of TTA, P_{HA}, is represented by:

$$P_{\mathrm{HA}} = \frac{[\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}}} = D_{\mathrm{HA}}\left(1 + \frac{K_{\mathrm{a}}}{[\mathrm{H}^+]}\right) \qquad (1)$$

where D_{HA} denotes the distribution ratio of TTA.

As discussed above, the equilibrium among the species is not sensitive to pH below pH 5. When the apparent dissociation constant of TTA[10], $K_{\mathrm{a}} = 6 \cdot 10^{-7}$, is introduced, the distribution ratio is effectively equal to the distribution coefficient of TTA below pH 4.

Since the distribution ratio is essentially constant in the range 10^{-3}–10^{-1} M TTA, it can be concluded that neither an association of TTA molecules nor a change in keto–enol equilibrium occurs in the organic phase. Consequently, an initial concentration of 0.01 M TTA solution was adopted and at least 4 runs were carried out for each solvent at pH below 4. The average values of the distribution coefficients found (log P_{HA}) are shown in Table I. The distribution coefficients in the ester solvent systems are higher than those in inert solvent systems ($P_{\mathrm{HA}} = \sim 70$) or alcohol systems ($P_{\mathrm{HA}} = \sim 60$). The esters should therefore be superior solvents in chelate extraction systems.

Correlation between distribution coefficient of TTA and solubility parameter of organic solvent

Although ester solvents have permanent dipoles, the contribution of orientation and induction effects to the cohesive energies is extremely small. For instance, in the case of ethyl acetate, the contribution of dipole–dipole interaction is about 1%[8]. Accordingly, the relation established on the basis of regular solution theory in the inert solvent system should also be applicable to the ester system.

The relationship between the distribution coefficient of the enol form of TTA and the solubility parameter of the organic solvent is expressed[1] by the following equation:

$$\log P_{\mathrm{x}} = \frac{V_{\mathrm{e}}}{2.30\,RT}(\delta_{\mathrm{aq}} - \delta_{\mathrm{org}})(\delta_{\mathrm{aq}} + \delta_{\mathrm{org}} - 2\delta_{\mathrm{e}}) \qquad (2)$$

where P_{x} represents the distribution coefficient in terms of mole fraction, and V and δ

represent the molar volume and the solubility parameter of a species, respectively. Although the aqueous phase is not a regular solution, this equation is valid for inert solvent systems by adopting an empirical value of 16.3_5 as a solubility parameter of the aqueous solution[1]. If the possibility of interaction between TTA and ester is neglected, this empirical value can also be applied to the present systems. Various species participate in the distribution coefficients of TTA shown in Table I, which are therefore *apparent* values, and do not show the true distribution coefficients of a single species of TTA. In order to confirm the validity of eqn. (3), attention was given to the enol form of TTA, and the distribution coefficient of this form, P_e, was calculated by the following equation from the measured distribution coefficient and the enol ratio which was determined by a simple NMR measurement.

$$P_e = \frac{K_e}{K_a}\,\frac{P_{HA}}{1+K_{org}} \tag{3}$$

where K_{org} is the equilibrium constant of the keto–enol tautomerism in the organic phase ($K_{org}=[\text{Keto}]/[\text{Enol}]$), and K_e is the dissociation constant of the enol form of TTA[10] ($K_e=5\cdot 10^{-5}$).

The solubility parameters of several ester solvents have not yet been reported, nor have values for heat of vaporization, from which the solubility parameter could be calculated. However, if it is accepted that molecular interaction in esters is not essentially different from that in inert solvents, then the heat of vaporization of an ester at 25° may be estimated from the boiling point of the ester by means of the empirical equation (4)[11], and then the solubility parameter (eqn. (5))[11] can be calculated:

$$\Delta H_{298}{}^{v}(\text{cal/mole}) = -2950+23.7\,T_b+0.020\,T_b{}^2 \tag{4}$$

$$\delta=\left(\frac{\Delta H^{v}-RT}{V}\right)^{\frac{1}{2}} \tag{5}$$

where T_b and V represent the boiling point and the molar volume of liquid, respectively. Before the application of eqn. (4) to esters with unknown solubility parameters, the above treatment was confirmed for esters of known solubility parameter[12].

In the case of ethyl acetate, however, as its mutual solubility with water is fairly large, the solubility parameter of the two phases in equilibrium is different from that of pure ester and the original aqueous solution, hence a correction is necessary. The solubility of water in ethyl acetate is 3.30 g/100 g at 25°, while that of ethyl acetate in water is 8.08 g/100 g[13]. If there is no specific interaction between ethyl acetate and water molecules, then the solubility parameters of both phases equilibrated with each other can be calculated by means of eqn. (6) from the mutual solubility data to be $\delta_{aq\cdot equil}=15.8$ and $\delta_{org\cdot equil}=9.3$,

$$\delta_m=\phi_A\delta_A+\phi_B\delta_B \tag{6}$$

where δ_m represents the solubility parameter of mixed solvent and ϕ the volume fraction of components A and B in the mixed solvent.

In order to confirm the relationship shown by eqn. (2) for ester systems, log $P_{x,e}/(\delta_{aq}-\delta_{org})$ was plotted against δ_{org} as shown in Fig. 2. The straight line was drawn by postulating the molar volume of the enol form of TTA as 160 cc[1]. The relationship obtained is obviously satisfactory. For ethyl acetate, the deviation was large when mutual solubility was ignored; when a correction was made, the value was reasonable, hence the treatment described above seems appropriate. Even in the ester systems in which some interaction between TTA and solvent cannot be ignored, it seems valuable to correlate the distribution coefficient of TTA with the solubility parameter of solvent. Furthermore, the relationship observed in ester systems is similar to that in inert solvent and alcohol systems.

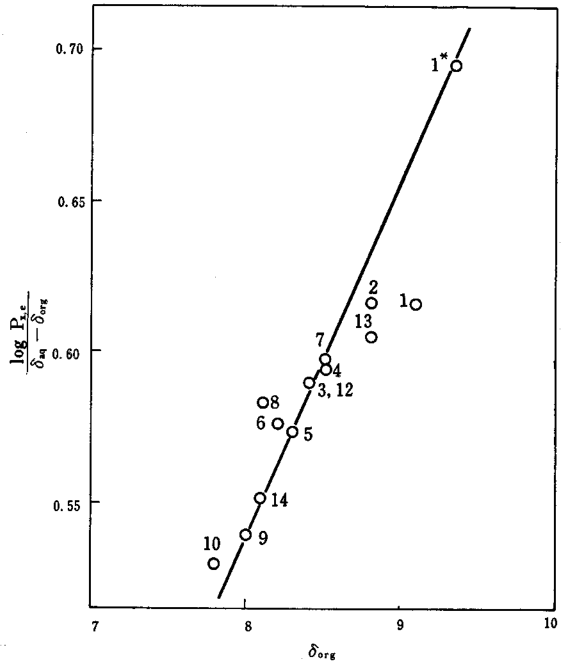

Fig. 2. Correlation between distribution coefficient of TTA and solubility parameter of solvent. * Corrected for mutual solubility.

Correlation between distribution coefficient of TTA and its scandium chelate

Before comparison of the distribution coefficient of the scandium chelate with that of TTA, it should be confirmed that the measured distribution coefficient exhibits the distribution coefficient of a fixed single species.

The formation and distribution of the scandium chelate can be shown as follows:

$$\mathrm{Sc}^{3+} + n\mathrm{A}^- \overset{\beta_n}{\rightleftharpoons} \mathrm{ScA}_n^{(3-n)+}$$

$$\mathrm{ScA}_{3\,\mathrm{aq}} \overset{P_\mathrm{M}}{\rightleftharpoons} \mathrm{ScA}_{3\,\mathrm{org}}$$

$$\mathrm{ScA}_{3\,\mathrm{org}} + j\mathrm{HA}_\mathrm{org} \overset{K_j}{\rightleftharpoons} \mathrm{ScA}_3 \cdot j\mathrm{HA}_\mathrm{org}$$

$$D_\mathrm{M} = \frac{P_\mathrm{M}\beta_3[\mathrm{A}^-]_\mathrm{aq}{}^3\{1 + \Sigma K_j[\mathrm{HA}]_\mathrm{org}{}^j\}}{1 + \Sigma\beta_n[\mathrm{A}^-]_\mathrm{aq}{}^n} \tag{7}$$

The distribution ratios of scandium were determined at various initial TTA concentrations or at different hydrogen ion concentrations. The results obtained for several esters plotted against pA ($= -\log[A^-]_{aq}$) are shown in Fig. 3; straight lines with slopes of -2.7–-3 were obtained for each solvent. Even when various initial concentrations of TTA solution were used and the pH values were different, straight lines of the same slope were obtained. Consequently, under these experimental conditions, the sole extractable scandium chelate is ScA_3 and there is no adduct formation with TTA. It was shown that the extraction of scandium by the solvent alone was negligible.

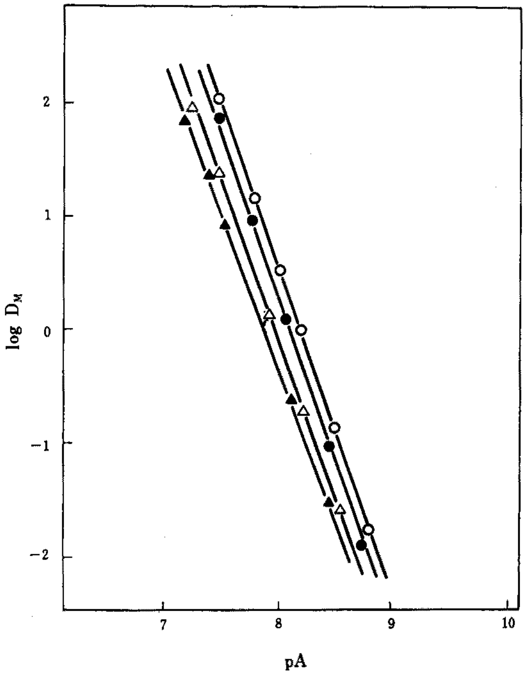

Fig. 3. Distribution ratio of Sc–TTA chelate as a function of pA. Ionic strength, 0.10 (H,Na)ClO_4; 25°. (●) ethyl acetate, pH = 2.06; (○) isopropyl acetate, pH = 2.04; (△) butyl propionate, [HA] = 0.01 *M*; (▲) butyl butyrate, [HA] = 0.01 *M*.

If the nature of an interaction between solute and solvent molecules is the same for two solutes, a chelating agent and its metal chelate, the following correlation is expected between the distribution coefficient of chelating agent (P_{HA}) and of metal chelate (P_M) in ester solvent system.

$$\log P_M = n \log P_{HA} + \text{const.} \tag{8}$$

The slope, n, of this correlation is connected with the ratio of molar volume of a chelating agent to that of metal chelate, and $n = 2.7$ was obtained in inert solvent systems[2,3] as well as in alcohol systems[5].

Since the distribution coefficient of the scandium chelate is extremely large, it is almost impossible to determine experimentally. It is obvious from eqn. (7), however, that the distribution ratio is a simple function of pA. At a definite pA, accordingly, the distribution ratio is proportional to the distribution coefficient. The distribution ratios at pA = 8.0 for each solvent are shown in Table I (6th column).

When the results of Table I are plotted as in Fig. 4, a linear relationship of slope *ca.* 2.7 is obtained. It is confirmed, accordingly, that the relationship shown by eqn. (8) is valid in the present system also.

The distribution coefficient of the metal chelate is actually compared with that of the enol form of TTA rather than that of the total TTA. Therefore, the distribution ratios of the scandium chelate were plotted against the distribution coefficient of the enol form of TTA (Fig. 5); the relationship with a slope of 2.7 is again clear.

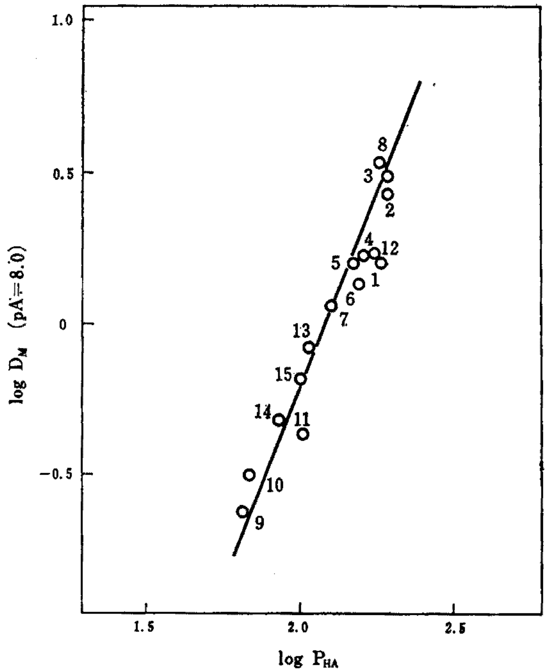

Fig. 4. Correlation between the distribution coefficients of TTA and its scandium chelate.

For practical applications, the apparent distribution coefficient, which includes a contribution of distribution of both enol and keto forms of TTA, can be correlated directly with the distribution coefficient of a metal chelate. For instance, in the cases of benzyl acetate and ethyl benzoate, the enol ratio of which could not be determined, values close to a straight line were obtained in Fig. 4.

In conclusion, it appears more valuable to correlate the distribution coefficient of a species with the solubility parameter of the solvent rather than to relate it to other physical and chemical properties. Since there is a clear correlation between the distribution coefficient of a chelating agent and that of the typical metal chelate, the distribution of this metal chelate into another solvent can be estimated.

The authors are grateful to Professor K. SETO and Dr. T. WAKAHAYASHI for their interest in this study, and to Professor Y. KITAHARA for advice on the NMR

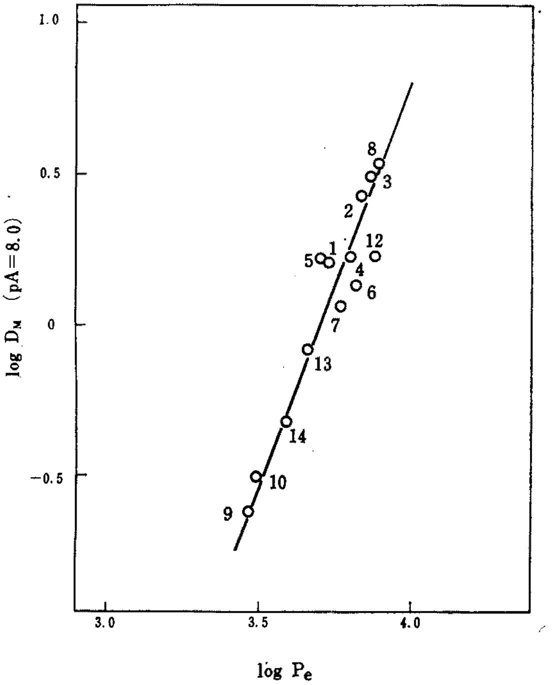

Fig. 5. Correlation between distribution coefficients of the enol form of TTA and its scandium chelate.

measurement. Thanks are also due to Misses K. TAKAIZUMI and H. ASANO for assistance in the experimental work.

SUMMARY

The distribution ratios of TTA and its scandium chelate between aqueous perchlorate solutions ($\mu = 0.1$) and 15 ester solvents including ethyl acetate were determined at 25°. A good correlation was found between the distribution coefficients of TTA and the "solubility parameter" of the ester solvents. The relationship between the distribution coefficients of the scandium chelate (P_M) and those of TTA (P_{HA}) was shown to be, $\log P_M = n \log P_{HA} + \text{const}$. The distribution of this chelate into another ester can thus be predicted.

RÉSUMÉ

On a déterminé les coefficients de partage du TTA et de son chélate avec le scandium, entre solutions aqueuses perchlorate et 15 solvants (esters) comprenant l'acétate d'éthyle. On observe une bonne corrélation entre coefficients de partage du TTA et le paramètre solubilité des esters. Le rapport entre coefficients de partage chélate scandium (P_M) et ceux de TTA (P_{HA}) correspond à $\log P_M = n \log P_{HA} + \text{const}$. On peut ainsi prévoir le partage de ce chélate dans d'autres esters.

ZUSAMMENFASSUNG

Die Verteilungskoeffizienten von TTA und seiner Scandium-Chelate zwischen wässrigen Perchloratlösungen ($\mu = 0.1$) und 15 Ester einschliesslich Äthylacetat wurden bei 25° untersucht. Es wurde eine gute Beziehung zwischen den Verteilungskoeffizienten P von TTA und den "Löslichkeitsparameter" der Ester gefunden. Der mathematische Zusammenhang lautet: $\log P_M = n \log P_{HA} + \text{const.}$ (P_M = Scandium-Chelat, P_{HA} = TTA). Die Verteilung dieser Chelate mit anderen Estern kann damit vorausgesagt werden.

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YTTRIUM 8-HYDROXYQUINOLINATES

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Among the earliest investigations on yttrium 8-hydroxyquinolinate were those by MANNELLI[1], who precipitated the complex from an aqueous solution of yttrium nitrate. Gravimetric and titrimetric procedures were suggested and it appeared that satisfactory recovery of yttrium as the 8-hydroxyquinolinate could be obtained from solutions containing acetic acid and ammonia. JACKSON[2] also carried out investigations into the precipitation of yttrium 8-hydroxyquinolinate and concluded that there was no evidence for the existence of a stoichiometric complex. The concentration of reactants and the temperatures of precipitation were varied but results were still unsatisfactory. In 1955, MURTHY *et al.*[3] also investigated the determination of yttrium with 8-hydroxyquinoline. These workers obtained satisfactory recovery of yttrium after precipitation from solutions containing acetic acid and ammonia in the pH range 5–6. The precipitate was dried at 100±5° for 4–8 h and weighed as $Y(C_9H_6NO)_3$. Bromometric titration confirmed the composition of the complex. The absorption spectra of this complex were also investigated in various organic solvents in the wavelength range, 300–400 nm. Limited conformity to Beer's Law was obtained in chloroform, acetone and carbon tetrachloride.

In 1956, WENDLANDT[4] carried out thermogravimetric studies on yttrium 8-hydroxyquinolinate and concluded that the complex could be weighed as YQ_3, where $Q = C_9H_6NO$, after drying at 110°, or as yttria, after ignition.

As a result of the conflicting reports in the literature on the determination of yttrium by 8-hydroxyquinoline, it was decided to investigate the preparation of yttrium 8-hydroxyquinolinate by direct precipitation and from homogeneous solution. The results of this investigation, as well as thermogravimetric and spectroscopic studies are outlined in this paper.

EXPERIMENTAL

Chemicals

Standard yttrium solution. A known amount of yttrium oxide, Y_2O_3 (Specpure, Johnson, Matthey and Co. Ltd., London) was dissolved in warm concentrated nitric acid, the solution was evaporated to incipient dryness and the residue dissolved in a known volume of distilled water. The solution was standardised by precipitating the hydroxide with concentrated ammonia solution, igniting and weighing as the oxide.

8-Acetoxyquinoline. A suitable amount of 8-acetoxyquinoline (Burdick and

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Jackson Laboratories, Michigan) was dissolved in the minimum amount of acetone as required.

8-Hydroxyquinoline. Laboratory-grade 8-hydroxyquinoline, without further purification, was used as a 5% solution in acetic acid.

Instrumentation

Perkin–Elmer Infracord, Model 137 spectrophotometers were used for all infrared measurements, ranges 2.5–15 μ and 12.5–25.0 μ.

A Hilger–Watts Uvispek H700/307 spectrophotometer was used for all absorptiometric measurements. Diffuse reflectance spectra were obtained by using the above instrument with Diffuse Reflectance Attachment H740.

Thermogravimetric data were obtained with a thermobalance constructed as described by DUVAL[5].

Precipitation of yttrium 8-hydroxyquinolinate by conventional means

Preliminary investigations. A suitable temperature for the reaction was found to be 70°. A 3-fold excess of 8-hydroxyquinoline dissolved in glacial acetic acid (5% solution) was used to precipitate the metal. The pH of the solution was adjusted with concentrated ammonia solution. No precipitation occurred below pH 3.9 and satisfactory recovery of yttrium was found in the pH range 5.2–6.0 (Table I). All further investigations were carried out at pH 5.5.

TABLE I

EFFECT OF PH ON THE PRECIPITATION OF YTTRIUM 8-HYDROXYQUINOLINATE BY CONVENTIONAL MEANS

(Weight of yttrium taken, 22.25 mg; incipient precipitation occurred at pH 3.9)

pH	4.2	4.5	4.8	5.2	5.5	6.0
Y found (mg)	10.50	16.66	20.05	22.26	22.27	22.25

TABLE II

PRECIPITATION OF YTTRIUM BY CONVENTIONAL MEANS

Yttrium taken (mg)	*Wt. of complex expected on basis of* YQ_3 *(mg)*	*Wt. of complex found (mg)*	*Error (mg)*
11.12	65.1	65.2	+ 0.1
11.12	65.1	65.4	+ 0.3
22.25	130.3	130.6	+ 0.3
22.25	130.3	130.4	+ 0.1
33.37	195.4	195.1	— 0.3

Procedure. Take 5 ml (5–50 mg Y^{3+}) of a standard yttrium solution and add a 3-fold excess of 8-hydroxyquinoline in acetic acid solution. Dilute the mixture to 100 ml. Adjust the solution to pH 5.5 with concentrated ammonia solution and heat at 70° for 3 h. Filter the yellow precipitate through a sintered glass crucible, wash with a minimum of distilled water (50 ml), and dry at 100 ± 5° for 4–8 h.

The results obtained in an examination of the completeness of the precipitation are shown in Table II.

Analysis: Calculated for $Y(C_9H_6NO)_3$: C, 62.19; H, 3.48%; 8-hydroxyquinoline/yttrium ratio, 3.00. Found: C, 62.56; H, 3.51%; 8-hydroxyquinoline/yttrium ratio[6], 3.00.

These results clearly indicate that yttrium is precipitated by conventional means as YQ_3, and confirm the work of MURTHY *et al.*[3].

Precipitation of yttrium 8-hydroxyquinolinate from homogeneous solution

Preliminary investigations showed that the most suitable conditions for precipitation of yttrium 8-hydroxyquinolinate were in the presence of a 2.5-fold excess of 8-acetoxyquinoline (assuming the precipitate to have the composition YQ_3) and an acetic acid medium. No precipitate formed below pH 6.5. Quantitative precipitation of yttrium occurred at pH 8.5 after heating at 70° for 3 h. The precipitate obtained was lemon-yellow in colour and had much better physical characteristics than that obtained by conventional precipitation.

Procedure. Dissolve 400 mg of 8-acetoxyquinoline in 45 ml of 1:1 acetic acid solution, add 5 ml (5–50 mg) of a standard yttrium solution and dilute to 100 ml. Adjust the mixture to pH 8.5 with concentrated ammonia solution and heat at 70° for 3 h. Filter the lemon-yellow precipitate, wash with a minimum of distilled water, and dry at 100 ± 5° for 2–4 h.

The results obtained in an examination of the completeness of the precipitation are shown in Table III.

TABLE III

PRECIPITATION OF YTTRIUM FROM HOMOGENEOUS SOLUTION

Yttrium taken (mg)	*Wt. of complex expected on basis of YQ_3 (mg)*	*Wt. of complex expected on basis of $YQ_3 \cdot HQ$ (mg)*	*Complex found (mg)*
8.89	52.1	66.6	66.2
8.89	52.1	66.6	66.5
22.23	130.2	166.5	166.5
22.23	130.2	166.5	166.4
22.23	130.2	166.5	166.9
22.23	130.2	166.5	165.4

These results indicate that yttrium 8-hydroxyquinolinate is precipitated from homogeneous solution with the composition, not of YQ_3, but rather as $YQ_3 \cdot HQ$.

Analysis: Calculated for $Y(C_9H_6NO)_3 \cdot C_9H_7NO$: C, 64.88; H, 3.78%; 8-hydroxyquinoline/yttrium ratio, 4.00. Found: C, 64.66; H, 3.85%; 8-hydroxyquinoline/yttrium ratio[6], 3.98.

Before the conclusion that yttrium can be determined gravimetrically as the 8-hydroxyquinolinate was drawn, it was first decided to carry out thermogravimetric studies on the complexes. These are described and discussed below.

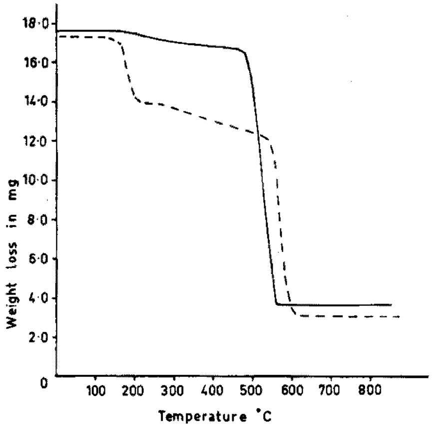
Thermogravimetric analyses of yttrium 8-hydroxyquinolinates

Previous investigations were carried out by WENDLANDT[4] on the yttrium 8-hydroxyquinolinate prepared by conventional means. Three main stages were observed in the thermolysis curve: (i) a 1% loss of weight above 175°, (ii) oxidation of the organic material between 370° and 525°, and (iii) formation of the oxide at 740°.

WENDLANDT concluded that yttrium could be weighed as YQ_3 or after ignition to the oxide.

Thermogravimetric curves for the two yttrium 8-hydroxyquinolinates obtained in the present work are shown in Fig. 1.

Yttrium 8-hydroxyquinolinate prepared by conventional means. The complex prepared by conventional means was found to be thermally stable up to about 170°.



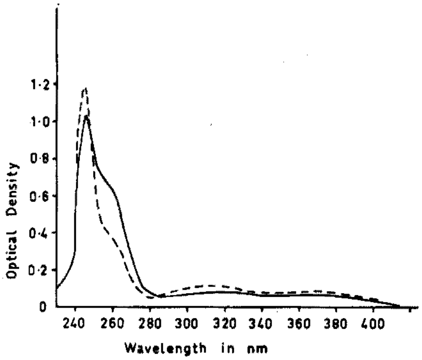


Fig. 1. Thermogravimetric curves for yttrium 8-hydroxyquinolinates. Full line: YQ_3; broken line: $YQ_3 \cdot HQ$. Heating rate: 300°/h.

Fig. 2. UV–visible absorption spectra of yttrium 8-hydroxyquinolinates in chloroform. Full line: YQ_3; broken line: $YQ_3 \cdot HQ$.

Above 170°, a 2% weight loss occurred until the remaining organic material was oxidised between 450° and 560°. The oxide was formed at about 600° and no further weight loss occurred above this temperature. As the temperature limit of the furnace was 900°, the pyrolysis curve was not examined beyond 850°. These results agree closely with WENDLANDT's observations[4]. Similarly, it was concluded that yttrium could be weighed as YQ_3 or after ignition to the oxide.

Yttrium 8-hydroxyquinolinate prepared from homogeneous solution. Thermal analysis of the yttrium 8-hydroxyquinolinate precipitated from homogeneous solution showed that this complex is less stable than the complex prepared by conventional means. The complex is thermally stable up to 125°, where the first weight loss occurs. Between 160° and 210° a loss in weight corresponding to one molecule of 8-hydroxyquinoline is recorded and a constant weight level corresponding closely to the composition YQ_3 is obtained between 210° and 260°. Above 260° a slow decomposition occurs until the remaining organic material is oxidised between 525° and 620°. Above 620° the oxide is formed and no further weight loss is observed up to 850°.

From these results it was concluded that yttrium can be determined by weighing as $YQ_3 \cdot HQ$ after drying at $100 \pm 5°$ or after ignition to the oxide. Furthermore, it is apparent that the extra molecule of 8-hydroxyquinoline is fairly loosely bound within the molecular crystal as it is removed at much lower temperatures than the remaining ligands and thus, this complex is structurally different from the complex prepared by conventional means.

Infrared measurements

Yttrium 8-hydroxyquinolinates prepared by conventional means, and by precipitation from homogeneous solution were examined in the range 4000–400 cm^{-1} by means of the potassium bromide disc and nujol-mull techniques.

The differences which occur between the two spectra are small and occur mainly in the 850–700 cm^{-1} region and in the long wavelength region around 500 cm^{-1}.

The bands in the 850–700 cm^{-1} region are due to ring vibrations and C–H deformations[7] and no valuable information concerning the structure of the compounds can be deduced from this region. However, it was observed that the band at 502 cm^{-1} in the sample prepared conventionally is shifted to 500 cm^{-1} in the spectrum of the sample prepared from homogeneous solution. Also, the bands at 500 cm^{-1} and 489 cm^{-1} in the latter spectrum show an increase in intensity compared to the corresponding bands in the former spectrum.

In the region around 500 cm^{-1}, a number of workers[8,9] have assigned bands to metal–nitrogen stretching frequencies for various complexes. It is supposed, therefore, that the two major peaks around 500 cm^{-1} in the chelates investigated here are also due to metal–nitrogen stretching. Further, changes in this region for the complex prepared from homogeneous solution would appear to be due to the binding of the extra molecule of 8-hydroxyquinoline. As there is no change in the peak attributed to metal–oxygen stretching[10] at 910 cm^{-1}, it is suggested that the extra molecule of 8-hydroxyquinoline in the complex prepared from homogeneous solution is weakly bound through the nitrogen atom.

Ultraviolet–visible absorption spectra of yttrium 8-hydroxyquinolinates

Previous investigations on the absorption spectra of yttrium 8-hydroxyquinolinate prepared by conventional means were carried out by MURTHY *et al.*[3]. The spectra were examined in the range 300–400 nm in chloroform, acetone and carbon tetrachloride.

In the present work, the absorption spectra of the two yttrium 8-hydroxyquinolinates were examined in the range 200–500 nm with chloroform as the solvent.

As the yttrium ion has an empty *d*-orbital, one would expect the ultraviolet–visible absorption spectra of the yttrium 8-hydroxyquinolinates to be similar to each other, with most of the bands occurring in the ultraviolet region.

The absorption spectra for the two yttrium 8-hydroxyquinolinates are shown in Fig. 2. As predicted, the spectra are similar to each other, the only difference being in the intensities at peak wavelengths. The absorption bands occur mainly in the ultraviolet region at 245, 258, 317 and 370 nm. Thus, the absorption spectra of the yttrium 8-hydroxyquinolinates are very similar to the absorption spectra of other metal 8-hydroxyquinolinates where the metallic ions contain no electrons in the *d*-orbitals[11]. Accordingly, the characteristic bands obtained for yttrium 8-hydroxyquinolinates are due to combined 8-hydroxyquinoline ligands whose absorption bands have been shifted along the wavelength scale.

Diffuse reflectance spectra of yttrium 8-hydroxyquinolinates

The diffuse reflectance spectra of the two yttrium 8-hydroxyquinolinates were examined in the range 200–1000 nm (Fig. 3). It can be seen that there is a considerable difference between the diffuse reflectance spectra of yttrium 8-hydroxyquinolinates and the absorption spectra in chloroform. This indicates that on dissolution in chloroform, the two yttrium 8-hydroxyquinolinates produce the same species in solution despite the individual structures in the solid state. If YQ_3 was the species present in solution, the diffuse reflectance spectrum of the compound YQ_3 would be expected to be similar to the absorption spectrum of the same compound in chloroform. However, the results show that this assumption is not correct; they indicate rather that co-ordination with the solvent is taking place, and that the species produced is contributing mainly to the absorption spectrum in solution.

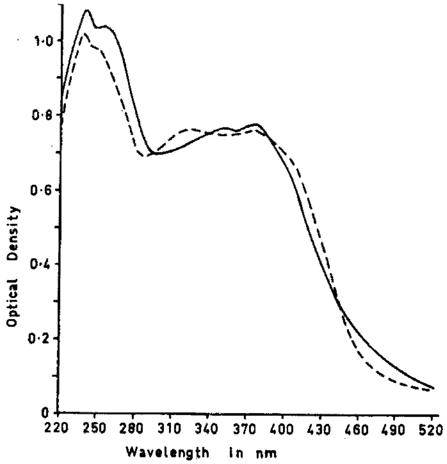


Fig. 3. Diffuse reflectance spectra of yttrium 8-hydroxyquinolinates. Full line: YQ_3; broken line: $YQ_3 \cdot HQ$.

CONCLUSIONS

Precipitation by direct means with 8-hydroxyquinoline can be utilized for the determination of yttrium, and the complex has a definite stoichiometry, $YQ_3 \cdot HQ$. Thermal analysis confirms that yttrium can be determined either conventionally or from homogeneous solution by weighing the 8-hydroxyquinolinates after drying at 110° or after ignition to the oxide.

Thermogravimetric analysis also shows that the complex prepared from homogeneous solution is different from the conventionally prepared complex and is less stable above 125°. The extra molecule of 8-hydroxyquinoline is removed at much lower temperatures than the other ligands indicating that it is fairly loosely bound within the molecular crystal.

The infrared spectroscopic studies on the compound prepared from homogeneous solution show no absorption peaks from free 8-hydroxyquinoline, which indicates that this is a definite compound and not a mixture of YQ_3 and excess of 8-hydroxyquinoline. It was hoped that the infrared spectra might indicate sufficient differences between the two compounds to draw definite conclusions about their structures.

However, as the above results show, the spectral differences are small, so that the only conclusion is that the chelates are structurally similar.

The ultraviolet–visible absorption spectra of the complexes are similar and indicate that the absorption bands are due to combined organic ligand. Also, there is strong evidence that, on dissolution in chloroform, the same species is produced which possibly involves co-ordination with the solvent. This was confirmed by the diffuse reflectance spectra.

SUMMARY

The preparation of two yttrium 8-hydroxyquinolinates, one by conventional means and the other by precipitation from homogeneous solution, was investigated. Analytical data indicated that the complex prepared conventionally corresponds to $Y(C_9H_6NO)_3$, and the complex prepared by precipitation from homogeneous solution corresponds to $Y(C_9H_6NO)_3 \cdot C_9H_7NO$. Thermogravimetric analyses, infrared, ultraviolet–visible and diffuse reflectance spectroscopic studies were carried out on both compounds. They were shown to be very similar structurally.

RÉSUMÉ

On examine la préparation de deux hydroxy-8-quinoléates d'yttrium, l'un par la méthode conventionelle, l'autre obtenu par précipitation en solution homogène. Le premier correspond à la formule $Y(C_9H_6NO)_3$, l'autre à $Y(C_9H_6NO)_3 \cdot C_9H_7NO$. Ces deux composés sont examinés par analyses thermogravimétriques, spectroscopie dans l'infra-rouge, l'ultraviolet, le visible et réflectance diffuse. On constate que leur structure est très similaire.

ZUSAMMENFASSUNG

Die Darstellung von zwei Yttrium-8-hydroxychinolaten durch konventionelle Verfahren und durch Fällung aus homogener Lösung wurde untersucht. Die analytischen Daten zeigten, dass der Komplex, der auf übliche Weise hergestellt wurde, die Zusammensetzung $Y(C_9H_6NO)_3$ und der Komplex, welcher aus homogener Lösung gefällt wurde, die Zusammensetzung $Y(C_9H_6NO)_3 \cdot C_9H_7NO$ besitzt. Thermogravimetrische Analysen, Infrarot-, Ultraviolett-, sichtbar- und diffuse reflektionsspektroskopische Untersuchungen wurden für beide Verbindungen durchgeführt. Daraus ergab sich, dass sie beide sehr ähnliche Struktur besitzen.

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SHORT COMMUNICATIONS

A direct amperometric method for continuous determination of low concentrations of iodine in aqueous solutions

A kinetic investigation[1] of the bromate–iodide and iodate–iodide reactions required an analytical method for continuous measurement of 10^{-6}–10^{-5} M iodine in aqueous iodide solution. The linearity of amperometric response to concentration change is well known[2,3]. In the case of iodine, it has been utilised for end-point detection in coulometric titrations[4]. Direct amperometry has also been applied to the determination of low concentrations of reagents which catalyze iodine-producing or iodine-destroying reactions[5]; the time taken for a defined current increment is measured, or the slopes of current–time plots in the absence and presence of catalyst are compared. Various examples are available in the literature[6,7]. Linear bi-amperometry without calibration was used recently to determine the hydrogen ion dependence of the iodate–iodide reaction rate[8], but the amperometric method does not appear to have been applied to the continuous monitoring of iodine concentration.

When a steady state is reached for a fast electrochemical reaction at a rotating electrode or at an electrode in a stirred solution, the electrolysis current becomes diffusion-controlled. When the potential is sufficiently negative, the limiting diffusion current reached is proportional to the concentration of the electroactive species in the bulk solution. A base electrolyte should be present to prevent significant electromigration of the measured species, and other factors such as the position and surface area of the indicator electrode and the liquid flow or stirring rate should be constant. A simplified theory[2,9] predicts

$$i_l = \frac{nFADC^0}{\delta_0} \tag{1}$$

where i_l is the limiting diffusion current, A the indicator electrode area, D and C^0 the diffusion coefficient and bulk solution concentration of the electroactive species, F the Faraday, n the number of electrons associated with the electrode reaction and δ_0 the effective diffusion layer thickness. Experimentally, this linear dependence on concentration is found to be true for a limited range of concentrations. Sensitivity may be improved by increasing A or by stirring the solution more efficiently to reduce δ_0.

For the determination of iodine in the presence of excess of iodide, the reaction can be formulated as:

$$2\,e^- + I_3^- \rightarrow 3\,I^-; \quad E_0 = 0.54\text{ V} \tag{2}$$

which is fast at a platinum cathode. The counter electrode may be an unpolarizable reference electrode which can sustain a small current flow, *e.g.*, the Ag/Ag$^+$ (0.1 M) electrode ($E = 0.74$ V) used in the present study, or another platinum electrode at which the reaction is the reverse of that shown in eqn. (2). This latter reaction is not diffusion-limited under these conditions because of the large iodide concentration.

A simple potentiostat[10] is adequate to maintain the potential of the indicator electrode at *ca.* -0.5 V with respect to a Ag/Ag$^+$ counter electrode, or -0.15 V with respect to a similar platinum electrode[4].

The experiments were carried out in the presence of several other potentially electroactive species. The reactions of perchlorate[11], thiosulphate[11] and oxygen are slow and do not interfere. The reduction of iodate is slow except when catalyzed by iodide ions at a sufficiently high concentration[10,12]; because the concentrations were adjusted to make the rate of the iodate–iodide reaction slow, no catalysis could occur.

Apparatus

The indicator electrode was a platinum wire of 0.5-mm diameter extending 2.5 cm from a glass mount. The Ag/Ag$^+$ (0.1 *M*) counter electrode was contained in a half-cell compartment closed at the bottom by a 2-cm capillary containing an agar gel–sodium nitrate salt bridge; the gel was replaced periodically because silver ions slowly diffused into it. The tops of both electrodes were fitted with ground-glass cones for positioning in the 5-necked reaction flask. This closed vessel, containing usually 200 ml of solution, was thermostatted at 25.00±0.05° in a water bath and stirred by a glass link stirrer at a constant rate of 500 rev./min. The upper end of the barrel of an Agla micrometer syringe was fitted with a bored rubber stopper

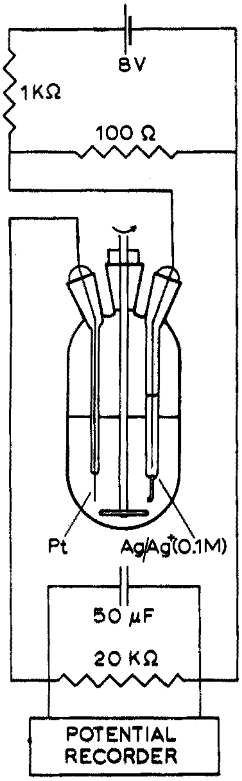

Fig. 1. Cell and circuit for direct iodine amperometry.

allowing insertion in one of the reaction flask sockets so that the syringe needle was below the surface of the solution.

A simple potentiostatic circuit (Fig. 1) maintained the platinum indicator electrode at a potential which gave rise to an amperometric current proportional to the iodine concentration; this was chosen by inspection of current–voltage curves at various iodine concentrations. A high resistor was used in place of a galvanometer to determine the current, as in the amperometric titration end-point method of POTTER AND WHITE[13]. The potential developed across the dropping resistor by the linear response current was applied to a potential recorder (Metrohm model E336) used on the 0–250 mV range. The potential impressed on the platinum electrode was -0.7 V with respect to the counter electrode at zero indicator current; although this potential decreased as the current increased, the change did not affect the linearity of response in the iodine concentration region required. The 50-μF capacitor was included in parallel with the potential recorder to eliminate the alternating signal due to vibration transmitted from the stirrer to the indicator electrode.

Operation and calibration

To initiate the iodine-producing reaction, potassium iodide solution was added to a mixture of an acid buffer (pH 3–6) and potassium iodate or potassium bromate solution in the reaction vessel. Reactant concentrations were chosen ($\nless 10^{-4}\,M$) so that iodine was produced at a constant rate. The rate of iodine production in a solution of ionic strength 1.0 (with sodium perchlorate) at 25° may be calculated[1] as follows:

$$\frac{d[I_2]}{dt} = 9.0 \cdot 10^8\,[H^+]^2[I^-]^2[IO_3^-]\ \text{mole l}^{-1}\,\text{sec}^{-1}$$

When the iodine concentration reached $2 \cdot 10^{-6}\,M$ (A in Fig. 2), the potential–time plot became linear and remained so until a concentration of $1 \cdot 10^{-5}\,M$ had been reached (B). The slope of line AB was proportional to the rate of iodine production by the reaction under investigation. Calibration was carried out individually for

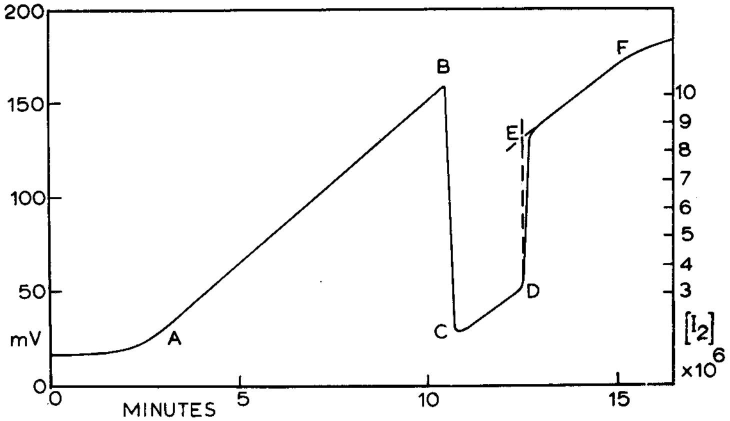

Fig. 2. Smoothed recorder trace of determination of the rate of iodine production (AB) and calibration (DE). (A,C) lower limit of linearity; (B) thiosulphate addition; (D) iodine addition; (F) upper limit of linearity.

each kinetic run because of the slight dependence of the proportionality constant on the cell geometry and stirring speed. A small volume of 0.1 N sodium thiosulphate solution was added to the reaction vessel to reduce the iodine concentration to its lowest detectable level (BC); the concentration then increased again at the same rate as previously owing to the continuation of the iodine-producing reaction (CD). Standard iodine solution (usually 0.25 ml of $3 \cdot 10^{-3}$ M) was added rapidly from the syringe burette, and the "step" in the plot, DE, enabled the potential change to be related to the amount of iodine added; duplicate calibrations agreed within 3%.

Discussion

The simple circuit used in this work measures iodine concentrations in the range $2 \cdot 10^{-6}$–$1 \cdot 10^{-5}$ M. Modifications to the circuit, stirring speed and cathode area allow other concentration ranges to be investigated; improvement of the circuit and recording instrument would permit a wider linear range. Coulometric iodine generation[14] would enable a more accurate calibration to be made. The present method was designed to suit the conditions of continuous iodine production at a constant rate by a kinetic method in a known initial volume. The procedure could be modified for other purposes such as the determination of low iodine concentrations in a continuous liquid flow.

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The volatilities of some lead β-diketonates

The literature contains numerous reports of volatile compounds of various metals[1], but little work has been conducted on lead. The low-molecular-weight lead alkyls are not too stable thermally, and attempts by Clark[2] to prepare fluorinated lead alkyls using fluoroalkyl Grignard or fluoroalkyl lithium reagents plus lead(II) chloride were unsuccessful. Tetra(perfluorovinyl)lead has been synthesized[3]. This substance boils at 51–52° under 8-mm pressure, but it is not too stable thermally. For a number of metals, one of the most fruitful routes to a volatile compound is the preparation of β-diketone derivatives. In many instances the substitution of fluorine for hydrogen atoms in these compounds increases the volatility and sometimes enhances the thermal stability.

Menzies[4] has prepared bis(2,4-pentanedionato)lead(II) by reaction of lead(II) oxide with the β-diketone in dry toluene. He notes that the substance showed signs of volatilizing on heating. This present study was undertaken to determine the volatilities and thermal stabilities at 100° of a number of fluorinated and non-fluorinated lead β-diketonates. It was thought that this study might increase the number of metal β-diketonates which could be employed in gas chromatography.

Experimental and results

β-Diketones. The β-diketones 2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione, and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione were obtained from Pierce Chemical. These materials were purified by drying over sodium sulfate followed by distillation. The 7-methyl-2,4-octanedione was prepared by Schweitzer and Willis[5] and 1,1,1,2,2,6,6,6-octafluoro-3,5-hexanedione and 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione were obtained from Scribner[6]. The procedure of Johnson *et al.*[7] was em-

TABLE I

β-DIKETONES USED IN PREPARING LEAD COMPOUNDS

No.	*Compound*	*B.p. (°)*
1	2,4-Pentanedione	139 (760 mm)
2	1,1,1-Trifluoro-2,4-pentanedione	107 (760 mm)
3	1,1,1,5,5,5-Hexafluoro-2,4-pentanedione	63–65 (760 mm)
4	3-Methyl-2,4-pentanedione	170–172 (760 mm)
5	3-Isopropyl-2,4-pentanedione	180–183 (740 mm)
6	2,2-Dimethyl-3,5-hexanedione	68–70 (16 mm)
7	1,1,1-Trifluoro-5-methyl-2,4-hexanedione	28–30 (1–2 mm)
8	1,1,1-Trifluoro-5,5-dimethyl-2,4-hexanedione	36–37 (1–2 mm)
9	1,1,1,2,2,6,6,6-Octafluoro-3,5-hexanedione	80 (760 mm)
10	2,2-Dimethyl-3,5-heptanedione	65–66 (6 mm)
11	2,2,6,6-Tetramethyl-3,5-heptanedione	58–64 (3–4 mm)
12	1,1,1,2,2-Pentafluoro-6-methyl-3,5-heptanedione	38–39 (12 mm)
13	1,1,1,2,2,-Pentafluoro-6,6-dimethyl-3,5-heptanedione	49 (6 mm)
14	1,1,1,2,2,3,3-Heptafluoro-4,6-heptanedione	39–42 (15–16 mm)
15	1,1,1,5,5,6,6,7,7,7-Decafluoro-2,4-heptanedione	105 (760 mm)
16	1,1,1,2,2,6,6,7,7,7-Decafluoro-3,4-heptanedione	26–27 (3–4 mm)
17	7-Methyl-2,4-octanedione	82 (6 mm)
18	1,1,1,2,2,3,3,-Heptafluoro-4,6-octanedione	51–53 (15–16 mm)
19	1,1,1,2,2,3,3-Heptafluoro-7-methyl-4,6-octanedione	44–45 (6–7 mm)
20	1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione	43–49 (2–4 mm)
21	1,1,1,2,2,6,6,7,7,8,8,8-Dodecafluoro-3,5-octanedione	52–58 (3–4 mm)

ployed to prepare 3-methyl-2,4-pentanedione and 3-isopropyl-2,4-pentanedione. All other β-diketones were synthesized according to the general method of ADAMS AND HAUSER[8] with modifications as recommended by BENSON[9]. All the β-diketones with their boiling points are listed in Table I.

Preparation of lead chelates. The following general procedure was used for the preparation of the lead compounds of the β-diketones. An anhydrous solution of the appropriate β-diketone was made in dry toluene. The toluene had been dried over over tetraphosphorus decaoxide for at least 48 h and had been distilled at 111° under a dry nitrogen atmosphere. The toluene solution of the β-diketone was heated to a slow reflux with an excess of powdered lead metal for 4–21 h. The time of the reaction was usually long in the hope that most of the β-diketone would react. The reaction mixture was then cooled, the lead was filtered off, and the solution was vacuum-distilled to remove the toluene and any excess of β-diketone. The residue was vacuum-dried. In all procedures extreme care was taken to exclude water since it is known that some low-molecular-weight β-diketonates of lead tend to hydrolyze readily. Purifications of the residues were made by recrystallization and by sublimation. The latter process was not effective on all the compounds, but worked quite well for those prepared from the following β-diketones: 6, 7, 8, 9, 11, 12, 13, 14, 15, 18, 19, 20 (see Table I for β-diketones corresponding to these numbers). Table II presents the chemical analyses and melting points of the lead β-diketonates prepared. The calculated analyses were computed by assuming in each instance the anhydrous bis(β-diketonato)–lead(II) compound. The numbers in the first column correspond to the β-diketones given in Table I.

TABLE II

ANALYTICAL RESULTS, MELTING POINTS AND VAPOR PRESSURE OF β-DIKETONATES PREPARED FROM THE VARIOUS β-DIKETONES

No.	*Calculated analyses*			*Experimental analyses*			*M.p. (°)*	*T. (°) for 1 mm V.P.*
	C	*H*	*F*	*C*	*H*	*F*		
1	29.4	3.45	0.0	29.4	3.5	0.0	159 decomp.	95
2	23.4	1.6	22.2	23.5	1.6	22.1	146 decomp.	72
3	19.3	0.3	36.7	18.45	0.5	36.8	156	67
4	No sublimation, only decomposition						85 decomp.	
5	No sublimation, only decomposition						87 decomp.	
6	34.3	5.8	0.0	36.5	5.45	0.0	73	62
7	29.5	2.8	20.0	30.3	3.1	22.0	158	89
8	32.2	3.4	19.1	32.0	3.2	18.9	193	118
9	20.0	0.3	42.1	20.2	0.4	41.9	135	49
10	No sublimation						48	
11	42.6	6.6	0.0	46.4	6.4	0.0	123	79
12	28.7	2.4	28.4	28.5	2.2	28.3	84	76
13	31.0	2.9	27.25	31.1	2.9	27.3	129	60
14	23.6	1.1	37.3	23.7	1.05	37.1	139	95
15	20.5	0.25	46.25	20.35	0.3	46.2	123	55
16	No lead product isolated; very low β-diketone yield							
17	No lead product isolated							
18	26.0	1.6	36.0	26.1	1.8	35.6	107	78
19	20.1	2.1	34.6	27.95	2.0	34.7	63	53
20	30.1	2.5	33.4	29.6	2.6	34.9	72	[a]
21	Very slight sublimation						—	

[a] 0.6 mm at 68°.

Vapor pressure measurements. The temperatures at which all of the readily sublimable compounds exhibited vapor pressures of 1 mm of mercury were measured by a technique similar to that proposed by SMITH AND MENZIES[10] and modified by TRUEMPER[11]. The data obtained are listed in Table II.

Thermal stability measurements. The thermal stabilities of all the readily sublimed compounds were checked at 100°. The following compounds showed signs of slight decomposition after heating at this temperature for 24 h in sealed glass vials: 2, 3, 7, 11, 12, 14. A darkening of the material was employed as a sign of decomposition. All others showed no observable decomposition under these conditions.

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Spectrophotometric titration of aliphatic amines with cinnamic anhydride

A spectrophotometric method for the determination of aliphatic amines has recently been developed[1] in which the amine is acylated with *trans*-cinnamic anhydride, the excess of reagent is hydrolyzed, and the cinnamide is extracted into chloroform for spectrophotometric analysis. The difference in spectral properties between cinnamic anhydride and cinnamides suggested that the separation step of the analysis might be eliminated by carrying out a direct titration of the amine with the anhydride, the progress of the titration being followed spectrophotometrically.

REYNOLDS *et al.* have described photometric titrations of primary aliphatic amines with 2-ethylhexanal (to form the Schiff base) as the titrant[2], and of aromatic amines with acetic anhydride as the titrant[3].

Materials

Trans-cinnamic anhydride (J. T. Baker Chem. Co.) was recrystallized three times from benzene; m.p. 134–6°. Acetonitrile (Fisher Scientific Co., catalog no. A-21) was refluxed over phosphorus pentoxide and then distilled from phosphorus pentoxide through a packed column[4]; b.p. 81–81.5°. Amines (Aldrich and Eastman products) were purified by distillation to constant boiling point. 0.02 *M trans*-cinnamic anhydride titrant was freshly prepared by dissolving 55.66 mg of cinnamic anhydride in enough purified acetonitrile to make 10.0 ml.

Apparatus

Absorbance measurements were made with a Cary 15 recording spectrophotometer. Titrations were done in a 50-ml photometric titration flask[5], a flow-through cylindrical 1-cm cuvette being connected to the circulation flask with glass tubing and short lengths of rubber tubing. Titrant was delivered from a 2-ml micrometer buret (Roger Gilmont Instruments), the tip of which passed through a rubber stopper in the mouth of the titration flask.

Procedure

Acetonitrile (24 ml) was delivered into the titration flask and the cuvette was firmly positioned in the light path. A 1.0-ml aliquot of an amine sample solution, containing about 20 μmoles of amine/ml (in acetonitrile) was added to the flask. Titrant was added and the solution was stirred magnetically; stirring ensures homogeneity, but is also necessary to circulate the solution to the cuvette. Absorbance was monitored, at a fixed wavelength, until it assumed a constant value, when a reading was taken. Further titrant was then added. Usually three absorbance readings were taken before the end-point and three after the end-point. A titration plot was made of absorbance against titrant volume; the end-point is marked by the intersection of the two straight line segments.

Results and discussion

Figure 1 shows the absorbance tracing in a typical titration. Although the second-order rate constants for the reaction between amines and *trans*-cinnamic anhydride are quite large[1], the reaction rates are not high because the reactant concentrations are quite low in these systems. The decay in absorbance after each titrant addition is clearly visible in the Figure. After the fourth addition of titrant, the reaction is at its slowest, because with the slight excess of anhydride the amine concentration is driven to a very low value. The approach to a constant absorbance after the fifth and sixth additions is controlled by the circulation rate in the titration assembly. The appearance of the titration plot is determined by the wavelength at which measurements are made. Figure 2 shows a titration plot of data taken at 320 nm.

Table I lists analytical results for the titration of seven amines. These amines were also analyzed by the earlier cinnamoylation method[1] and by perchloric acid-catalyzed acetylation[6], and the results of the three methods were consistent (the slow-reacting amines tended to give slightly higher results in the photometric titration procedure).

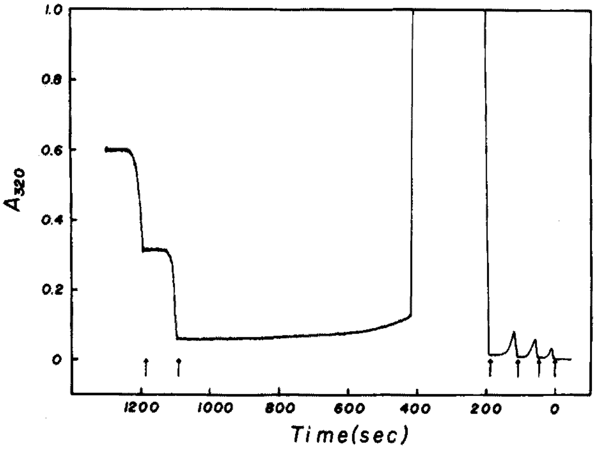

Fig. 1. Recorder tracing of absorbance as a function of time during the titration of *n*-butylamine. Titrant additions are marked by arrows.

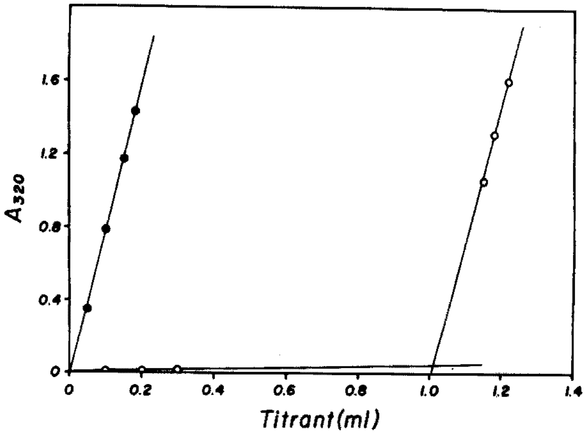

Fig. 2. Spectrophotometric titration of 20 μmole of *n*-butylamine. (●) blank titration; (○) sample titration.

The total titration time ranges from 15 min (for the highly reactive piperidine) to 70 min (for the very slow benzylamine); for most amines a titration takes about 25 min. In an effort to reduce this time, several substances were tested as catalysts. Perchloric acid appears to catalyze the reaction, but it seems to lead to a reaction between the anhydride and the solvent. Trichloroacetic acid, diphenylphosphate, and pyridine did not give useful catalytic effects, and indeed, diphenylphosphate reduces the reaction rate markedly. Reaction in dioxane is much slower than in acetonitrile.

Titration of 20 μmole samples (corresponding to $8 \cdot 10^{-4}$ moles/l in the titration solution) gives standard deviations usually in the range 0.5–2.0%. Reduction of the sample size to 5 μmole ($2 \cdot 10^{-4}$ moles/l) is feasible, with some loss in precision.

Some selectivity is achieved because of differences in rates of acylation. Thus *n*-butylamine could be titrated in the presence of an equal quantity of *tert*-butylamine

TABLE I

SPECTROPHOTOMETRIC TITRATION RESULTS[a]

Amine	*% Purity*	
	Mean[b]	*Standard deviation*
n-Butylamine	96.7	0.56
n-Hexylamine	97.9	0.10
n-Octylamine	99.1	0
Benzylamine	99.8	1.90
β-Phenethylamine	99.6	0.10
Diethylamine[c]	101.0	1.91
Piperidine[c]	98.8	0.35

[a] At 320 nm unless otherwise noted.
[b] Mean of 4–6 determinations.
[c] At 325 nm.

without interference. A 10-fold excess of aniline did not significantly interfere in the titration of *n*-butylamine. Similarly, a 4000-fold excess of methanol caused no interference. Some reaction of these potential interfering substances with excess of reagent does of course occur after the end-point, and the proper absorbance reading was obtained by extrapolating the absorbance back to the time of titrant addition. Water interferes significantly.

The direct spectrophotometric titration of aliphatic amines with *trans*-cinnamic anhydride is a simple technique applicable to small samples. Its principal disadvantage is the slowness of reaction time; its advantages are its sensitivity and, in part, its selectivity.

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Spectrophotometric determination of iron with 2,4-dihydroxyacetophenone

2,4-Dihydroxyacetophenone has been used as a reagent for the detection of iron(III) by COOPER[1] and for the titrimetric determination of copper by RAMANUJAM[2]. The present communication describes a study of the iron(III)–2,4-dihydroxyacetophenone chelate and its utilization in a selective method for the spectrophotometric determination of iron.

Apparatus and reagents

A Unicam SP-500 spectrophotometer was used. Matched 1-cm silica cells were used for absorbance measurements. A Beckman pH meter, Model H2 was used for all pH determinations.

Standard iron(III) solution. Dissolve 40. 385 g of iron(III) nitrate nonahydrate in 1 l of distilled water. Prepare weaker solutions by dilution.

Reagent solutions. 2,4-Dihydroxyacetophenone was synthesised by the method of COOPER[3]. A solution of DHA in 40% ethanol was used in all experiments. The solution is stable for several weeks and does not absorb light in the visible range of the spectrum.

All other reagents were analytical grade and were used without further purification.

Properties of the chelate

The absorption spectrum of the reddish-violet iron(III)–2,4-dihydroxyacetophenone complex formed at pH 2.9 is shown in Fig. 1. The optimum pH for complex formation is 2.9–3.0. The complex becomes reddish brown above pH 3.0, but is then unstable. The complex shows a maximum absorbance at 470 nm, the molar absorptivity being $2.10 \cdot 10^3$. The colour is formed instantaneously, and the maximum absorbance develops 30 min after the pH adjustment; the colour is then stable for 10 h. The absorbance of the complex is unaffected by the order of addition of the reagents.

Composition and stability of the complex

Four methods were employed: the mole ratio method[4], the continuous varia-

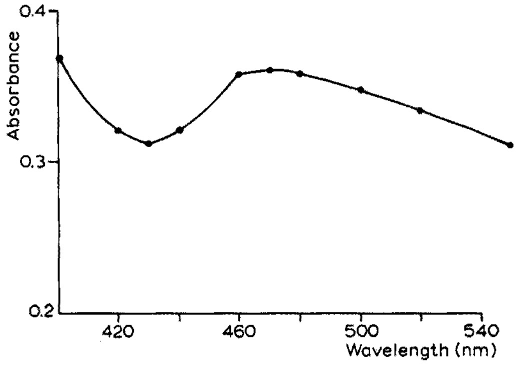

Fig. 1. Absorption spectrum of the iron(III)–2,4-dihydroxyacetophenone complex at pH 2.9. 2 ml of 0.01 M iron(III) nitrate, 20 ml of 0.01 M reagent, $\mu = 0.1$ M $NaClO_4$, final volume 50 ml.

tions method[5], the slope ratio method[6] and the logarithmic method of Bent and French[7]. All the data were obtained for the formation of the complex at pH 2.9 in media adjusted to an ionic strength of 0.1 with sodium perchlorate, with the absorbance measurement at 470 nm. The data for the continuous variations method are shown in Fig. 2. When 0.01 *M* reagent solution was used, the other methods also indicated that a 1:1 complex was formed. The complex is probably a divalent cation.

Stability constants were calculated from the data of the mole ratio and continuous variation methods in the usual way. The two methods gave results for *K* of $8.4 \cdot 10^2$ and $8.3 \cdot 10^2$, respectively, for ionic strengths of 0.1.

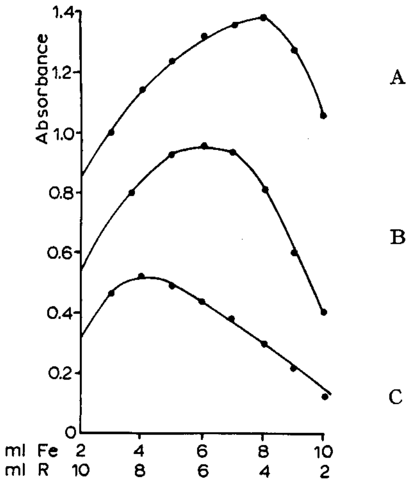

Fig. 2. Composition of the iron(III)–2,4-dihydroxyacetophenone complex by the method of continuous variation. *x* ml 0.01 *M* iron(III) nitrate + 12−*x* ml reagent (0.02 *M* in plot A, 0.01 *M* in plot B, 0.005 *M* in plot C) + 5 ml 1 *M* $NaClO_4$. Final volume 50 ml. pH 2.95.

Recommended procedure

Transfer 0.25–5.0 ml aliquots of standard 0.01 *M* iron(III) solution (*ca.* 140 μg–2.8 mg Fe) to 50-ml volumetric flasks, add 7.5 ml of a 0.1 *M* solution of the reagent in 40% ethanol, mix well and adjust the pH to 2.95. Dilute to volume with distilled water and mix thoroughly. Measure the absorbance at 470 nm after 30 min, against iron(III) blank.

Study of variables and interferences

Beer's law was obeyed between 1.0 and 56.0 p.p.m. of iron in the final measured solution; lower and higher concentrations were not investigated. The optimum concentration range for determinations[8] was 5.3–18.0 p.p.m. The sensitivity[8] was 0.084 μg Fe/cm² for $\log I_0/I = 0.001$. To study the reproducibility, six solutions corresponding to 11.2 p.p.m. of iron at the final dilution were analysed by the recommended procedure; the standard deviation was found to be 0.95%.

The effect of 32 ions was investigated. The following ions had no effect on the absorbance of the complex at the 11.2 p.p.m. iron level when present in a 1000 p.p.m. concentration: Al^{3+}, Ba^{2+}, Be^{2+}, Cd^{2+}, Ca^{2+}, Fe^{2+}, Pb^{2+}, Mg^{2+}, Mn^{2+}, K^+, Na^+, Cs^+, Sr^{2+}, Th^{4+}, Zn^{2+}, NH_4^+, Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}; 500 p.p.m. concentrations of Cr^{3+},

Co^{2+}, Ni^{2+}, UO_2^{2+}, Br^-, 250 p.p.m. of silver, 100 p.p.m. of iodide, and 5 p.p.m. of copper(II) and bicarbonate could be tolerated. Phosphate, fluoride, citrate and oxalate interfered at all levels. Thus 2,4-dihydroxyacetophenone provides a selective determination of iron(III). Since the absorbance values of the complex are practically constant in the spectral range 460–480 nm, the method is suitable for use with simple filter photometers.

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Folgetitrimetrische Bestimmung von Calcium und Magnesium mit ÄDTA in äthanolhaltiger Lösung

Die stufenweise kompleximetrischen Bestimmungen von Calcium und Magnesium gegen Farbindikatoren werden entweder nur mit Dinatriumäthylendiamintetraacetat (ÄDTA)[1] oder in Kombination mit anderen Chelatbildnern[1,2] ausgeführt. Diejenigen Methoden, die andere Chelatbildner benötigen, setzen entweder die Anwesenheit von Tarnungsmitteln und ein sorgfältiges Einhalten des pH-Wertes, der Ammoniakkonzentration und des Calcium–Magnesiummengenverhältnisses[1] voraus, oder sie erfordern eine vorhergehende orientierende Calciumbestimmung[2]. Bei den Methoden, bei denen die Elemente direkt mit ÄDTA titriert werden, müssen störende Anionen, wie z.B. Phosphat, Oxalat u.a., abwesend sein. Durch Magnesiumhydroxidadsorption und Kohlenstoffdioxidabsorption verursachte Störungen werden jedoch nicht ausgeschaltet. In dieser Arbeit wird eine folgetitrimetrische Methode beschrieben, welche die angeführten Schwierigkeiten möglichst beseitigt.

Auf Grund der Hinweise von SCHWARZENBACH UND ACKERMANN[3], fanden wir in früheren Arbeiten[4], dass in 60%-igem Äthanol der log $K_{MgY^{2-}}$-Wert grösser wird, wodurch der Farbwechsel schärfer und die Ergebnisse besser werden. Es wurde deshalb die Gesamtmenge von Calcium und Magnesium durch direkte ÄDTA-Titration gegen Methylthymolblau in 60%-igem Äthanol beim pH-Wert 8, unter Verwendung minimaler Ammoniakmengen, mit scharfem Farbwechsel bestimmt. Die geringe Ammoniakmenge puffert die Probelösung[5] unwesentlich, so dass in der zweiten Stufe dieser Folgetitration in derselben Probelösung ein pH von 13, durch Kaliumhydroxidzugabe leicht erreicht werden kann. Das Magnesium fällt dann als Hydroxid und die freigesetzte ÄDTA-Menge wird mit Calciummasslösung gegen Methylthymolblau-Fluorexon Mischindikator titriert.

Durch diese Arbeitsweise wird die Adsorption von Calciumionen an dem Magnesiumhydroxid und die Fällung von Calciumcarbonat, durch Kohlendioxidabsorption verhindert. Das Äthanol verhindert auch die Indikatoradsorption am Magnesiumhydroxid und vermindert die Löslichkeit des Niederschlages, so dass der Farbumschlag scharf ist.

Bei wesentlich kleineren Äthanolkonzentrationen als 60%, ist die Stabilität der Chelate zu klein und die Löslichkeit des Magnesiumhydroxides zu gross, so dass der Farbumschlag undeutlich wird. Bei höheren Äthanolkonzentrationen fallen die Metallsalze aus, wodurch der Farbumschlag schleppend wird.

Da die Chelatbildungsreaktionen in äthanolhaltiger Lösung verzögert ablaufen, muss bei 60 bis 70° titriert werden.

Methylthymolblau wird in wässriger Lösung durch Spuren von Kupfer(II) blockiert[6]. Äthanol verhindert diese Blockierung. Deshalb konnte die Folgetitration auch in Anwesenheit von geringen Kupfer(II)- und anderen Schwermetallmengen vorgenommen werden. Die vorgeschlagene Methode erlaubt auch die Gegenwart sonst störender Anionen und Kationen und die Anwendung der üblichen Maskierungsmittel.

Reagentien

Die Bestimmungen wurden mit 0.05 *M*, 0.01 *M* und 0.005 *M* Lösungen durchgeführt.

Die Lösungen von ÄDTA, Calciumchlorid und Magnesiumsulfat wurden in der üblichen Weise hergestellt.

Die 0.01 *M* und die 0.005 *M* Lösungen erhielt man durch Verdünnen 0.05 *M* Lösungen. Die Gehalte der Magnesiumsulfatlösungen wurden durch Titration mit ÄDTA gegen Methylthymolblau in äthanolhaltiger Lösung[4], die der Calciumchloridlösungen gegen Methylthymolblau-Fluorexon Mischindikator[6] bestimmt.

Alle Lösungen wurden mit bidestilliertem Wasser bereitet und in Polyäthylengefässen aufbewahrt.

Arbeitsvorschrift

In ein 100 ml Becherglas werden 3 bis 6 ml Magnesiumsulfat- und 6 bis 3 ml Calciumchlorid-Stammlösung gegeben, so dass die Gesamtmenge 9 ml beträgt. Danach wird 10 ml 96%-iger Äthanol und 5 mg Methylthymolblau Indikatormischung (1:100 mit gepulvertem Kaliumnitrat) zugesetzt, worauf sich die schwach saure Lösung hellgelb färbt. Nach Zugabe von 1–2 Tropfen konz. Ammoniaklösung schlägt bei einem pH-Wert von ungefähr 8 die Farbe der Lösung nach blau um. Bei 60° wird die Gesamtmenge von Calcium und Magnesium durch direkte Titration mit ÄDTA bis zum Farbwechsel von Blau nach bleibendem Hellgrau bestimmt.

Anschliessend werden 20 ml Äthanol und 3 Tropfen 0.2%-ige wässerige Auramin Indikatorlösung[7] zugesetzt, worauf sich die Lösung gelb färbt. Danach wird soviel wässerige 30%-ige Kaliumhydroxidlösung zugegeben, bis sich die Lösung grau färbt. Der pH-Wert ist dann etwa 12. Dann setzt man weitere 0.8 ml Kaliumhydroxidlösung zur Ausfällung des Magnesiumhydroxyds zu. Die Lösung wird auf etwa 70° erwärmt, 5 mg Methylthymolblau-Fluorexon Mischindikator (0.3 g Fluorexon und 0.29 Methylthymolblau mit 50 g gepulvertem Kaliumnitrat) zugefügt und die durch das Magnesium freigesetzte ÄDTA-Menge mit Calciumchloridmasslösung bis zum Farbwechsel von Hellrot nach bleibendem Blaugrün bestimmt.

Der Calciumgehalt wird aus der Differenz der ersten und der zweiten Titrationsergebnisse berechnet.

Die Ergebnisse der Bestimmungen sind in der Tabelle I zusammengefasst.

TABELLE I

ERGEBNISSE DER FOLGETITRIMETRISCHEN BESTIMMUNG VON CALCIUM UND MAGNESIUM MIT ÄDTA IN 60%-IGER ÄTHANOLISCHER LÖSUNG

Molarität der Lösungen	*Gegeben (mg)*		*Gefunden (mg)*		*Relativer Fehler in %*[a]		*Standard Deviation*[b]	
	Ca	*Mg*	*Ca*	*Mg*	*Ca*	*Mg*	*Ca*	*Mg*
0.05	12.00	3.378	11.96	3.399	—0.31	—0.50	0.10	0.057
	6.000	7.156	5.964	7.213	—0.66	+0.80	0.01	0.024
	12.00	14.59	11.97	14.66	—0.25	+0.46	0.00	0.04
0.01	4.800	1.459	4.787	1.479	—0.28	+1.35	0.012	0.012
	2.400	2.918	2.402	2.926	—1.02	+0.27	0.045	0.012
0.005	2.074	1.186	2.061	1.195	—0.61	+0.77	0.003	0.003

[a] Mittelwert von neun Bestimmungen.
[b] Aus neun Bestimmungen berechnet.

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Iron(III) complex interference in the iodometric determination of hydrogen peroxide

The iodometric determination of hydrogen peroxide according to the reaction:

$$2\,H^+ + H_2O_2 + 2\,I^- = I_2 + 2\,H_2O$$

is well established[1]. The oxidation is relatively slow and ammonium molybdate solution is usually added as catalyst; for most purposes this is perfectly satisfactory. However, it has been found that small concentrations of iron(III) complexes constitute a serious interference in the analysis of dilute hydrogen peroxide solutions under certain conditions. Interfering complexes include iron(III) porphyrins and the proteins, catalase, methaemoglobin and metmyoglobin. When interference occurs, titration figures are higher than expected, indicating that the production of iodine is in excess of that expected from the iodide–peroxide reaction. The effect does not occur in the absence of iron(III) complexes, nor apparently, in the presence of simple aqua-iron(III) ion. It is not due to a stoichiometric reduction of the iron(III) complex, since this would have a negligible effect under the operating concentrations.

The determination of hydrogen peroxide in the presence of iron compounds has important applications in catalytic and biological assay, *e.g.*, in studies of the iron(III) haemoproteins, catalase and peroxidase, and the catalytic decomposition of hydrogen peroxide. In addition, the use of iron compounds as peroxidatic agents, *i.e.*, as catalysts for the oxidation of various substrates by hydrogen peroxide, has been the subject of many investigations, particularly with regard to technological applications. The determination of hydrogen peroxide in such systems is therefore of considerable importance and has a wide field of interest. The iodometric technique is particularly suited to such studies because (a) starch end-points are extremely sharp even at low peroxide concentrations, (b) end-point detection with other oxidants may be masked by extraneous coloured iron species, and (c) spectrophotometric techniques may not be suitable because of the high optical absorptions of iron complexes.

The interference noted in this communication is particularly serious since its magnitude may not be large enough to be obvious, but sufficiently large to destroy the value of quantitative results. A method of preventing the interfering reaction by a judicious choice of conditions is reported below.

Experimental

The iron(III) complexes used were haemin chloride (iron(III) protoporphyrin IX), bacterial catalase, metmyoglobin and methaemoglobin. Haemin was prepared from defibrinated blood by the method of FISHER[2] and recrystallized once. Aqueous haemin solutions were made by standard techniques[3], and allowed to stand before use so that haemin (A)[3] was the active reagent. Catalase was prepared from *M. lysodeikticus*, and metmyoglobin and methaemoglobin were commercially obtained. Hydrogen peroxide was 85% w/v unstabilized material (Laporte Chemicals Ltd).

Hydrogen peroxide was titrated iodometrically in the usual way with freshly prepared starch solution indicator in sulphuric acid medium. There is some variation in the standard texts as to the optimum quantity of molybdate required for catalysis[1]. Molybdate catalyses not only oxidation of iodide by hydrogen peroxide, but also oxidation by molecular oxygen, hence a large excess of molybdate must be avoided.

Under the conditions given below, no autoxidation could be detected even when test solutions were exposed to the atmosphere for several hours. The concentration of hydrogen peroxide to be determined also influences the quantity of molybdate to be added. For very low concentrations (*ca.* 10^{-3} M), it is necessary to increase the molybdate concentration so that the iodide–peroxide reaction is complete within a short time. In this work, 3 drops of 20% solution were added in each case (total volume, *ca.* 10 ml).

Titrations were made with and without iron(III) complex present but otherwise under identical conditions, so that results were directly comparable. Care was taken to acidify test solutions *before* addition of iron(III) complex to avoid catalytic decomposition of hydrogen peroxide. All measurements were made at ambient temperature. Test solutions containing iron(III) complex were deep green before titration. In such solutions, end-point detection was difficult but not impossible with starch indicator and 0.1 N sodium thiosulphate solution. When titration was carried out in the absence of starch (with iodine as self indicator) solutions were blue at the end-point and remained blue after addition of excess of thiosulphate.

Results

In every case when iron(III) complex was present, the titration figure was higher than expected when the commonly recommended conditions[1] were used. A few specimen results are given in Table I, referring to haemin and catalase. At low peroxide concentrations, a short time of standing is necessary for full development of iodine. The level of interference was found to be dependent upon the reaction time (Table I).

TABLE I

INTERFERENCE BY THE IRON(III) COMPLEXES, HAEMIN AND CATALASE, IN THE DETERMINATION OF HYDROGEN PEROXIDE

	Concn. of iron(III) complex (M)	*Reaction time (min)*	*Acid concn. (N)*	*mMoles H_2O_2 found*	*% Error*
Haemin	10^{-5}	15	1.0	0.257	+ 2
	0	15	1.0	0.253	
	10^{-5}	15	1.0	0.095	+ 6
	0	15	1.0	0.090	
	10^{-5}	15	1.0	0.061	+ 9
	0	15	1.0	0.056	
	10^{-5}	15	1.0	0.038	+ 26
	0	15	1.0	0.030	
	10^{-5}	20	1.0	0.065	+ 14
	0	20	1.0	0.057	
	10^{-5}	60	1.0	0.068	+ 19
	0	60	1.0	0.057	
	10^{-5}	15	1.5	0.057	+ 6
	0	15	1.5	0.054	
	10^{-5}	15	2.0	0.057	0
	0	15	2.0	0.057	
Catalase	10^{-7}	15	1.0	0.060	+ 5
	0	15	1.0	0.057	
	10^{-7}	15	1.0	0.092	+ 2
	0	15	1.0	0.090	
	10^{-7}	15	1.0	0.033	+ 13
	0	15	1.0	0.029	

Qualitative experiments showed that methaemoglobin and metmyoglobin caused similar effects. The data in Table I also illustrate how the interference increases at longer reaction times and decreases (to zero) as the pH is lowered.

Discussion

The level of interference is serious for the determination of small amounts of hydrogen peroxide in the presence of trace quantities of iron(III) complexes (Table I). The absolute error is approximately constant (for constant reaction time) and the percentage error therefore increases as the hydrogen peroxide concentration decreases. In determinations of hydrogen peroxide, reaction conditions could be such that the interference would not be noticed, but would nevertheless seriously affect quantitative data.

The interference by iron(III) complexes is explained in terms of a reaction between molybdate and iodide to give a reduced molybdenum species and free iodine. Titration figures are thus higher than expected. The observed effects can only be explained if it is assumed that the molybdate oxidation of iodide is catalysed by iron(III) complexes. This idea has been verified and is considered in detail elsewhere[4]. The effect is especially noteworthy in view of the very small concentrations of iron(III) complex involved (see Table I). The reduced molybdenum species is molybdenum blue but solutions appear green in the presence of iodine. After addition of excess of sodium thiosulphate, the blue species is clearly observable.

In an investigation of the haemin-catalysed oxidation of iodide by molybdate[5], the rate of oxidation has been shown to vary in quite a remarkable way with pH. The rate of oxidation is maximal near pH 1, is zero at pH 2 and is very small below pH 0. Experiment has shown that below pH -0.3 (*i.e.*, 2 *N* acid) no oxidation could be detected after 15 min. This is illustrated in Table I, where at 2 *N* acid concentration, no interference was found. The effect has also been shown to depend markedly on molybdate concentration[5]. Again, the rate of oxidation passes through a maximum corresponding to 0.02 *M* molybdate at pH 1.

It is clear from the maxima involved in the dependence of rate of catalytic oxidation on pH and molybdate concentration, that interference could be minimized by working at very low or very high acid concentrations, or alternatively, at very low or very high molybdate concentrations. Significant change of molybdate concentration is not feasible since high concentrations may involve atmospheric oxidation of iodide and very low concentrations may not be sufficient to catalyse the hydrogen peroxide–iodide reaction. Similarly this reaction would be affected if the pH were increased. Significant lowering of pH has no adverse effects and would minimize interference. Before addition of molybdate catalyst, sufficient acid must be added to ensure that the *final* acid concentration after titration is at least 2 *N*. With this slight modification, the iodometric technique is capable of high precision in the determination of hydrogen peroxide in the presence of iron(III) complexes.

Recommended procedure

The initial hydrogen peroxide concentration should be between 0.1 *M* and 0.005 *M*. Add 25 ml of 5 *N* sulphuric acid to 10 ml of the hydrogen peroxide solution in a 100-ml conical flask, followed by a suitable quantity (3-fold excess) of 5% potassium iodide solution and 3 drops of 20% ammonium molybdate solution. Stopper the flask and allow to stand for 20 min. Titrate with 0.1 *N* sodium thiosulphate solution to the starch end-point (for small concentrations of hydrogen peroxide, 0.01 *N* thiosulphate can be used with little deterioration in the end-point).

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Anal. Chim. Acta, 43 (1968) 343–346

Compleximetric titration of phosphate with lanthanum as precipitant

A new compleximetric method for the determination of phosphate in the presence of chloride, sulfate, alkali and alkaline-earth metals is described. The usual compleximetric methods for phosphate, which are based on the precipitation of magnesium ammonium phosphate and titration of the precipitate with EDTA in the presence of eriochrome black T[1], are unsatisfactory for small amounts of phosphate because of the high solubility of magnesium ammonium phosphate. A method for phosphate determination based on precipitation of thorium phosphate and titration of the excess of thorium with EDTA in the presence of xylenol orange indicator has been described[2], but it is necessary to filter off the precipitate before titration, whereas in the proposed method, filtration is not required, and the method is therefore shorter and more accurate.

Lanthanum can be accurately titrated with EDTA at pH 5.0 (acetate buffer) in the presence of xylenol orange[3]; alkali and alkaline-earth metals do not interfere at this pH. Lanthanum phosphate precipitates at pH 4.5[4] while alkaline-earth phosphates do not. It is therefore possible to precipitate all the phosphate with an excess of lanthanum and back-titrate with 0.1 *M* EDTA at pH 5.0 in the presence of xylenol orange indicator without filtration. This procedure was successfully used with solutions containing 50–300 mg of phosphate in 50 ml of solution.

In another series of experiments, 0.01 *M* lanthanum and 0.01 *M* EDTA were used. The end-point was even sharper than with more concentrated solutions because less precipitate was formed. As little as 1 mg of phosphate in 50 ml of solution could be accurately titrated.

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In the presence of sulfate, the results obtained for phosphate were high, probably because double salts of lanthanum sulfate with the alkali and alkaline-earth sulfates[5] were formed; these double sulfates are soluble in water, but do not react stoichiometrically with EDTA. However, when some EDTA (about 10 ml) was added before the addition of lanthanum, accurate results were obtained for phosphate. Presumably, the presence of EDTA prevents the formation of the double sulfates.

The precision of the method is in the range 0.03–1.1% and the accuracy is ± 1%. Concentrations as high as 1930 p.p.m. Cl^-, 480 p.p.m. Mg^{2+}, 800 p.p.m. Ca^{2+}, 1100 p.p.m. Na^+, 1920 p.p.m. SO_4^{2-} and 2740 p.p.m. Ba^{2+} do not interfere with the method.

Procedure

(a) Without sulfates. Acidify 50 ml of solution which may contain chloride, alkali and alkaline-earth metals, but not sulfate, with a few drops of concentrated hydrochloric acid. Then add 20 ml of 0.1 *M* lanthanum chloride solution, previously standardized against 0.1 *M* EDTA standard solution, followed by 9 drops of aqueous 0.1% xylenol orange solution, and adjust the pH to 5.0 by addition of 10 ml of acetate buffer (3:7 0.2 *M* acetic acid–0.2 *M* sodium acetate) and a few drops of concentrated ammonia solution (color red). A white precipitate is formed. Add 1 drop of pyridine and titrate with 0.1 *M* EDTA until a yellow color is obtained. Add another drop of pyridine; if the color reverts to red, add more EDTA until a yellow end-point is reached. The titration should be done under daylight fluorescent lamp illumination. It is very helpful to use another solution, which was previously titrated on the same day, as a color comparison.

(b) In presence of sulfate. After acidification of the solution, add 10 ml of 0.1 *M* EDTA standard solution and then a measured excess of 0.1 *M* lanthanum chloride. Raise the pH to 5.0 and titrate with EDTA as described. Small amounts of phosphate (1–10 mg) may be determined if 0.01 *M* lanthanum chloride and 0.01 *M* EDTA are used.

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Use of a pyrolytic boron nitride thimble in determining oxygen by the inert gas fusion method

It is not uncommon in the determination of oxygen by carrier gas fusion to experience high and erratic oxygen blanks. Operator technique is undoubtedly vital in achieving a reasonably low, stable blank. The principal source of this blank is the carbon monoxide formed by the high-temperature reaction of the carbon-black insulation with the quartz crucible thimble:

$$SiO_2 + 2\,C \xrightarrow[\Delta]{} 2\,CO + Si.$$

This reaction is accelerated by the formation of cracks developed in the carbon-black insulation and by local hot spots. These hot spots can be caused by tin deposits on the quartz thimble which couple with the induction field. The tin which diffuses through the carbon black and deposits on the quartz thimble, derives from the capsules used as sample containers. The introduction of samples containing alkali elements will cause similar high erratic blanks owing to diffusion of the alkali metal to the quartz thimble and the alkali reaction with the quartz.

Recently, a pyrolytic boron nitride (PBN) crucible thimble has been used in carrier gas fusion determinations of gas in metals to reduce the oxygen blank[1,2]. The principal advantages of the PBN thimble over the conventional quartz thimble are its high temperature stability (2500° in inert atmosphere, 1000° in air or oxygen) and its lack of oxygen content[3]. This report will describe certain modifications to the previously described system and their application to commercially available instrumentation.

Instrumentation and procedure

The blank studies were conducted with a LECO No. 534-300 Analyzer. The graphite reaction crucible (No. L4401, Carbon Products Division, Union Carbide Corporation), carbon-black packing (LECO No. 501-092) and tin capsules (LECO No. 501-59) were routinely used materials.

The pyrolytic boron nitride crucible thimble, ring, and funnel (No. H-5520, H-5521 and H-5522, respectively) were products of this laboratory.

The combustion sections, furnace packing, and related operations were preformed according to the LECO instruction manual[4] with the following exceptions: the quartz crucible thimble, and funnel drop tube were replaced by the corresponding parts in PBN; a pyrolytic boron nitride ring was placed over the carbon-black packing as shown in Fig. 1.

The system was purged of adsorbed oxygen by gradually heating the reaction crucible to 2500–2600° while maintaining a flow of 0.4 l/min of argon through the furnace section. The reaction crucible was held at this temperature for 20–30 min after which the normal operating temperature was maintained.

The system blank was determined by dropping an empty tin capsule from the loading head into the graphite crucible which was held at 2350°, after a preliminary 2-min equilibrium of the total system. The blank reading was taken 5 min after the start of the combustion.

Discussion

When the quartz crucible thimble is used, great care and proper techniques

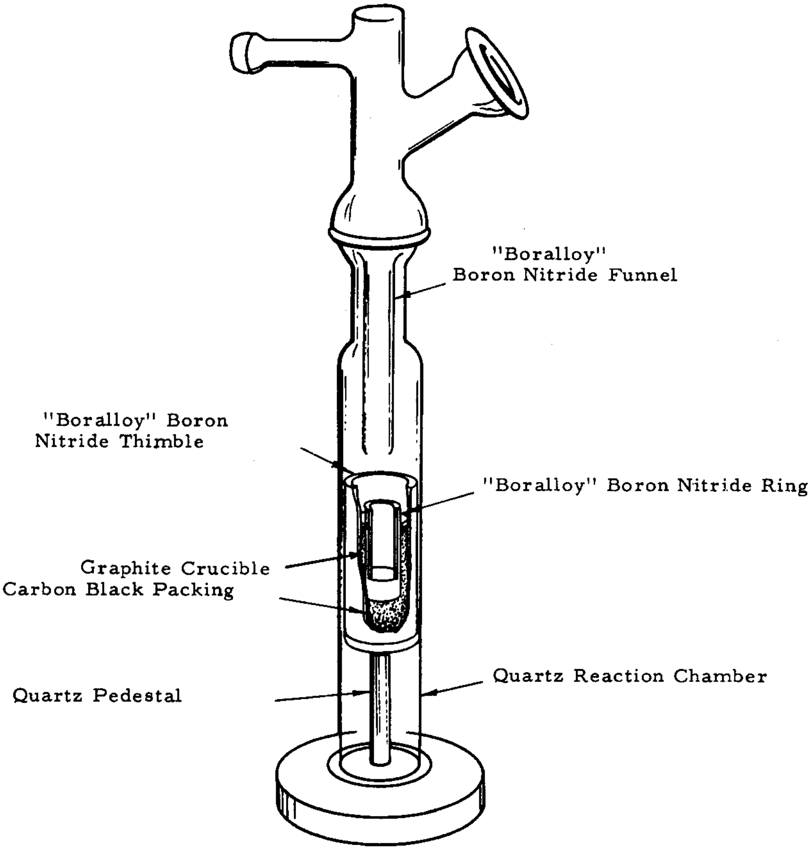

Fig. 1. Combustion section with "Boralloy" thimble–ring–funnel.

are necessary if a low and reproducible oxygen blank is to be achieved. One of the most critical steps is in the packing of the combustion crucible. The graphite combustion crucible is floated on a carbon-black insulating blanket which is held in the quartz thimble. The carbon black is used to insulate the quartz from the high temperatures produced in the combustion crucible. If the carbon black is packed too tightly and outgassed too rapidly, cracks can develop in the pack and expose the quartz thimble to a higher temperature, resulting in a higher oxygen blank. Too tight a pack can also cause the pack to couple with the electromagnetic field, decreasing the temperature attainable in the combustion crucible. This condition could also increase the temperature to which the quartz is exposed and could cause an increased blank. Packing the carbon black too loosely also contributes to crack formation in the pack and exposes the quartz to a higher temperature, resulting in a higher blank.

Replacing the quartz thimble with a pyrolytic boron nitride (PBN) thimble which is free of oxygen eliminates this source of oxygen and reduces the severity of the problem of precise packing. The PBN has higher thermal stability than the quartz and is better able to withstand any incidentally increased temperature, hence the need for great care in packing the carbon black around the graphite crucible is strongly reduced.

The carbon-black insulation is necessary so that the PBN thimble does not receive the full temperature of the graphite reaction crucible. Without the carbon-black insulation, such a high temperature in the presence of the carbon atmosphere would result in carbide formation on the surface of the PBN thimble which would couple with the electromagnetic field and decrease the power available to the graphite crucible. However, under normal conditions, the PBN thimble is not exposed to the higher temperature and does not react in this way. Carbide on the crucible can be easily removed by wiping with a soft cloth or washing with a detergent and test-tube brush. Tin deposits can be dislodged by careful use of a spatula.

The PBN drop funnel was installed when it was noted that the bottom end of the quartz funnel became etched after a period of time. This etching increases the danger that the sample dropping through the funnel will strike the funnel wall and dislodge a minute particle of the glass and carry it into the reaction crucible causing unexplainable erratic results. Use of the PBN drop funnel eliminated this potential problem. More recent thermal conductivity read-out systems with different sample drop mechanisms obviate the need for the PBN funnel.

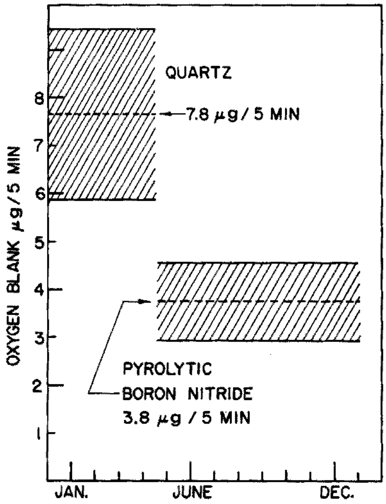

Fig. 2. Oxygen blank of "Boralloy" thimble *vs.* quartz thimble.

During the initial degassing operation, it is not uncommon for some of the carbon-black packing to be blown out of the thimble and into the glass connecting system. This puffing has been eliminated by use of PBN ring placed over the carbon black (see Fig. 1). Use of PBN ring helps to keep the system clean, reduces the chance for carbon black to get into the reaction crucible, and helps to reduce degassing time.

The experimental oxygen blank values representing the total micrograms of oxygen extracted from all furnace components and the empty tin capsule were measured at 2350° and are shown in Fig. 2. The level and stability of the oxygen blank found for both thimbles is shown. These studies were conducted over a period of one year with both the quartz and the pyrolytic boron nitride thimble.

The average 5-min oxygen blank using the PBN thimble was 3.8 μg of oxygen, a 50% decrease over the blank average of 7.8 μg of oxygen found for the quartz thimble. A marked improvement in blank reproducibility was also achieved with the PBN thimble; the standard deviation for the PBN thimble oxygen blank was 0.82 μg of oxygen compared with 1.8 μg oxygen for the quartz thimble. Both the reduced blank and the improved blank stability will be important for operators doing parts-per-million oxygen analyses.

The significant reduction of the oxygen blank level and the increased stability of the oxygen blank show the value of using the pyrolytic boron nitride thimble in commercially available carrier gas fusion analyzers. The PBN thimble has been in use in our instrument for over two years without apparent damage or deleterious effects. This long life has more than offset the initial cost of the PBN crucible. In addition, use of the PBN thimble saves time in operator training, crucible packing, degassing and down time.

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The determination of micro-concentration gradients on the surfaces of solid samples by means of the laser-microprobe

The elucidation of some modern technological problems frequently requires the determination of concentration gradients of impurities and added substances in the solid phase of materials, down to a spatial resolution of 50 μ or better.

The boron-10 isotope of any boron contained in steel used for reactor purposes will undergo a nuclear reaction with the formation of helium which causes embrittlement. As part of a programme of evaluating steels for this purpose it became necessary to know how the boron was distributed. The electron-microprobe was of no avail in resolving this problem and since previous work had shown that it was possible to detect $5 \cdot 10^{-12}$ g boron with the laser-microprobe this device was used for the investigation.

The laser-microprobe used was a commercially produced equipment (Jarrell Ash, Inc.) in which a 30 nsec pulse of wavelength 6943 Å is generated by means of a Q-switched ruby laser. The pulse of intense light emitted by the laser rod is focussed by means of a metallurgical microscope on to a pre-selected area of the sample. Energy is dissipated on the surface of the sample at the rate of 2 MW in an area 50 μ in diameter; photon energy is absorbed by the sample and about 1 μg is vaporised. The plume of the vapour rising from the sample is then allowed to shortcircuit 2 graphite electrodes on which there is a capacitive standing voltage. The spectra of the impurity elements produced by the resulting spark are then recorded by means of a quartz spectrograph of medium dispersion with a Kodak 0-0 photographic plate.

The particular type of steel examined consisted of a 20/25 niobium-stabilised material, micrographs of which showed the presence of austenite grains about 50 μ in diameter interspersed with coarse precipitates of variable size but averaging 100 × 20 μ. It was considered that the boron was contained in the precipitates and series of determinations were carried out on the two phases present in the steel sample.

In order to obtain some idea of the level of boron present, standards were synthesised by grinding and successive dilution of known amounts of boron carbide with a matrix consisting of the appropriate proportions of the oxides of iron, chromium, nickel and niobium. The standards were pelleted and subjected to laser-microprobing. Variations in the weights of samples and standards vaporised were compensated to some extent by the use of iron as an internal standard. Cathode-ray microphotometry was used to determine the intensity ratio of Fe 2495.9 and B 2496.8 and a linear calibration was obtained over the range 10–1000 p.p.m. of boron. Laser shots were taken on each of six areas corresponding to the precipitate and austenite areas and the typical results obtained for one specimen are shown in Table I.

TABLE I

LASER-MICROPROBE ANALYSIS OF 20/25 NIOBIUM-STABILISED STEEL SPECIMEN NO. 249

Area	*B content (p.p.m.)*	*Area*	*B content (p.p.m.)*
"Precipitate" area 1	450	"Austenite" area 1	50
"Precipitate" area 2	250	"Austenite" area 2	<10
"Precipitate" area 3	200	"Austenite" area 3	10
"Precipitate" area 4	400	"Austenite" area 4	<10
"Precipitate" area 5	350	"Austenite" area 5	<10
"Precipitate" area 6	100	"Austenite" area 6	<10

Mean boron content of all areas by *laser-microprobe* = 150 p.p.m.
Boron content by *chemical analysis* = 160 p.p.m.

Because of the high resolution and correspondingly small sample weight, it was not possible to obtain an independent check on the accuracy of this method, but it is of interest to note that the boron content obtained by chemical determination on a massive sample was in good agreement with the average figure obtained by the twelve laser determinations. At first, this agreement was thought to be fortuitous but subsequent examinations of other samples have produced similar results. Whilst it cannot be said that this technique represents a method for the quantitative determination of boron in a microgram of steel, the indications are that the results obtained are probably of semi-quantitative significance and they have proved of value in elucidating metallurgical problems that could not be resolved by other means.

A similar technique has also been used for the determination of thallium concentration gradients in potassium iodide crystals and the distribution of uranium absorbed on to refractory oxides.

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Calcein blue as a fluorescent adsorption indicator in the direct titration of silver ions

Numerous adsorption indicators for the argentimetric titration of halide and thiocyanate and for the determination of silver have been described[1]. Calcein blue, first prepared by WILKINS[2], is a large polarizable molecule and thus would probably be strongly adsorbed. It was first used as an indicator for the compleximetric titration of metal ions with EDTA[3], and has been proposed for the fluorimetric determination of calcium, magnesium and iron in the same solution[4]. KIRKBRIGHT AND STEPHEN[5] screened the residual fluorescence of calcein blue by adding a few drops of rhodamine B in the compleximetric determination of calcium. Calcein blue has not previously been used as a fluorescent adsorption indicator. In this paper, the properties of calcein blue which make it a good fluorescent adsorption indicator are discussed and a direct determination of silver is described. Fluorescent quenching is easily detected, besides being convenient and sensitive.

Reagents and apparatus

Calcein blue was obtained from G. Frederick Smith Chemical Company, Columbus, Ohio. All other reagents were of analytical grade and were used without further purification. All solutions were prepared with deionized water.

Measurements of spectra were made with a Beckman Spectrophotometer Model DBG. A Corning Expandomatic pH meter Model 12 with No. 41260 Beckman glass electrode and a saturated calomel electrode were used for pH measurements. A Coleman Electronic Photofluorimeter equipped with a Galvanometer Model 22 and a Precision Scientific water bath with controls were used for some fluorimetric readings at different pH and temperature. An ultraviolet box[6] was used for the titrations.

Procedures

Fluorescent changes with pH and temperature. The pH of solutions containing *ca.* 0.0053 g of calcein blue in 50.0 ml of aqueous solution was varied from 2 to 12 with potassium hydroxide and hydrochloric acid. The relative fluorescence of these solutions was obtained. The same solutions were used to study the changes in relative fluorescence in the temperature range 17°–80°.

Comparison of relative fluorescences of calcein blue and silver–calcein blue at different pH. Mixtures containing 10.0 ml of 0.001 *M* silver nitrate, 10.0 ml of 0.5% gelatin and 1.0 ml of 0.02% calcein blue were placed in different 25-ml volumetric flasks. The pH was adjusted to values ranging between 1.87 and 12.73 with 0.5 *M* nitric acid and 0.05 *M* potassium hydroxide. The mixtures were diluted to volume with deionized water. The percent relative fluorescence was read immediately after 30 min.

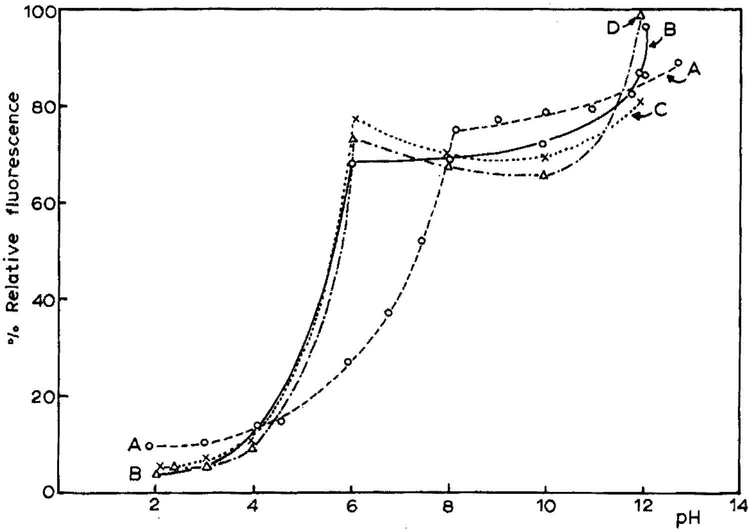

Fig. 1. Fluorescence of silver–calcein blue and calcein blue at different pH and temperature. (A) Silver–calcein blue; (B) calcein blue, $5.0 \cdot 10^{-3}$ g/50.0 ml H_2O, 23°; (C) as B but at 48.2°; (D) as B but at 80°.

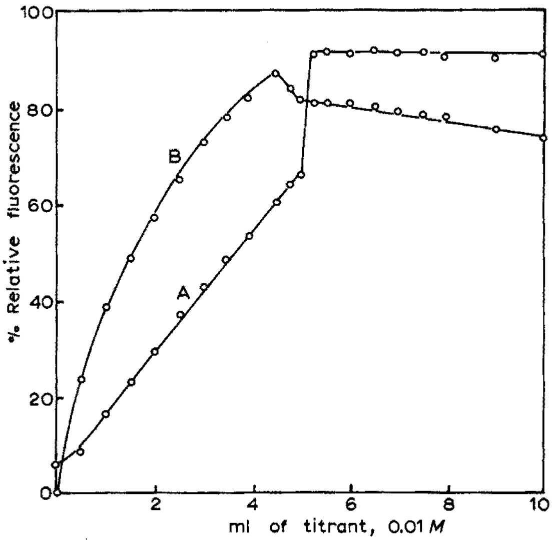

Fig. 2. Titration curves. (A) 5.0 ml of 0.01 *M* $AgNO_3$ *vs.* 0.01 *M* KI as titrant; (B) 5.0 ml of 0.01 *M* KI *vs.* 0.01 *M* $AgNO_3$ as titrant. Each solution mixture contains 1.0 ml of 0.5% gelatin, 3 drops of 0.50 *M* nitric acid and 1 drop of 0.02% calcein blue.

The plots of percent relative fluorescence *versus* pH of the silver–calcein blue mixtures and that of calcein blue alone at three different temperatures are shown in Fig. 1.

Ultraviolet spectra at different pH. The solutions used contained about 0.0012 g of calcein blue in 50.0 ml of deionized water and the pH was varied from 2.08 to 11.88.

Titration curves. A solution containing silver nitrate was titrated with standard potassium iodide and the relative fluorescence of the mixture at various stages of titration was read at room temperature. A reverse titration was also done. Plots of percent relative fluorescence *versus* the volume of titrant in each case are shown in Fig. 2.

Recommended procedure for the determination of silver. To 10.0 ml of 0.001–0.01 *M* silver nitrate solution add 10.0 ml of freshly prepared and well-dissolved 0.5%

TABLE I

TITRATIONS OF SILVER NITRATE WITH POTASSIUM IODIDE

($AgNO_3$ used: 10.0 ml. Gelatin used: 10.0 ml (0.5%))

pH	*$AgNO_3$ (M)*	*Calcein blue (drops)*	*KI (ml)*	*KI (M)*	*End-point*	
2.18	0.001	3	1.01(2)[a]	0.010	d[b]	
2.22	0.010	20	10.00	0.010	d	
2.97	0.001	3	10.50	0.001	d	indistinct
3.89	0.001	2	1.00	0.010	d	very sharp
4.00	0.001	10	10.11(11)	0.001	d	good
4.00	0.010	80–200	10.26(3)	0.010	d	poor
4.09	0.001	1	1.00	0.010	d	very sharp
4.43	0.001	5–10	10.06(2)	0.001	d	good
5.15	0.001	3	1.10(2)	0.010	d	good
5.45	0.001	40	1.00(2)	0.010	r	very sharp
5.45	0.100	5	0.70	0.100	d	premature
5.75	0.0001	20	—(3)	0.001	r	indistinct
5.92	0.001	20	1.01(2)	0.010	r	good
5.93	0.001	10–20	1.02(2)	0.010	r	very sharp
5.95	0.001	20	10.02	0.001	r	good
6.33	0.001	2	1.02(2)	0.010	r	good
6.38	0.0001	2	—	0.001	r	indistinct
6.38	0.0001	2	—	0.010	r	indistinct
7.23	0.001	40	1.00	0.010	r	
10.27	0.001	1–10	10.23(3)	0.001	r	
12.60	0.001	5	10.20(5)	0.001	d	
13.20	0.001	20	10.50(3)	0.001	d	
Modified titrations						
0.01	0.001[c]	10	10.0(3)	0.001	d	sharp
5.65	0.001[d]	20	1.02	0.010	d	
7.45	0.001[d]	5	1.02	0.010	d	
10.02	0.010[e]	20	10.2(7)	0.010	d	
10.27	0.001[d]	1–10	10.24	0.001	d	
10.37	0.001[f]	1–10	9.90	0.001	d	
10.39	0.001[g]	20	10.00	0.001	d	
12.60	0.001[d]	0.5	10.38(6)	0.001	d	

[a] Number in parentheses indicates multiple titrations.
[b] d = disappearance of fluorescence; r = reappearance.
[c] $9 \cdot 10^{-3}$ *M* KIO_4, 0.02–0.03 g of $K_2S_2O_8$ and 3 ml of sulfuric acid added.
[d] Rhodamine B (0.003%) added.
[e] 2 ml of ammonia liquor added.
[f] $9 \cdot 10^{-3}$ *M* KIO_4, 2 ml of ammonia liquor added.
[g] $9 \cdot 10^{-3}$ *M* KIO_4, 2 ml of ammonia liquor and 0.02 g of $K_2S_2O_8$ added.

gelatin solution. Adjust the pH to 4–6 with potassium hydroxide or nitric acid. Add 10–20 drops of freshly prepared aqueous 0.02% calcein blue solution and titrate rapidly inside an ultraviolet box with standard 0.001–0.01 *M* potassium iodide to the disappearance of the brilliant blue fluorescence if the pH is about 4–5.5, and the reappearance of the removed fluorescence above this pH. Place a black background below the titration vessel and stir magnetically.

Results and discussion

The results of some titrations at different pH values and concentrations are shown in Table I. The structure of the compound at the end-point of the titration was elucidated by investigations on changes of relative fluorescence and spectra at different pH. The relative fluorescence of calcein blue in aqueous solution was greatest above pH 11; it changed only slightly below pH 4, but increased sharply above pH 6 and again at pH 11.9 (Fig. 1). The curves obtained are characteristic of calcein blue and are different from those of other calcein-type indicators observed in this laboratory. As the temperature was increased, the relative fluorescence did not change substantially below pH 4, but again increased rapidly at a temperature of about 40° and pH 6 (Fig. 1).

There were changes in the wavelength of maximum absorption in the ultraviolet spectra of calcein blue in aqueous solution at different pH. In acid, the peak is at 323 nm at pH 2.08, and at 327 nm at pH 3.87. In alkaline medium, the peak shifts to longer wavelengths: 360 nm at pH 9.80 and 362 nm at pH 11.88. This shows dissociation at both extreme pH ranges. Between pH 6.05 and 7.95, a broad band and a lower peak are observed.

A neutral molecule of calcein blue is assumed at pH 4–6; at other pH values, ionic forms exist. The change in fluorescence at pH 4–6 may be due to protons gained or lost by the precipitate. In an acidic medium, the neutral indicator is preferentially adsorbed on the excess of silver at the precipitate surface with the release of a proton. After the equivalence point, excess of iodide ions are adsorbed and the proton is regained by the calcein blue accompanied by an increase in pH and relative fluorescence. Calcein blue is used in this paper as an amphiprotic fluorescent adsorption indicator. The results obtained in these studies conform with the findings of earlier workers on other adsorption indicators[7,8]. The presence of gelatin prevents the coagulation of the precipitate and premature end-points. The addition of rhodamine B as a screening agent does not markedly improve the end-point.

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