ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 45, No. 1, 1–204, March 1969
Published monthly

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)**

Subscription price: $ 17.50 or Dfl. 63.— per volume plus postage. Total subscription price for 1969: $ 87.50 or Dfl. 315.— plus postage. Additional cost for copies by airmail available on request. For subscribers in the U.S.A. and Canada, 2nd class postage paid at Jamaica, N.Y. For advertising rates apply to the publishers.

Subscriptions should be sent to:

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 45, No. 1, March 1969

A FLUORIMETRIC ENZYMIC METHOD FOR THE ASSAY OF MIXTURES OF ORGANIC ACIDS

Rapid fluorimetric methods are described which involve six enzyme systems for the determination of mixtures of 21 organic acids. Lactate (Types II and IV), malate, glutamate, isocitrate, and β-hydroxybutyrate dehydrogenases are used, coupled with NAD, phenazine methosulfate and resazurin, in a fluorimetric procedure for the determination of acetic, adipic, benzilic, butyric, D-α- and D-β-hydroxybutyric, chloroacetic, DL-citric, formic, L-glutamic, glutaric, glycolic, threo-D-isocitric, L-lactic, L-malic, malonic, oxalic, phthalic, DL-succinic and L-tartaric acids in the approximate concentration range of 0.1–500 μg with an accuracy and precision of about 2%. The rate of production of the highly fluorescent resorufin is equated to the concentration of the acid.

G. G. Guilbault, S. H. Sadar and R. McQueen,
Anal. Chim. Acta, 45 (1969) 1–12

PHOSPHORESCENCE AND FLUORESCENCE SPECTROMETRY OF PHENYL-SUBSTITUTED SILANES

The fluorescence and phosphorescence spectral characteristics of twelve phenyl-substituted silanes have been determined; phosphorescence lifetimes are also presented. Limits of detection by fluorimetry and phosphorimetry are compared and the possibility of luminescence assay is discussed. Fluorimetry and phosphorimetry are shown to be complementary in achieving the highest analytical sensitivities.

E. S. Moyer and W. J. McCarthy,
Anal. Chim. Acta, 45 (1969) 13–19

THE EFFECT OF CONCENTRATION ON THE OPTIMAL BURNER HEIGHT IN THE DETERMINATION OF COPPER AND MANGANESE BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

(in French)

The concentration of the element to be analyzed is shown to affect the height of the zone of maximum atomic population in atomic absorption spectroscopy. This effect particularly influences the shape of the calibration curves. It varies according to the elements and the type of the flame; the cases of copper and manganese are discussed in detail.

M. de Waele and W. Harjadi,
Anal. Chim. Acta, 45 (1969) 21–25

ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR

PART I. CONSTRUCTION AND OPERATION OF ATOM RESERVOIR

A highly efficient carbon filament atom reservoir is described for use in atomic absorption and atomic fluorescence spectroscopy. Atomisation of minute samples of aqueous solutions occurs on a 1–2 mm carbon filament electrically heated by the passage of *ca.* 100 A at 5 V in an inert atmosphere within a simple glass chamber. With the elements tested so far there are no memory effects and the carbon filament is self-purging and may be used repeatedly for the same or other analyses. The device operates with an inexpensive transformer unit and is so compact that it may easily be fitted in the place of the burner–nebuliser unit on any commercial atomic absorption equipment and operated with perfect safety without flame extractors or precautions against fire or electrocution hazards. Analyses are completed within 5 sec and may be repeated every 2 min. As little as 10^{-15} g of magnesium may be determined with a precision of better than 30%.

T. S. West and X. K. Williams,
Anal. Chim. Acta, 45 (1969) 27–41

DETERMINATION OF PHOSPHORUS, ARSENIC OR SILICON BY ATOMIC ABSORPTION SPECTROMETRY OF MOLYBDENUM HETEROPOLY ACIDS

A method is described for the determination of trace amounts of phosphorus, arsenic or silicon by atomic absorption spectrometry. The heteropoly-molybdo acids of phosphorus, arsenic and silicon were formed and selectively separated by means of solvent extraction, and the molybdenum present in the organic phase was determined by atomic absorption spectroscopy with a nitrous oxide–acetylene flame. The method is rapid, simple and accurate and is essentially free from interferences.

T. V. Ramakrishna, J. W. Robinson and P. W. West,
Anal. Chim. Acta, 45 (1969) 43–49

THE DETERMINATION OF NANOGRAM AMOUNTS OF CHROMIUM IN URINE BY X-RAY FLUORESCENCE SPECTROSCOPY

Nanogram amounts of chromium can be extracted as oxinate into chloroform. By treatment of the chloroform layer with 3 M hydrochloric acid, oxinates of other elements and excess of reagent are removed, leaving a chloroform solution of the chromium chelate only. This solution is concentrated and transferred to the top of a small brass rod acting as sample holder. The intensity of the X-ray fluorescence of the Cr $K\alpha$ line is measured with curved crystal optics. Chromium amounts greater than 5 ng can be detected. The application of the procedure to the analysis of the chromium content of urine is demonstrated.

K. Beyermann, H. J. Rose, Jr. and R. P. Christian,
Anal. Chim. Acta, 45 (1969) 51–55

THE SOLVENT EXTRACTION OF ZINC(II) WITH ALIPHATIC MONOCARBOXYLIC ACIDS

Extractions of 10^{-3}–10^{-7} M zinc from aqueous 0.1 M sodium perchlorate solutions into organic media (benzene, chloroform, 4-methyl-2-pentanone) with the aid of 1–10-carbon aliphatic monocarboxylic acids and 1-aminobutane have been studied. Extraction is increased by increases in acid molecular weight, acid concentration, pH, and 1-aminobutane concentration. The extractions are independent of zinc concentration. Detailed studies on the hexanoic-acid systems have led to identifications of possible aqueous and organic species and to the calculation of some equilibrium constants.

G. K. Schweitzer and F. C. Clifford,
Anal. Chim. Acta, 45 (1969) 57–63

THE PARTITION AND DIMERIZATION OF OCTANOIC ACID IN SEVERAL ORGANIC–AQUEOUS SYSTEMS

The partition and dimerization constants of octanoic acid between five organic solvents and 0.1 M sodium perchlorate solution have been measured over the organic concentration range of $10^{-4.1}$–$10^{0.9}$ M with carbon-14 labelled acid. The partition and dimerization constants for the five organic solvent systems were determined to be 1830 ± 85 and negligible for 1-hexanol, 1150 ± 47 and negligible for 4-methyl-2-pentanone, 148 ± 15 and 286 ± 18 for chloroform, 47 ± 6 and 320 ± 86 for benzene, and 4.6 ± 0.4 and 5940 ± 1890 for hexane.

G. K. Schweitzer and D. K. Morris,
Anal. Chim. Acta, 45 (1969) 65–70

THE EXTRACTION OF URANIUM(VI) AND COBALT(II) FROM HYDROCHLORIC ACID SOLUTIONS BY CYCLOHEXYL- AND BENZYLALKYLAMINES

The partition of uranium(VI) and cobalt(II) between hydrochloric acid solutions and solutions of cyclohexyl- and benzylalkylamines in benzene has been investigated at different conditions. The effects of amine structure and organic solvent on the extractions have also been examined. It is found that cyclohexyl- and benzylalkyl tertiary amines are more efficient extractants for uranium and cobalt than secondary amines; a benzyl group is essential for promoting the extraction efficiency; the efficiency is reduced when the alkyl chain is branched and is strongly influenced by the kind of organic solvent used as diluent.

T. Sato,
Anal. Chim. Acta, 45 (1969) 71–80

DISTRIBUTION COEFFICIENTS AND THE CATION-EXCHANGE BEHAVIOUR OF ELEMENTS IN HYDROCHLORIC ACID–ETHANOL MIXTURES

Cation-exchange equilibrium distribution coefficients with Bio-Rad AG50W-X8, a sulfonated polystyrene resin, are presented for 45 elements in hydrochloric acid–ethanol media. The acid concentration range 0.1–3.0 M and the ethanol concentration range 0–95% are covered. The elements are arbitrarily arranged in tables according to their coefficients in aqueous hydrochloric acid. Possibilities for separations inherent in the system are demonstrated by elution curves for the multicomponent systems Fe(III)–U(VI)–Ca(II)–La(III); Cd(II)–Zn(II)–Fe(III)–Ca(II)–Ba(II); and In(III)–Ga(III)–Be(II)–Al(III)–Y(III). Some aspects in the elution behaviour of various elements are discussed.

F. W. E. Strelow, C. R. van Zyl and C. J. C. Bothma,
Anal. Chim. Acta, 45 (1969) 81–92

SOURCES OF ERROR IN THE USE OF ARSONIUM REAGENTS

PART II. THE ULTRAVIOLET SPECTRA OF TETRAPHENYL- AND TRIPHENYLMETHYLARSONIUM SALTS AND TRIPHENYLARSINE OXIDE

Arsonium salts have characteristic ultraviolet absorbance spectra with several sharp absorbance peaks in the 2400–2800 Å region. When they are estimated or identified by their absorption spectra, care must be taken to measure the peak maximum positions to within ±1 Å in order to obtain reliable wavelength or absorbance values. The peak positions can be significantly shifted by change of solvent or the presence of coprecipitated impurities, especially triphenylarsine oxide.

K. W. Loach,
Anal. Chim. Acta, 45 (1969) 93–99

THE SEPARATION AND DETERMINATION OF COBALT(II) AND COBALT(III)

A method for the separation and determination of cobalt(II) and (III) has been developed. The acetylacetonate complexes of cobalt are utilized for the separation, and analytical measurements are made by atomic absorption or visible absorption spectrophotometry. The sample is reacted with hot acetylacetone and diluted with 20% acetic acid. The cobalt(III) complex is separated by extraction with benzene. The benzene layer is then diluted with *n*-pentanol and the cobalt(III) concentration is determined by atomic absorption spectrophotometry. The cobalt(II) concentration can be determined in the 20% acetic acid layer by atomic absorption. In the absence of other metals which form colored acetylacetonate complexes, the cobalt(III) concentration can be determined by visible absorption spectrophotometry directly on the 20% acetic acid solution. The total cobalt concentration can be determined by any acceptable method for cobalt and the cobalt(II) concentration then obtained by difference.

J. E. Hicks,
Anal. Chim. Acta, 45 (1969) 101–108

DETERMINATION OF STABILITY CONSTANTS OF POLYNUCLEAR TTHA COMPLEXES BY MEANS OF A DIGITAL COMPUTER

The complex formation between triethylenetetraminehexaacetic acid (TTHA) and lead(II), zinc(II) and cadmium(II) has been studied by means of potentiometric pH titrations. The stability constants of $PbHA^{3-}$, PbA^{4-}, Pb_2A^{2-}, $ZnHA^{3-}$, ZnA^{4-}, Zn_2A^{2-}, $CdHA^{3-}$, CdA^{4-} and Cd_2A^{2-} complexes have been calculated by means of a high-speed digital computer. The numerical procedure used is applicable to all problems of this type. A program for the calculations, written in FORTRAN, is given.

W. Lund,
Anal. Chim. Acta, 45 (1969) 109–119

POTENTIOMETRIC TITRATIONS WITH ION-EXCHANGE MEMBRANE ELECTRODES

PART IV. A FURTHER STUDY OF EXPERIMENTAL VARIABLES

The effects of various experimental parameters on the shapes of potentiometric titration curves obtained with ion-exchange membrane electrodes are described. Particular attention is given to the nature of the reference solution, the pretreatment and capacity of the membrane, the effect of counter ions, and the effects of varying concentrations of titrant and titrand, as well as of inert electrolytes. The analytical aspects of the methods are discussed.

F. P. IJsseling and E. van Dalen,
Anal. Chim. Acta, 45 (1969) 121–132

SEPARATION OF URANIUM FROM PHOSPHORIC ACID BY REVERSED-PHASE COLUMN CHROMATOGRAPHY

Uranium and phosphate can be quantitatively separated on a column containing tri-*n*-butyl phosphate on silica gel. Phosphate can be eluted with saturated aluminum nitrate solution before the elution of uranium with water. The procedure is simple, rapid and versatile.

G. W. Heunisch,
Anal. Chim. Acta, 45 (1969) 133–136

DETERMINATION OF TRACES OF HYDROGEN, NITROGEN AND OXYGEN IN AQUEOUS SOLUTIONS BY GAS CHROMATOGRAPHY

Traces of hydrogen, nitrogen and oxygen in water can be determined by stripping the gases from water samples of up to 30 ml with a helium stream. The stripped gases are absorbed from the helium on molecular sieve 5A pellets at liquid nitrogen temperature; at room temperature, the gases are desorbed from the molecular sieve and determined by gas chromatography. Carbon monoxide, methane and argon can be determined simultaneously.

A. Tolk, W. A. Lingerak, A. Kout and D. Börger,
Anal. Chim. Acta, 45 (1969) 137–142

THE SPECTROPHOTOMETRIC DETERMINATION OF TWO OXIDATION STATES OF MULTIVALENT ELEMENTS

(in French)

Chloroplatinate can be determined in very dilute solution ($\sim 10^{-5}$ *M*) spectrophotometrically at 262 nm even in the presence of platinum(II). The latter can be determined at 216 nm only if the concentration of platinum(IV) in the solution is relatively small. Tellurium(IV) can be determined in 4 *N* hydrochloric acid solution at 250 nm in the presence of tellurium(VI), which can be also determined after extraction of tellurium(IV) by tributyl phosphate and reduction with concentrated hydrochloric acid.

M. Haïssinsky and A. Raitz,
Anal. Chim. Acta, 45 (1969) 143–147

SPECTROPHOTOMETRIC DETERMINATION OF OZONE IN THE PRESENCE OF CHLORINE COMPOUNDS

(in German)

Ozone reacts with the manganese(II) diphosphate complex in acidic media, to form a violet-coloured complex which can be used for the photometric determination of ozone in waters. Procedures for concentrations greater than 1 mg O_3/l in drinking and industrial waters are described; at the 4.30 mg O_3/l level, the standard deviation was 2.42%. Ozone can be determined in the presence of chlorine, chlorine dioxide, hypochlorite, chlorite, chlorate and perchlorate.

P. Hofmann and P. Stern,
Anal. Chim. Acta, 45 (1969) 149–155

THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE

PART VII. THE ANALYSIS OF IRON ORES AND SLAGS

A scheme is described for the analysis of iron ores and slags by atomic absorption spectrophotometry. Methods are given for the determination of silicon, aluminium, magnesium, calcium, titanium and manganese in both materials; methods for determining sodium and potassium in iron ores, and total iron, chromium and vanadium in slags are also given. The samples are decomposed by a mixture of hydrofluoric, hydrochloric and nitric acids. Analytical data for standard samples are given.

F. J. Langmyhr and P. E. Paus,
Anal. Chim. Acta, 45 (1969) 157–162

ELECTRONICALLY MODULATED MICROWAVE-EXCITED ELECTRODELESS DISCHARGE TUBES AS SOURCES IN ATOMIC ABSORPTION SPECTROSCOPY

Electronic modulation of a selected range of electrodeless discharge tubes is achieved by superimposing a 50 Hz component on the d.c. potential of the anode of the magnetron valve. The effect of modulation is favourable and the usual methods of tube preparation are satisfactory. The source spectra for lead, mercury, silver, thallium and tin are compared with those for the corresponding hollow-cathode lamps and the analytical atomic absorption working curves obtained with the various sources are compared. The sources for lead and tin give considerably higher sensitivity and a wider working range than the hollow-cathode lamps because of the absence of continuous background or non-absorbing lines near the resonance line. The mercury source behaves similarly, probably because of less self-reversal.

R. F. BROWNER, R. M. DAGNALL AND T. S. WEST,
Anal. Chim. Acta, 45 (1969) 163–170

AN INVESTIGATION OF THE SOLUBILITY OF SOME FLUORIDES IN 38.5% HYDROFLUORIC ACID

(Short Communication)

F. J. LANGMYHR AND R. WENDELBORG,
Anal. Chim. Acta, 45 (1969) 171–172

THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE

PART V. THE ANALYSIS OF FERROSILICON

(Short Communication)

F. J. LANGMYHR AND P. E. PAUS,
Anal. Chim. Acta, 45 (1969) 173–176

THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE

PART VI. THE ANALYSIS OF FELSPARS

(Short Communication

F. J. LANGMYHR AND P. E. PAUS,
Anal. Chim. Acta, 45 (1969) 176–179

PRECISION DETERMINATION OF GADOLINIUM IN CADMIUM FLUORIDE BY NEUTRON ACTIVATION ANALYSIS

(Short Communication)

R. H. MARSH AND W. ALLIE,
Anal. Chim. Acta, 45 (1969) 179–182

A STUDY OF THE MECHANISM OF THE ADSORPTION ON COLUMNS OF SALTS

THE SORPTION OF EUROPIUM ON CADMIUM OXALATE

(Short Communication)

D. L. Massart,
Anal. Chim. Acta, 45 (1969) 183–186

ON ANALYTICAL CURVES AND LIMITS OF DETECTION IN PHOSPHORIMETRY

(Short Communication)

J. D. Winefordner and L. V. S. Hood,
Anal. Chim. Acta, 45 (1969) 186–187

SELECTIVE ESTIMATION OF BERYLLIUM WITH MORIN CRAYON ON THE RING OVEN

(Short Communication)

P. W. West and E. Jungreis,
Anal. Chim. Acta, 45 (1969) 188–190

DETERMINATION OF SULPHITE ION (OR SULPHUR DIOXIDE) BY ATOMIC ABSORPTION SPECTROSCOPY

(Short Communication)

E. Jungreis and Z. Anavi,
Anal. Chim. Acta, 45 (1969) 190–192

SOLVENT EXTRACTION OF THALLIUM(I) WITH HEXANOIC ACID

(Short Communication)

G. K. Schweitzer and R. H. Stevens,
Anal. Chim. Acta, 45 (1969) 192–195

SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH BITHIONOL

(Short Communication)

A. G. Fogg, A. Gray and D. Thorburn Burns,
Anal. Chim. Acta, 45 (1969) 196–198

COLORIMETRIC DETERMINATION OF PERIODATE WITH BENZHYDRAZIDE

(Short Communication)

A. M. Escarrilla, P. F. Maloney and P. M. Maloney,
Anal. Chim. Acta, 45 (1969) 199–201

THE MASS SPECTRA OF ORGANIC MOLECULES

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

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

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

MASS SPECTROMETRIC ANALYSIS OF SOLIDS

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

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

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Still available:

MASS SPECTROMETRY AND ITS APPLICATIONS TO ORGANIC CHEMISTRY

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

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Photoluminescence of Solutions

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Volume Two, Part B is devoted to physical separation methods. After an account of the theory and practise of liquid chromatography in columns, the volume continues with a lengthy treatment of gas chromatography.
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.

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**Elsevier
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Company** Amsterdam London New York

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ANALYTICA CHIMICA ACTA

Vol. 45 (1969)

ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 45 (1969)

PRINTED IN THE NETHERLANDS

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A FLUORIMETRIC ENZYMIC METHOD FOR THE ASSAY OF MIXTURES OF ORGANIC ACIDS

G. G. GUILBAULT, S. H. SADAR AND R. McQUEEN
Department of Chemistry, Louisiana State University in New Orleans, New Orleans, La. 70122 (U.S.A.)

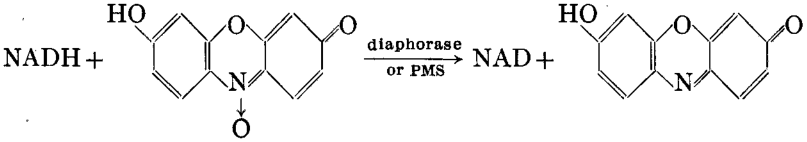
(Received October 31st, 1968)

Most analytical methods for the determination of macro quantities (> 10 mg) of organic acids depend on the acidic properties of the carboxy group. Simple mixtures of organic acids that differ in acidity can be titrated potentiometrically in aqueous or nonaqueous solution. Many proposals have been made for the separation of acids by physical methods, *i.e.*, partition between immiscible solvents, azeotropic distillation and gas chromatography[1–4]. The latter does not yield satisfactory separations unless the acids are first esterified. There are no good analytical methods available for the direct analysis of several organic acids present in microconcentrations (0.1–100 μg) in a mixture.

Enzymic methods have been proposed for the determination of various single component organic acids, such as lactic, malic and glutamic. Surveys of these methods can be found in reviews by Guilbault[5,6], and a book by Bergmeyer[7].

Recently Guilbault and Kramer[8] described a simple, rapid fluorimetric method for measuring the activity of dehydrogenases. The method was based on the conversion of the non-fluorescent material, resazurin, to the highly fluorescent compound resorufin, in conjunction with the nicotinamide adenine dinucleotide-reduced nicotinamide adenine dinucleotide (NAD–NADH) system. An increase in sensitivity of 1–2 orders over conventional fluorimetric or colorimetric procedures involving NADPH or NADH formation was demonstrated.

$$\text{acid} + \text{NAD} \xrightarrow{\text{dehydrogenase}} \text{ketoacid} + \text{NADH}$$



(non-fluorescent) (fluorescent)

In this study six dehydrogenase systems were used for the detection and determination of 21 organic acids. With malate, glutamate, β-hydroxybutyrate, isocitrate and lactate (types II and IV) dehydrogenases, coupled with NAD, phenazine methosulfate (PMS) and resazurin, procedures were developed for 0.1–500 μg of acetic, adipic, benzilic, butyric, D-α- and D-β-hydroxybutyric, chloroacetic, DL-citric, formic, L-glutamic, glutaric, glycolic, threo-D-isocitric, L-lactic, L-malic, malonic, oxalic, phthalic, DL-succinic and L-tartaric acids, and mixtures thereof. The rate of production of the highly fluorescent compound, resorufin, is equated to the concentration of the acid. An increase in sensitivity of at least one order of magnitude over fluorimetric methods based on NADH or NADPH formation was obtained in the assay of all acids[5-7,9].

EXPERIMENTAL

Reagents

Substrates. Resazurin (Eastman Organics Co., Rochester, N.Y.). A stock $2 \cdot 10^{-4}$ *M* solution was prepared in methyl cellosolve. This solution should be nonfluorescent, with a bluish-red hue. It is stable indefinitely.

Nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP), obtained from Calbiochem Co., were 86.3% and 70.1% pure, respectively. Stock $2 \cdot 10^{-4}$ *M* solutions were prepared in triply distilled water. If refrigerated these solutions are stable for one week.

Phenazine methyl sulfate. An aqueous stock 10^{-3} *M* solution of the purified substance (Sigma Chemical, St. Louis) is stable for 4 days if kept refrigerated in a dark bottle.

Solutions of all acids were prepared by dissolving the C.P. acid in triply distilled water to a concentration of 0.1 *M*. The solutions were adjusted to pH 7 with sodium hydroxide before use. All optically active acids were obtained from Sigma (St. Louis) and were the natural isomers in most cases: threo-D(+)-isocitric, L(+)lactic, L(+)malic, L(−)tartaric, L(+)glutamic, D-α- and D-β-hydroxybutyric. Citric acid (Sigma) was a DL-mixture. Other non-optically active acids (acetic, formic, butyric, etc.) were obtained in the highest available purity from Eastman (Rochester) or Sigma.

Enzymes

All enzymes were assayed by standard conventional spectrophotometric methods, and the activities found are reported below.

β-Hydroxybutyrate dehydrogenase, β-OH-BuDH (Boehringer Mannheim Corp., Rhodopseudomonas spheroides). A 1 mg/ml solution was prepared in 33% ammonium sulfate. Activity = 3 units/mg (one unit is that amount which catalyzes the oxidation of 1 μmole of D-β-hydroxybutyrate per min at pH 7.3 and 37°).

Glutamate dehydrogenase, GDH (Sigma Chemical, bovine liver, Type II). A 1 mg/ml solution was prepared in triply distilled water. Activity = 2.7 units/mg (one unit catalyzes the oxidation of 1 μmole of L-glutamate at pH 7.6 and 25°).

Lactate dehydrogenase, LDH (Sigma Chemical, Type II from rabbit muscle, activity 400 units/mg, and Type IV from Baker's yeast, 10 units/mg). A 1 mg/ml solution of Type II was prepared in 33% ammonium sulfate; a 1 mg/ml solution of Type IV was prepared in water. Definition of units: one unit of Type II converts 1 μmole of pyruvate to lactate per minute at pH 7.5 and 37°; one unit of Type IV oxidizes 1.0 μmole of L-lactate to pyruvate at pH 8.4 and 37°.

Malic dehydrogenase, MDH (Sigma, pig heart, Type I). A 1 mg/ml solution was prepared in 33% ammonium sulfate, activity 56 units/mg. One unit converts 1 μmole of oxalacetate and β-NADH to malate and β-NAD at pH 7.5 and 25°.

Isocitrate dehydrogenase, ICDH (Sigma, pig heart, Type IV). A 1 mg/ml solution was prepared in water, activity 3 units/mg. One unit converts 1 μmole of threo-D-isocitrate to α-ketoglutarate at pH 7.4 and 37°.

Diaphorase (Type III, Sigma). A solution was prepared by diluting 1 ml of diaphorase to 10 ml with 33% ammonium sulfate, pH 7.7.

All enzyme solutions were stable for 2 days if refrigerated when not in use.

Buffers

Tris buffer. Tris(hydroxymethyl)aminomethane (Sigma). A 0.5 *M* solution, pH 9.5 and a 0.1 *M* solution, pH 7.0, were prepared. These solutions are stable indefinitely.

Phosphate buffer, 0.1 M, pH 6.5. This solution is stable indefinitely.

Hydrazine–glycine buffer. 1 *M* glycine–0.4 *M* hydrazine, pH 9.5. This solution is stable for 2 weeks.

Apparatus

All fluorescence measurements were made with an Aminco Bowman spectrophotofluorimeter (SPF), equipped with a thermoelectric cooler to maintain a constant temperature. The resorufin produced was measured at excitation and emission wavelengths of 560 and 580 nm. Although the excitation and emission wavelengths are close together, scattered radiation was not found to be a problem as was pointed out in a previous paper[8].

Procedures

Determination of acids with GDH, LDH-II, MDH and β-OH-BuDH. Place 1 ml of the acid to be determined (neutralized to pH 7) in a clean dry cuvette, then add 1 ml of glycine–hydrazine buffer (tris buffer for analysis of L-lactic acid with LDH and L-glutamic acid with GDH), pH 9.5, 0.1 ml of $2 \cdot 10^{-4}$ *M* NAD, 0.1 ml of $2 \cdot 10^{-4}$ *M* resazurin and 1 ml of 10^{-3} *M* phenazine methyl sulfate. (Diaphorase for benzilic acid.) Place the cuvette in the instrument, adjust the temperature to 30° and zero the instrument. Withdraw the cuvette, add 0.1 ml of the appropriate dehydrogenase (Table I), invert to mix, place the cuvette back in position, and record the change in fluorescence with time, ΔF/min. Determine the concentration of acid present from a calibration plot of ΔF/min *vs.* acid concentration.

Determination of D-isocitric acid. To 1 ml of a neutral solution of the threo-D-isocitric acid to be determined, add 1 ml of phosphate buffer, pH 6.5, 0.5 ml of magnesium chloride ($1 \cdot 10^{-2}$ *M*), 0.1 ml of NADP (10^{-3} *M*), 0.1 ml of resazurin ($2 \cdot 10^{-4}$ *M*) and 1 ml of phenazine methyl sulfate (PMS) (10^{-3} *M*). Adjust the temperature of the fluorimeter to 35° and zero the instrument. At time zero add 0.2 ml of a 0.3 mg/ml solution of isocitric dehydrogenase and record the change in fluorescence with time, ΔF/min. The concentration of isocitric acid is calculated from a calibration plot as described above.

Determination of L-lactic acid with LDH-IV. To 1 ml of a solution of unknown L-lactic acid concentration (neutralized to pH 7) add 1.0 ml of tris buffer, pH 7.0, and 0.3 ml of resazurin ($2 \cdot 10^{-4}$ *M*). Adjust the fluorescence to read zero and adjust the temperature to 37°. Add 0.1 ml of a 22 mg/ml solution of LDH-IV and record the rate of change in fluorescence, ΔF/min. The concentration of L-lactic acid present is calculated as described above.

Determination of isocitric dehydrogenase. The activity of isocitric dehydrogenase

TABLE I

LIST OF ACIDS DETERMINABLE

Acid	*Enzyme (buffer)*[a]	*Range (μg/ml)*	*Interferences*
Acetic	MDH	10–200	Adipic (> 100 μg), benzilic, butyric, D-α-OH and β-OH-butyric (> 100 μg), chloroacetic (> 100 μg), DL-citric (> 150 μg), formic, glutaric (> 100 μg), glycolic, D-isocitric, L-malic, oxalic, phthalic, DL-succinic, D-tartaric (> 200 μg)
Adipic	MDH	110–2500	Same as acetic
Benzilic[b]	MDH	5–500	Same as acetic
Butyric	MDH	10–250	Same as acetic
D-α-Hydroxybutyric	MDH	100–1500	Same as acetic
	LDH-IV* (T,7)	2–50	L-Lactic acid
D-β-Hydroxybutyric	β-OH-BDH	1–75	DL-Citric (> 10 μg)
Chloroacetic	MDH	100–2500	Same as acetic
DL-Citric	MDH	150–600	Same as acetic
	LDH-II	50–500	L-Glutamic, glycolic, D-isocitric, L-lactic, L-malic (> 300 μg), oxalic
	GDH	25–300	L-Glutamic, glycolic, D-isocitric, L-lactic (> 100 μg), L-malic, oxalic (> 100 μg)
	β-OH-BDH*	10–110	D-β-OH-Butyric
Formic	MDH	10–500	Same as acetic
L-Glutamic	GDH (T, 9.5)	1–100	None[c]
Glutaric	MDH	100–2500	Same as acetic
Glycolic	GDH	20–300	Same as citric
	LDH-II*	2–75	Same as citric
	MDH	20–400	Same as acetic
D-Isocitric	ICDH* (P)	0.02–1.0	None
	GDH, LDH-II	10–250	Same as citric
	MDH	20–400	Same as acetic
L-Lactic	LDH-II (T, 9.5)	4–175	None[c]
	LDH-IV* (T,7)	0.2–10	D-α-OH-Butyric
L-Malic	GDH	10–200	Same as citric
	MDH*	0.1–2.0	Same as acetic
D-Malic	MDH	50–800	Same as acetic
Malonic	MDH	20–550	Same as acetic
Oxalic	MDH	30–600	Same as acetic
	LDH-II*	5–100	Same as citric
Phthalic	MDH	50–1000	Same as acetic
D-Tartaric	MDH	200–3000	Same as acetic

GDH = glutamate dehydrogenase; LDH = lactate dehydrogenase; II = type II; IV = type IV; MDH = malic dehydrogenase; ICDH = isocitric dehydrogenase; β-OH-BDH = β-hydroxybutyric dehydrogenase.

[a] All glycine–hydrazine buffer except as listed: T,7 = tris, pH 7; T, 9.5 = tris, pH 9.5; P = phosphate buffer, pH 6.5.

[b] Diaphorase used instead of phenazine methosulfate.

[c] Tris buffer, no hydrazine added.

* Best system for analysis.

can be determined under the conditions described above for the isocitric acid assay, except that a 10^{-3} M isocitric acid concentration is used. The activity of enzyme can be calculated from a plot of ΔF/min *vs.* enzyme concentration.

DISCUSSION AND RESULTS

Specificity of enzyme systems

Initial experiments were conducted to determine the specificity of various acid dehydrogenases. Some typical results obtained are indicated in Table II, which gives data on the relative rates of dehydrogenation (oxidation) of various acids using three different enzyme systems. The first two of these, lactic dehydrogenase, type II (rabbit muscle), and glutamate dehydrogenase (bovine liver) behave similarly with different acids, having no reaction with acetic, adipic, benzilic, butyric, D-α- and D-β-hydroxybutyric, chloroacetic, formic, glutaric, L-malic, malonic, phthalic, salicylic, DL-succinic, L-tartaric and amino acids (leucine, tryptophane, tyrosine, etc.). The order of decreasing reaction rate with LDH-II is glycolic acid > L-lactic

TABLE II

RELATIVE RATES[a] OF LACTIC, GLUTAMIC AND MALIC DEHYDROGENASE SYSTEMS

(Acid = 100 μg/ml; enzyme = 0.03 mg/ml)

Acid	*LDH-II system*[b]	*GDH system*[c]	*MDH system*[d]
Acetic	0	0	0.10
Adipic	0	0	0
Benzilic	0	0	0.12
Butyric	0	0	0.11
D-α-Hydroxybutyric	0	0	0.02
D-β-Hydroxybutyric	0	0	0.035
Chloroacetic	0	0	0.05
DL-Citric	0.03	0.04	0
Formic	0	0	0.15
L-Glutamic	0.16	0.35	0
Glutaric	0	0	0
Glycolic	0.53	0.12	0.18
D-Isocitric	0.16	0.18	0.23
L-Lactic	0.25	0.070	0
L-Leucine	0	0	0
L-Malic	0.01	0.13	0.25
D-Malic	0	0	0.052
Malonic	0	0	0.12
Oxalic	0.20	0.10	0.06
Phthalic	0	0	0.033
Salicylic	0	0	0
DL-Succinic	0	0	0.04
D-Tartaric	0	0	0
Tryptophan, tyrosine	0	0	0

[a] Expressed as ΔF/min.
[b] Glycine–hydrazine buffer; with tris buffer only L-lactic acid reacts.
[c] Glycine–hydrazine buffer; with tris buffer only L-glutamic acid reacts.
[d] Glycine–hydrazine buffer.

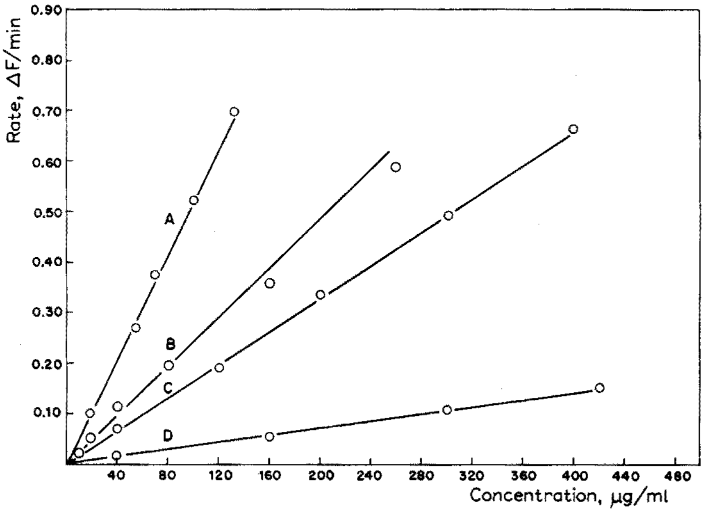


Fig. 1. Plot of ΔF/min *vs.* concentration of organic acid. Lactate (II) dehydrogenase system. All conditions optimum. (A) Glycolic acid; (B) L-lactic acid; (C) D-isocitric acid; (D) DL-citric acid.

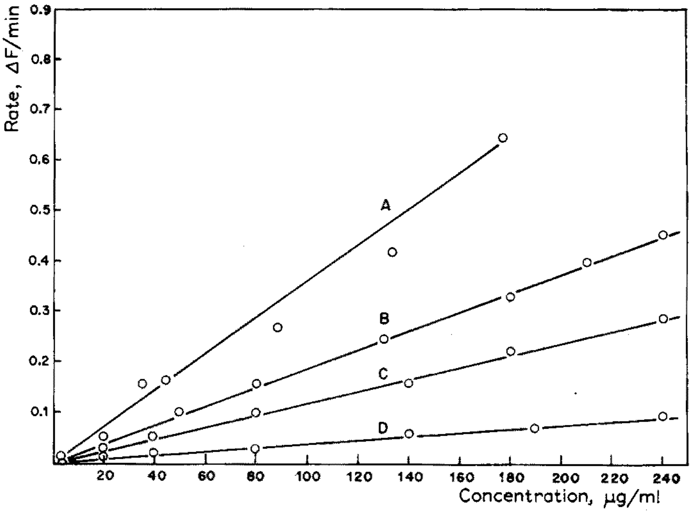
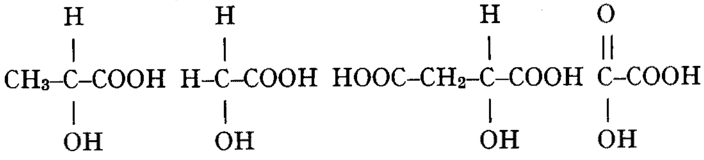


Fig. 2. Plot of ΔF/min *vs.* concentration of organic acid. Glutamate dehydrogenase system. All conditions optimum. (A) L-Glutamic acid; (B) D-isocitric acid; (C) glycolic acid; (D) DL-citric acid.

acid > oxalic acid > L-glutamic = D-isocitric acid > DL-citric acid > L-malic acid (Fig. 1 and Table II). Glycolic acid has a structure identical with lactic except for substitution of a hydrogen for a methyl group. The lack of specificity of lactate dehydrogenase is not surprising. MEISTER[10] has reported that a number of α-keto acids are reduced by rabbit muscle LDH: α-ketoglutamate, oxaloacetate, phenylpyruvate, α-ketobutyrate, α-ketocaproate, α-ketovalerate, etc.

Glutamate dehydrogenase catalyzes oxidations with



$$\mathrm{CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}{-}COOH}\qquad \mathrm{H{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}{-}COOH}\qquad \mathrm{HOOC{-}CH_2{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}{-}COOH}\qquad \mathrm{\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{C}}{-}COOH}$$

lactic glycolic malic oxalic

rates of the order L-glutamic > D-isocitric > L-malic > glycolic > oxalic > L-lactic > DL-citric acid (Fig. 2 and Table II). If phenylhydrazine is not added to react with the α-keto acid formed and thus ensure a more complete reaction from hydroxy- to keto-acid, then only L-lactic acid reacts in the LDH-II system and only L-glutamic acid in the GDH system. Thus, with tris buffer of pH 9.5, L-lactic and L-glutamic acids can be specifically determined with their respective dehydrogenases. Malic dehydrogenase (MDH) is a less specific enzyme, and many acids can be determined with this dehydrogenase. Good rates were obtained with all acids regardless of the buffer used: tris, glycine, or glycine with hydrazine added (Fig. 3 and Table II).

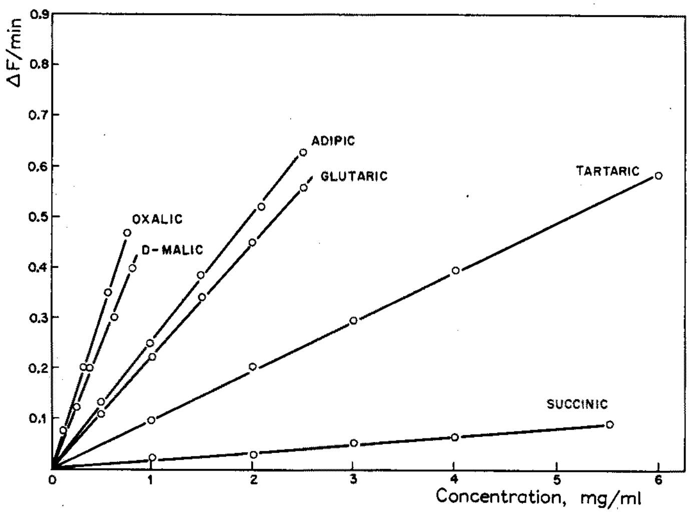


Fig. 3. Plot of ΔF/min *vs.* concentration of organic acid. Malate dehydrogenase system. All conditions optimum.

Lactate dehydrogenase Type IV from Baker's yeast is an enzyme which does not require the use of NAD or NADH. Electron acceptors such as hexacyanoferrate-(II) or methylene blue can be used, and are directly reduced. Initial experiments indicated that resazurin is a good electron acceptor and is reduced to the fluorescent resorufin:

$$\underset{\text{(non-fluorescent)}}{\text{L-lactate} + \text{resazurin}} \xrightarrow{\text{type IV LDH}} \underset{\text{(fluorescent)}}{\text{resorufin}} + \text{pyruvate}$$

This enzyme is more specific than the type II; only L-lactic acid and D-α-hydroxybutyric acids react, two acids which are not generally found together. Greater

TABLE III

TYPICAL DETERMINATIONS OF ACIDS

D-β-Hydroxybutyric acid[a]			L-Glutamic acid[b]			L-Lactic acid[c]		
Added (μg/ml)	*Found (μg/ml)*	*Rel. error (%)*	*Added (μg/ml)*	*Found (μg/ml)*	*Rel. error (%)*	*Added (μg/ml)*	*Found (μg/ml)*	*Rel. error (%)*
1.00	1.01	+ 1.0	5.00	4.95	− 1.0	0.500	0.510	+ 2.0
5.00	4.90	− 2.0	15.0	14.7	− 2.0	1.50	1.47	− 2.0
10.0	10.0	0.0	25.0	25.0	0.0	3.0	3.08	+ 2.7
50.0	51.0	+ 2.0	75.0	77.0	+ 2.2	5.00	4.85	− 3.0
75.0	74.0	− 1.5	100.0	102.0	+ 2.0	10.0	10.0	0.0
Av. rel. error		± 1.3			± 1.4			± 1.9

[a] Analysis with β-hydroxybutyric dehydrogenase in the presence of 1 mg/ml of L-glutamic, L-lactic, L-malic and D-α-hydroxybutyric acids.

[b] Analysis with glutamate dehydrogenase in the presence of 1 mg/ml of acetic, D-tartaric and D-β-hydroxybutyric acids.

[c] Analysis with lactate dehydrogenase Type IV in the presence of 1 mg/ml L-malic, L-glutamic and D-β-hydroxybutyric acids.

sensitivity was found with the type IV enzyme, also. As little as 0.2 μg/ml of L-lactic acid can be determined with LDH IV compared to 4 μg/ml with the type II enzyme.

Isocitric dehydrogenase, Type IV from pig heart, is a highly specific enzyme; of all the acids tried only threo-D-isocitric acid reacted with this enzyme. Thus a completely specific analysis of D-isocitric acid is possible.

β-Hydroxybutyrate dehydrogenase from Rhodopseudomonas spheroides is also a highly specific enzyme. Of all the acids tried (those listed in Table II) only D-β-hydroxybutyric and DL-citric acids reacted and were determinable. Even the D-α-hydroxy acid and butyric acid do not react. Since D-isocitric acid does not react, a specific method for DL-citric acid in the presence of D-isocitrate is possible.

Table I lists all the acids that can be determined by means of these 6 enzyme systems, together with the range of concentrations determinable, and the interferences. An asterisk indicates the best enzyme system for analysis. Some typical results for the analysis of acids are shown in Table III. With β-hydroxybutyrate dehydrogenase, 1–75 μg/ml of D-β-hydroxybutyrate were analyzed in the presence of 1 mg/ml concentrations of L-glutamic, L-lactic, L-malic and D-α-hydroxybutyric acids with an accuracy of ±1.3% and a precision of 2%. DL-Citric acid is the only interference (Table I), being determinable in the range 10–110 μg/ml with a precision and accuracy of about 2%.

L-Glutamic acid, in concentrations of 5–100 μg/ml, was determined with a precision and accuracy of about 1.5% in the presence of acetic, D-tartaric and D-β-hydroxybutyric acids. No interferences can be anticipated if tris buffer, pH 9.5, is used. Higher rates are observed with glycine–hydrazine buffer, however, and if the interfering acids (Table I) are known to be absent, analysis should be performed with this buffer system.

With lactate dehydrogenase, type IV, 0.4–10 μg/ml of L-lactic acid were determined in the presence of 1 mg/ml of L-malic, L-glutamic and D-β-hydroxybutyric acids with a precision and accuracy of 1.9%. Only D-α-hydroxybutyric acid interferes. With type II LDH, 4–175 μg/ml of L-lactic acid can be specifically determined in the presence of all acids including D-α-hydroxybutyric.

BLE IV

LYSIS OF A MIXTURE OF CITRIC, ISOCITRIC, LACTIC AND GLUTAMIC ACIDS

ed (μg/ml)				*Found (μg/ml)*			
Citric	D-*Isocitric*	L-*Lactic*	L-*Glutamic*	DL-*Citric*	D-*Isocitric*	L-*Lactic*	L-*Glutamic*
	1.00	10.0	10.0	10.1	1.00	9.90	10.2
	1.00	5.00	50.0	10.0	1.01	5.10	49.2
	1.00	10.0	50.0	9.9	0.980	10.1	51.0
	0.500	10.0	50.0	49.2	0.495	10.0	51.0

error (%)			
Citric	D-*Isocitric*	L-*Lactic*	L-*Glutamic*
.0	0.0	− 1.0	+ 2.0
.0	+ 1.0	+ 2.0	− 1.6
.0	− 2.0	+ 1.0	+ 2.0
.6	− 1.0	0.0	+ 2.0

TABLE V

ANALYSIS OF ISOCITRIC DEHYDROGENASE

Enzyme (units/ml)		*Rel. error (%)*
Added	*Found*	
0.000100	0.000103	+ 3.0
0.000789	0.000781	− 1.0
0.00789	0.00799	+ 1.2
0.0158	0.0162	+ 2.7
0.0307	0.0300	− 2.3
0.0675	0.0660	− 2.2
	Av. rel. error	± 2.1

A four-component acid mixture of DL-citric acid, D-isocitric acid, L-lactic acid and L-glutamic acid was analyzed, and the results are given in Table IV. The sample was divided into 4 equal parts, and analysis of each acid performed with a different dehydrogenase: β-hydroxybutyrate dehydrogenase for DL-citric acid, isocitric dehydrogenase for D-isocitric acid, lactate dehydrogenase Type II for L-lactic acid and glutamate dehydrogenase for L-glutamic acid. A phosphate buffer, pH 6.5, was used for ICDH, a glycine–hydrazine buffer (pH 9.5) for β-OH-BuDH and tris buffer (pH 9.5) for LDH and GDH. Essentially the same precisions and accuracies were obtained for the analysis of the mixture (Table IV) as were obtained in the analysis of the acid alone (Table III).

Finally a fluorimetric method was developed for the sensitive analysis of isocitrate dehydrogenase (Table V). As little as 10^{-4} units to 0.0675 unit of enzyme can be assayed by an initial reaction-rate method with a precision and accuracy of about 2%.

Effect of pH, buffer and other reagents

The lactate II, malate, glutamate and β-hydroxybutyrate dehydrogenase systems all work in the pH range 6–10. At low pH the α-keto acid is reduced to the hydroxy acid; at high pH the equilibrium is shifted in favor of formation of the keto acid.

$$\text{hydroxy acid} \underset{}{\overset{\text{dehydrogenase}}{\rightleftarrows}} \alpha\text{-keto acid} \xrightarrow{\text{hydrazine}} \text{hydrazone}$$

In order to use these dehydrogenase systems for the determination of the various hydroxy acids a pH of 9.5 was used in all determinations with either tris or glycine–hydrazine buffer. In general, higher rates were obtained with glycine–hydrazine, due to reaction of the α-keto acid with hydrazine to form a hydrazone. Some typical results obtained in the malate dehydrogenase system with various acids are given in

TABLE VI

EFFECT OF BUFFER ON DETERMINATION OF VARIOUS ACIDS WITH MALIC DEHYDROGENASE

(Acid = 0.35 mg/ml; enzyme = 0.03 mg/ml, pH = 9.5)

Acid	*Rate (ΔF/min)*		
	Tris	*Glycine*	*Glycine–hydrazine*
L-Malic	0.68	0.75	0.86
L-Tartaric	0.12	0.10	0.15
Acetic	0.12	0.14	0.16
Oxalic	0.20	0.22	0.26
Adipic	0.23	0.25	0.30

TABLE VII

VALUES OF THE MICHAELIS CONSTANTS FOR ENZYME–SUBSTRATE SYSTEMS

Substrate	*Enzyme*[a]	*K_m (mM)*[b]
D-Isocitric	ICDH	$5 \cdot 10^{-3}$
L-Lactic	LDH-II	2.1
	LDH-IV	0.30
D-α-Hydroxybutyric	LDH-IV	1.0
Glycolic	LDH-II	1.5
D-Isocitric	LDH-II	3.0
L-Glutamic	GDH	1.7
D-Isocitric	GDH	15.0
Glycolic	GDH	52.0
D-β-Hydroxybutyric	β-OH-BDH	1.5
DL-Citric	β-OH-BDH	3.0
L-Malic	MDH	0.030
Formic	MDH	25.0
Chloroacetic	MDH	50.0
Butyric	MDH	10.1
Oxalic	MDH	10.0
Acetic	MDH	6.6
L-Tartaric	MDH	20.0
D-Isocitric	MDH	7.5
Glycolic	MDH	9.0

[a] GDH = glutamate dehydrogenase; LDH = lactate dehydrogenase; II = type II; IV = type IV; MDH = malic dehydrogenase; ICDH = isocitrate dehydrogenase; β-OH-BDH = β-hydroxybutyrate dehydrogenase.

[b] Determined under optimum conditions as described in the text.

Table VI. With this enzyme system all acids reacted in either tris, glycine or glycine–hydrazine buffers, the rates being higher in the latter. With lactate and glutamate dehydrogenase only L-lactate and L-glutamate reacted in tris buffer. The rates of oxidation of these acids were higher in glycine–hydrazine, but several other acids were also oxidized in this buffer system, thus reducing the specificity.

The optimum pH values and buffer systems for the isocitrate and lactate IV dehydrogenase systems were pH 6.5 phosphate and pH 7.0 tris, respectively. Hydrazine was not needed in these two enzyme systems.

Phenazine methyl sulfate (PMS) and diaphorase are both good "coenzymes" that facilitate the transfer of a hydrogen atom in the fluorescence indicator reaction. PMS was used instead of diaphorase in all the dehydrogenase systems for the determination of all acids except benzilic which worked only with diaphorase. Comparable rates were obtained with PMS and diaphorase with all the other acids determined. PMS has two advantages over diaphorase, stability and cost. Solutions of PMS can be used for up to two weeks; diaphorase solutions must be prepared daily. Costwise, PMS is about 1/100 as expensive as diaphorase.

Michaelis constants and reaction products

The Michaelis constants for all the organic acids for each dehydrogenase system used were determined from standard Lineweaver–Burk plots of $1/V_0$ *vs.* $1/[S]$. Some of these constants are reported in Table VII. In all cases lower K_m values were found than have been previously reported in the literature because of the greater sensitivity achieved in the fluorimetric resorufin procedure. This is undoubtedly due, in part, to the shift in the equilibrium of the primary enzyme–substrate reaction by the hydrazone formation and by the resazurin–resorufin indicator reaction. Thus a K_m value of $5 \cdot 10^{-6}$ M for the D-isocitrate–isocitrate dehydrogenase system compares with a value of $2.5 \cdot 10^{-5}$ M obtained by the NADPH fluorimetric assay method. A K_m value of $3.0 \cdot 10^{-5}$ M was obtained for L-malic with malic dehydrogenase compared with a value of $5.5 \cdot 10^{-5}$ M obtained in previous studies[9].

Finally, attempts were made to identify the products of the oxidation of the organic acids. Gas chromatography, gas adsorption, thin-layer chromatography and other techniques were used. In the case of the α-hydroxy acids, the α-keto acid was the main product. In the case of citric, isocitric and glycolic acids, carbon dioxide was identified as an additional product. The main oxidation product from the non-hydroxy acids, formic, acetic, butyric, oxalic, etc., was carbon dioxide.

Although some of the results described on the "non-specificity" of some enzyme systems, *i.e.* malic and glutamic, are in disagreement with other biochemical studies[9], we believe that definite evidence has been given in proof that many other organic acids are catalytically oxidized by enzymes that are believed to be highly specific. Reproducible calibration plots of rate *vs.* concentration of these acids are presented (Figs. 1–3), Michaelis constants are calculated and the reaction products were identified. It can probably be concluded that, as other extremely sensitive assay procedures, such as the fluorescence method developed in this paper, become available, more detailed and meaningful information on enzyme specificity will result.

This work was presented at the 155th National Meeting of the ACS, San Francisco, 1968. The financial assistance of the National Science Foundation (Grant

No. GB 6325) and the Office of Saline Water, U.S. Department of the Interior (Grant No. 14-01-0001-1337) is gratefully acknowledged.

SUMMARY

Rapid fluorimetric methods are described which involve six enzyme systems for the determination of mixtures of 21 organic acids. Lactate (Types II and IV), malate, glutamate, isocitrate, and β-hydroxybutyrate dehydrogenases are used, coupled with NAD, phenazine methosulfate and resazurin, in a fluorimetric procedure for the determination of acetic, adipic, benzilic, butyric, D-α- and D-β-hydroxybutyric, chloroacetic, DL-citric, formic, L-glutamic, glutaric, glycolic, threo-D-isocitric, L-lactic, L-malic, malonic, oxalic, phthalic, DL-succinic and L-tartaric acids in the approximate concentration range of 0.1–500 μg with an accuracy and precision of about 2%. The rate of production of the highly fluorescent resorufin is equated to the concentration of the acid.

RÉSUMÉ

On décrit des méthodes fluorimétriques avec enzymes pour le dosage de mélanges d'acides organiques. On utilise des déhydrogénases de lactate (types II et IV), malate, glutamate, isocitrate et β-hydroxybutyrate, avec NAD, phénazine métosulfate et résazurine, pour le dosage des acides acétique, adipique, benzylique, butyrique, D-α- et D-β-hydroxybutyrique, chloroacétique, DL-citrique, formique, L-glutamique, glutarique, glycolique, threo-D-isocitrique, L-lactique, L-malique, malonique, oxalique, phtalique, DL-succinique et L-tartrique, à une concentration de 0.1 à 500 μg avec une exactitude et une précision d'environ 2%. La vitesse de production de la résorufine (fluorescence) est fonction de la concentration de l'acide.

ZUSAMMENFASSUNG

Es wird eine schnelle fluorimetrische Methode beschrieben, die enzymatische Systeme zur Bestimmung von Mischungen von 21 organischen Säuren verwendet. Lactat, Malat, Glutamat, Isocitrat und β-Hydroxybutyrat-Dehydrogenase werden verwendet zusammen mit NAD, Phenazinmethosulfat und Resazurin in einem fluorimetrischen Verfahren zur Bestimmung der verschiedensten Säuren. Im Konzentrationsbereich von etwa 0.1–500 μg betragen die Reproduzierbarkeit und Richtigkeit etwa 2%. Die Bildungsrate des sehr stark fluoreszierenden Resorufins ist etwa gleich der Konzentration der Säure.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

PHOSPHORESCENCE AND FLUORESCENCE SPECTROMETRY OF PHENYL-SUBSTITUTED SILANES

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(Received October 24th, 1968)

Fluorimetry and phosphorimetry have achieved broad analytical acceptance for trace analysis of wide varieties of organic compounds in a host of complex media[1]. Application of analytical luminescence techniques to inorganic compounds (excluding metal chelates and rare earth metals in solution) have been extremely limited. It is reasonable to expect high analytical sensitivities and selectivities for inorganic compounds. There are, however, many complicating features to consider when proposing luminescence analytical techniques for such compounds. Some of the more important spectroscopic problems which can be reasonably expected are mentioned below. If carbon skeletons are to be altered by insertion of heavy atoms such as silicon, then significantly shortened triplet lifetimes may be expected.

Furthermore, additional heavy atoms in the molecule, such as halogens, would further increase spin–orbit coupling and tend to shorten severely phosphorescence decay times. These drastic increases in the radiative triplet rate constant might result in increased quantum efficiencies for phosphorescence if intermolecular and intramolecular radiationless triplet deactivation rates remain approximately the same as in the non-heavy atom system[1].

Direct comparisons of fluorimetry and phosphorimetry by HOLLIFIELD AND WINEFORDNER[2] for anticoagulant analysis demonstrated that fluorescence and phosphorescence are complementary spectrometric techniques. Fluorimetry is inherently simpler than phosphorimetry; but phosphorimetry necessarily is the analytical method of choice when fluorescence is either insufficiently sensitive or selective.

It is therefore suggested that luminescence spectrometric techniques may be of considerable value in analytical studies of phenyl-substituted silanes. Further, it is probable that the additional spectroscopic information available through luminescence techniques may play an important role in structure elucidation and reaction kinetics studies of these general classes of phenyl-substituted silanes.

EXPERIMENTAL

Apparatus

An Aminco-Bowman Spectrophotofluorimeter (American Instrument Company, Silver Spring, Md.) equipped with an Aminco-Kiers rotating can phosphoroscope, an off-axis-ellipsoidal-mirror-source-condensing-system, and a 150-W xenon arc lamp were used for all fluorescence and phosphorescence measurements. A potted

TABLE I

LUMINESCENCE CHARACTERISTICS OF PHENYL-SUBSTITUTED SILANES

Front-surface illumination of neat liquid or solid[a]					*Fluorescence*[e]		*Phosphorescence*[h]		
Number	*Compound*	*Form*[b]	*Excitation*[c,d] *(nm)*	*Emission*[d] *(nm)*	*Excitation*[c] *(nm)*	*Emission*[c] *(nm)*	*Solvents*[i]	*Excitation*[c] *(nm)*	*Emission*[c] *(nm)*
1	Phenyltriethoxysilane	L	314 (I) 342 (II)	393	341	405	MEK	305	457 (I) 437 (II)
							P	308	434 (I) 462 (II) 488 (III)
2	Methylphenyldichlorosilane	L	296	337	336 (I) 361 (II)	411	MEK	306	456 (I) 434 (II) 486 (III) 407 (IV)
							P	286	465 (I) 441 (II) 490 (III)
3	Diphenyldiethoxysilane	L	329	359	334	357	MEK	305	462
							P	279	475
4	Dichlorophenyltrichlorosilane	L	344	402	397 (I) 410 (II)	465	MEK	[k]	[k]
							P	[k]	[k]
5	Diphenyldichlorosilane	L	348 (I) 291 (II)	376	350	372	MEK	302 (I) 283 (II)	458 (I) 480 (II)
							P	277	470
6	Diphenylmethylchlorosilane	L	345	358	343	363	MEK	298	453
							P	280	455
7	Phenyltrichlorosilane	L	317	400	345[f] 373[g]	422[f] 438[g]	P	280	436 (I) 408 (II) 463 (III)

8	Diphenyldi-methoxysilane	L	296 (I) 321 (II)	353	332[f] 333[g]	359[f] 375[g]	MEK P	308 278	457 471
9	Triphenyl-silane	S	306	352	337	394	MEK	300 (I) 270 (II) 235 (III)	435
							P	280	463
10	Diphenylsilane-diol	S	294 (I) 325 (II)	358	333	361	MEK	306 (I) 280 (II) 247 (III)	427
11	Triphenylchloro-silane	S	350	405	339	386	MEK	[l]	[l]
12	Tetraphenyl-silane	S	381 (I) 362 (II)	436	337	395	MEK	[l]	[l]

[a] All spectra were measured at room temperature with the solid sample accessory for the SPF.

[b] L, liquid; S, solid.

[c] Where resolvable fine structure is found, the order of decreasing relative intensity is indicated by numerals in parentheses.

[d] All spectra are uncorrected for instrument response.

[e] All spectra were measured at room temperature with the normal SPF fluorescence accessory. Methyl ethyl ketone was the solvent for all cases. Spectra are uncorrected for instrument response.

[f] High compound-to-solvent ratio: 3/7 (v/v).

[g] Dilute sample.

[h] All spectra were measured at 77°K with the normal phosphoroscope accessory. Spectra are uncorrected for instrument response.

[i] MEK = methyl ethyl ketone; P = pentane (technical).

[k] Very weak sample phosphorescence excitation is observed as a shoulder on the normal solvent phosphorescence excitation spectrum. Solvent emission completely obscured any weak sample phosphorescence.

[l] No observable phosphorescence.

RCA 1P28 multiplier phototube and a Houston Instrument HR-96 X-Y-T recorder were used for all determinations of luminescence excitation and emission spectra. Numerous slit arrangements in the SPF were employed for achieving either high analytical sensitivities (in which case very wide slits were used at the expense of resolution) or high spectrometric resolution (in which case very narrow excitation and/or emission slits were used at the expense of high analytical sensitivities).

Materials

All of the phenylsilane compounds were obtained from Alfa Inorganics, Inc. (Beverly, Mass.) in the highest purity available. Stock solutions of these compounds were prepared by dissolving the material in methyl ethyl ketone (MEK) for fluorescence studies and technical pentane or anhydrous ethyl ether for phosphorescence studies. All solvents were found to be satisfactory for luminescence use without further purification. Some evidence of background luminescence was observable at very high analytical sensitivities; however, this low background emission was found to be negligible under conditions of high spectral resolution and consequently has been neglected in the following discussion.

Procedure

Fluorescence, phosphorescence and front-surface excitation and emission spectra were recorded in the usual manner[1]. Limits of detection for each of the compounds were determined by preparing analytical curves through successive dilution of the stock solution. Many of the silanes undergo rapid photochemical decomposition when exposed for short periods of time to intense sunlight; therefore, precautions against exposure of the compounds to intense radiation are necessary. All neat liquids and solutions were stored in brown bottles in the dark.

RESULTS AND DISCUSSION

Luminescence characteristics of twelve phenyl-substituted silanes are presented in Table I. Several problems in sample preparation and handling were encountered during this study. All of the chlorine-containing silanes (with the exception of triphenylchlorosilane) undergo a color change upon exposure to intense sunlight; a yellow color is produced in both neat liquids and in MEK solutions. In the case of methyldichlorosilane there are significant alterations in the luminescence characteristics when the color change has taken place. In particular, the maximum for front-surface excitation shifts from 296 to 410 nm; the emission maximum changes from 337 to 462 nm. Fluorescence changes in MEK solution were also observed: excitation shifts from 336 to 397 nm, and emission shifts from 411 to 455 nm. It is suggested that slow photochemical decomposition may be the source of such significant shifts. Attempts to evaluate a rate for the reaction failed because of severe source instability problems; a fluorescence intensity *versus* time recording of the reaction progress showed slow but undeniable decay of luminescence at 411 nm. Simultaneously, the 397–455 nm excitation–emission pair slowly increased in fluorescence intensity. It should be noted that no emission was observed at 455 nm for fresh neat liquid or MEK solution; also no trace of 411-nm emission was detected after sufficient time for reaction had elapsed (about 2 h). With a more stable source of excitation the kinetics of these decompositions would be easily determined and rate constants and orders of reaction could be assigned; all of the kinetic studies could be accomplished with simple time *versus* fluorescence plots which are conveniently obtained from the instrument. None of the chlorine-free silanes displayed any apparent photochemical decomposition.

A severe shift in the fluorescence emission spectrum for diphenylmethylchlorosilane was observed for very concentrated MEK solutions. The shape of the fluorescence emission spectrum changed drastically as MEK solutions of this silane were diluted. Because the fluorescence excitation and emission spectra overlap considerably, reabsorption of emitted radiation appears to be the probable cause of the phenomenon.

Several large solvent shifts in fluorescence should be noted. Both phenyltrichlorosilane (PTCS) and diphenyldimethoxysilane (DPDXS) show large fluorescence excitation and emission wavelength changes as a function of concentration. At very high concentrations the maxima for PTCS fluorescence excitation and emission are 345 and 422 nm, respectively; while in dilute solution the values are 373 and 438 nm, respectively. For DPDXS the concentrated MEK solution has maxima for fluorescence excitation and emission at 332 and 359 nm; dilute solutions of DPDXS yield 333 and 375 nm, respectively. Such pronounced solvent shifts, especially for PTCS, are quite unusual and therefore lead to greatly enhanced selectivity for routine analytical procedures.

Phosphorescence decay plots were prepared for all compounds except those which did not phosphoresce to any appreciable extent (see Table I). In no case was strict first-order phosphorescence decay observed; inspection of the plot of log relative intensity *versus* time suggests at least some low intensity interference from solvent background phosphorescence. In all cases, solvent background phosphorescence decay times were less than 0.2 sec which was the shortest decay time observable with the time constant limitations of the electrometer–recorder readout used in this study. Consequently for those compounds with decay times greater than about 0.4 sec, a first order, *i.e.* linear, plot of log relative intensity *versus* time may be obtained by extrapolating the long time portion of the curve[1]. The first-order decay times obtained by eliminating this rapid, small contribution to the total decay time are given in Table II.

Analytical curves for the phenyl-substituted silanes by means of fluorescence and phosphorescence were prepared by successive dilution of stock solutions. Limits of detection and the concentration ranges of analytical utility for the silane analytical curves are given in Table III. It should be noted that in 8 of the 12 cases studied phosphorimetry is the analytical method of choice; for 3 cases fluorimetry is the preferred method of analysis. In only one case, tetraphenylsilane, was luminescence unable to provide a sensitive method for analysis. Several important observations regarding relative luminescence intensities and their relation to structure seem to be in order. Incorporation of the silicon atom into a largely carbon skeleton seems to reduce the absolute magnitudes of luminescence intensities; fluorescence seems to suffer a considerable decrease in intensity from what might be expected for the carbon analogs. Phosphorescence, on the other hand, benefits to a large extent through some increase in spin–orbit interaction, resulting in both larger intensities (with respect to fluorescence) and shorter triplet lifetimes. In particular, dichlorophenyltrichlorosilane has a triplet

TABLE II

PHOSPHORESCENCE DECAY TIMES OF PHENYL-SUBSTITUTED SILANES[a]

Number	*Compound*	*Decay time (sec)*[b]	
1	Phenyltriethoxysilane	2.7 (MEK)	2.8 (P)
2	Methylphenyldichlorosilane	3.2 (MEK)	2.4 (P)
3	Diphenyldiethoxysilane	1.9 (MEK)	1.7 (P)
4	Dichlorophenyltrichlorosilane	$<$ 0.2 (MEK)	$<$ 0.2 (P)
5	Diphenyldichlorosilane	2.4 (MEK)	1.85 (P)
6	Diphenylmethylchlorosilane	3.4 (MEK)	2.9 (P)
7	Phenyltrichlorosilane	$<$ 0.2 (MEK)	$<$ 0.2 (P)
8	Diphenyldimethoxysilane	2.4 (MEK)	2.5 (P)
9	Triphenylsilane	3.1 (P)	
10	Diphenylsilanediol	0.4 (MEK)	1.4 (E)
11	Triphenylchlorosilane	[c]	
12	Tetraphenylsilane	[c]	

[a] All decay times were measured at the maxima for phosphorescence excitation and emission with the phosphoroscope accessory for the SPF. Samples were thermostatted at 77°K.

[b] Decay times are taken as the time for the phosphorescence intensity to drop to 1/e of its initial value after termination of excitation radiation. The short decay component for solvent background luminescence was graphically removed from the experimentally obtained decay curve. MEK = methyl ethyl ketone. P = pentane. E = diethyl ether.

[c] Very weak sample phosphorescence excitation is observed as a shoulder on the normal solvent phosphorescence excitation spectrum. Solvent emission completely obscured any weak sample phosphorescence.

TABLE III

LIMITS OF DETECTION AND RANGES OF ANALYTICAL UTILITY FOR PHENYL-SUBSTITUTED SILANES

No.	*Compound*	*Limit of detection*[a,b]		*Range of utility*[c]	
		F	*P*	*F (decades)*	*P (decades)*
1	Phenyltriethoxysilane	$2 \cdot 10^{-2}$	$2 \cdot 10^{-3}$	1	3
2	Methylphenyldichlorosilane	N.A.U.	$7 \cdot 10^{-5}$	N.A.U.	1
3	Diphenyldiethoxysilane	$4 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	3	2
4	Dichlorophenyltrichlorosilane	$1 \cdot 10^{-1}$	$3 \cdot 10^{-6}$	1	5
5	Diphenyldichlorosilane	$5 \cdot 10^{-4}$	$6 \cdot 10^{-6}$	3	3
6	Diphenylmethylchlorosilane	$1 \cdot 10^{-3}$	$7 \cdot 10^{-7}$	2	2
7	Phenyltrichlorosilane	$8 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	2	3
8	Diphenyldimethoxysilane	$3 \cdot 10^{-2}$	N.A.U.	1.5	N.A.U.
9	Triphenylsilane	N.A.U.	$2 \cdot 10^{-5}$	N.A.U.	2
10	Diphenylsilanediol	$7 \cdot 10^{-4}$	N.A.U.	2	N.A.U.
11	Triphenylchlorosilane	$2 \cdot 10^{-5}$	N.A.U.	4	N.A.U.
12	Tetraphenylsilane	N.A.U.	N.A.U.	N.A.U.	N.A.U.

[a] F and P represent fluorescence and phosphorescence, respectively. N.A.U. = not analytically useful. Concentrations are given as ml of compound per ml of solvent or in the case of solid pure compounds, g per ml. See Table I for form of pure compound.

[b] Limit of detection is taken as the concentration at the intersection of the linear portion of the analytical curve and the average value of the background intensity.

[c] The range of analytical utility is the number of concentration decades over which the analytical curve is linear.

lifetime less than 0.2 sec but is one of the most intensely phosphorescing compounds studied.

In general, this study extends and confirms the observations of HOLLIFIELD AND WINEFORDNER[2] that fluorimetry and phosphorimetry are in fact complementary analytical tools and should be used interchangably rather than exclusively in order to achieve the optimum analytical results.

SUMMARY

The fluorescence and phosphorescence spectral characteristics of twelve phenyl-substituted silanes have been determined; phosphorescence lifetimes are also presented. Limits of detection by fluorimetry and phosphorimetry are compared and the possibility of luminescence assay is discussed. Fluorimetry and phosphorimetry are shown to be complementary in achieving the highest analytical sensitivities.

RÉSUMÉ

On a déterminé les caractéristiques spectrales de fluorescence et de phosphorescence de 12 silanes phényl-substitués, les durées de vie de phosphorescence sont aussi présentées. Les limites de détection par fluorimétrie et par phosphorimétrie sont comparées; on discute la possibilité de dosage par luminescence. On montre que la fluorimétrie et la phosphorimétrie sont complémentaires en atteignant les plus grandes sensibilités analytiques.

ZUSAMMENFASSUNG

Die charakteristischen Fluoreszenz- und Phosphoreszenz-Spektren von 12 phenylsubstituierten Silanen wurden bestimmt, ebenso die Lebensdauer der Phosphoreszenz. Die Nachweisgrenzen bei der Fluorimetrie und Phosphorimetrie werden verglichen und die Möglichkeiten der Luminiszenz diskutiert. Es zeigt sich, dass die Fluorimetrie und Phosphorimetrie beim Erreichen höchster analytischer Empfindlichkeit einander komplementär sind.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

EFFET DE LA CONCENTRATION SUR LA HAUTEUR OPTIMALE DE MESURE EN ABSORPTION ATOMIQUE DANS LA FLAMME

EXPERIENCE SUR LE CUIVRE ET LE MANGANESE

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(Reçu le 21 octobre, 1968)

Lors d'une recherche de suppression des interférences chimiques de la détermination du calcium par absorption atomique dans la flamme, il est apparu que la linéarité des courbes de calibrage (Absorbance/Concentration) se modifie suivant la hauteur du flux lumineux cathodique par rapport au brûleur et suivant la richesse du mélange air/acétylène utilisé.

RANN ET HAMBLY[1] ont montré qu'il existe une distribution spatiale spécifique des atomes dans la flamme. Les observations de ces auteurs, faites avec un équipement approprié, indiquent que la hauteur et les dimensions de la zone à population atomique maximum (ZPAM) varient également suivant le rapport des débits gazeux. Les observations faites font penser que cette zone varie également avec la concentration de l'élément à analyser.

CONDITIONS EXPÉRIMENTALES

Le calcium présente certaines caractéristiques (ionisation, effet important du rapport gazeux, ...) telles que la concentration ne puisse être seule invoquée. L'expérience a donc été réalisée d'abord avec le cuivre. Cet élément réunit les qualités suivantes indispensables à la mise en évidence du seul effet de la concentration:

1. son degré d'atomisation est élevé: 0.98[2];
2. la relation A/C est linéaire au moins jusqu'à 0.5 unité d'absorbance;
3. la sensibilité en absorption atomique est peu influencée par le rapport des débits gazeux. A riche/A pauvre = 0.93[1];
4. ZPAM est de faible dimension[1];
5. cet élément n'est pas ionisé puisque son potentiel d'ionisation (7.72 eV) est supérieur à 6 eV considéré comme celui d'une flamme air–acétylène.

Elle a été effectuée également avec le manganèse. Cet élément présente par rapport aux caractéristiques du cuivre les différences suivantes:

1. degré d'atomisation: 0.47;
2. ZPAM n'est pas connue.

L'appareillage utilisé est un Perkin Elmer 290; les caractéristiques de fonctionnement sont reprises au Tableau I.

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TABLEAU I

Elément / *Conditions*	*Cu*	*Mn*
Raie (Å)	3247	2795
Cathode	Cu/Mn	Cu/Mn
Courant (mA)	4	4
Fente résolution (Å)	2	2
Amortissement	3	1
Longueur de la flamme (cm)	5.5	5.5
Nbre fente du brûleur	1	1
Débit aspiration (ml/min)	3	3
Acétylène		
Pression (kg/cm^2)	0.6	0.6
Débit (l/min)	2.2	2.2
Air comprimé		
Pression (kg/cm^2)	3	3
Débit (l/min)	11/15	11/15

L'expérience a consisté à mesurer l'absorption de solution à 2, 8, 15 et 20 p.p.m. pour le cuivre, et 1, 4, 8 et 12 p.p.m. pour le manganèse, à différentes hauteurs, (5, 10, 15 et 20 mm) du flux lumineux au dessus du brûleur, en flamme air/acétylène. Deux rapports de débits ont été testés: 5.0 correspondant à une flamme riche lumineuse et 6.8 à une flamme pauvre. Les solutions ont été préparées à partir de solutions standards à 1000 p.p.m. Harleco. La même préparation de chaque solution a servi aux différentes mesures.

RÉSULTATS

Les moyennes de trois mesures (C.V. inférieur à 1%) ont été reportées aux Fig. 1 pour le cuivre et Fig. 2 pour le manganèse. Sur ces figures les traits pleins indiquent la relation observée, les traits en tiret, la relation linéaire supposée. Pour plus de clarté, les résultats enregistrés pour la flamme riche ont été groupés dans un diagramme et ceux de la flamme pauvre dans un autre.

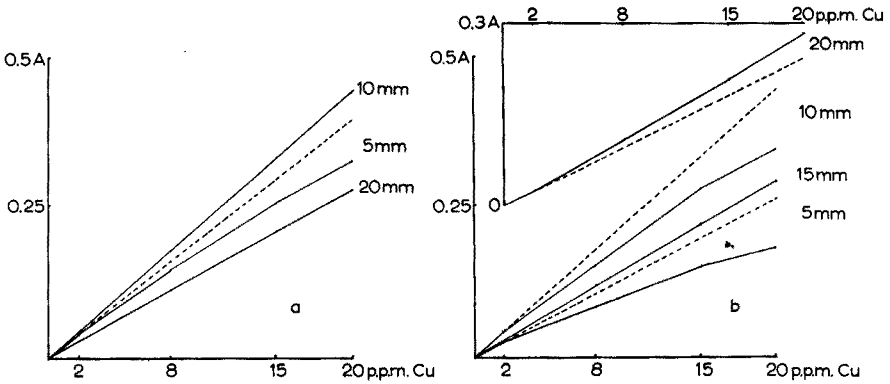

Fig. 1. Linéarité des courbes de calibrage (A/C) du cuivre en fonction de la hauteur du flux lumineux au dessus du brûleur. (a) Flamme pauvre (acétylène/air 0.15); (b) flamme riche (acétylène/air 0.2). En tiret: linéarité parfaite; en plein: courbe observée.

Plusieurs constatations peuvent être faites à partir de ces diagrammes. A une hauteur faible (5 mm), c'est à dire lorsque le flux lumineux traverse une partie du dard, aux extrémités de la fente du brûleur—ceci est du à la focalisation du flux au centre du brûleur—la relation A/C est logarithmique ou concave par rapport aux concentrations. A des hauteurs moyennes (10 ou 15 mm) la relation est arithmétique ou linéaire. A des hauteurs élevées (20 mm), en flamme riche, la relation a une allure géométrique ou convexe par rapport à la concentration. Le cuivre manifeste plus fortement cet effet que le manganèse. La flamme riche montre des écarts de linéarité plus importants.

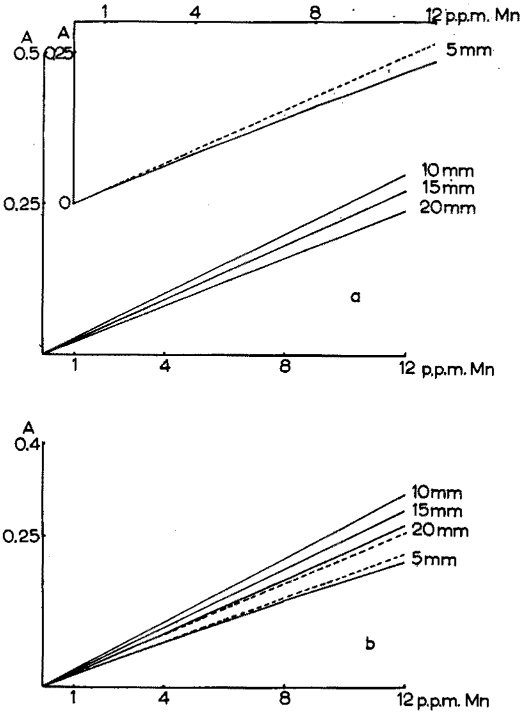

Fig. 2. Linéarité des courbes de calibrage (A/C) du manganèse en fonction de la hauteur du flux lumineux au dessus du brûleur. (a) Flamme pauvre; (b) flamme riche. En tiret: linéarité parfaite; en plein: courbe observée.

Ces constatations font penser que le flux lumineux, à hauteur faible, intercepte la totalité de la ZPAM dans le cas des faibles concentrations, mais seulement une partie des zones équivalentes aux plus fortes concentrations. A hauteur élevée, le flux cathodique intercepte la totalité de la ZPAM des fortes concentrations et une partie des zones équivalentes aux faibles concentrations. Autrement dit, la hauteur de la ZPAM varie proportionnellement avec la concentration.

DISCUSSION

On considère, en général, la dissociation en atome comme une fonction de la température du milieu. Cependant, on doit également considérer le temps pendant lequel un aérosol de l'échantillon est soumis à cette température. BAKER ET GARTON[3] estiment que le taux de vaporisation des résidus secs peut s'exprimer en temps de vaporisation ou temps de transit à travers la flamme. Ils estiment que la température atteinte par le résidu sec est un facteur important du taux de vaporisation.

Le temps de transit est étroitement lié à la vitesse d'écoulement des gaz conditionnée, elle, par la vitesse de propagation de la combustion[4].

Autrement dit, dans un mélange gazeux déterminé, on peut admettre que la distribution spatiale des atomes d'un élément donné est fonction de la vitesse de décomposition des résidus secs de l'aérosol, dont la hauteur de la ZPAM est un reflet.

Dans l'expérience réalisée pour chacun des éléments et chacun des types de flamme, la vitesse de dissociation ne dépend que de la concentration de l'élément choisi. En effet, la dilution des solutions exclut les effets physiques sur la nébulisation[5]. Les autres conditions étant hautement standardisées et constantes, la différence de concentration peut avoir joué un double rôle: à faible concentration, le résidu sec des gouttelettes de l'aérosol offre d'une part une plus grande surface et d'autre part, une masse totale plus faible qu'à forte concentration. L'augmentation de surface favorise l'échange thermique et la faible masse totale d'autre part ne nécessite qu'une partie plus faible de la quantité d'énergie thermique disponible. Ces deux phénomènes concourent à réduire le temps nécessaire pour que le résidu sec atteigne sa température de volatilisation complète. L'effet constaté peut être expliqué ainsi.

La différence entre le cuivre et le manganèse donne à penser que les caractéristiques de l'élément ont une importance. Plutôt que la différence de degré de dissociation—en effet, des observations semblables ont été faites pour le calcium qui a un degré de dissociation de 0.14[2]—on doit penser que cet effet est plus sensible pour les éléments à ZPAM de faible dimension et disparaît pour les éléments à ZPAM qui couvrent une surface plus allongée de la flamme tel le magnésium. Le manganèse n'ayant pas été repris par RANN ET HAMBLY[1] ceci n'a pas été prouvé mais est très vraisemblable.

La différence de comportement des deux types de mélanges gazeux peut s'expliquer d'une part par la différence de distribution de la température et par la différence même de température. En effet, la flamme riche a une température inférieure à la flamme pauvre et de plus son maximum est situé plus haut[1,4]. On doit donc normalement s'attendre à ce que la flamme riche soit plus sensible à cet effet puisque l'énergie thermique disponible est relativement moindre et autrement distribuée. De plus, les variations de réactions chimiques dans la flamme pourraient intervenir pour une part dans cette différence.

CONCLUSIONS

L'effet de la concentration en élément à analyser sur la linéarité de courbes de calibrage (A/C) suivant la hauteur de la zone soumise aux mesures d'absorption met une fois de plus en évidence le caractère complexe des phénomènes d'atomisation dans la flamme. L'importance des conséquences pratiques de cet effet sur l'analyse et la standardisation des conditions est grande.

De plus, on doit s'attendre à ce que des progrès puissent être obtenus par des systèmes augmentant soit la surface d'échange thermique par réduction des dimensions des gouttelettes de l'aérosol, soit le temps de transit des résidus secs dans la flamme et inversément. Enfin, il semble que comme il a été démontré en émission de flamme[6-8] et suggéré par **WILLIS**[5] et **DE WAELE**[9] en absorption atomique, il doit exister un optimum de débit en solution atteignant la flamme pour chaque élément et chaque type de flamme.

La participation de W. **HARJADI** à ce travail a été possible grâce à l'aide accordée par l'OECD.

RÉSUMÉ

Les auteurs ont constaté et tenté d'expliquer un effet de la concentration de l'élément analysé sur la hauteur de la zone à population atomique maximale en absorption atomique dans la flamme. Cet effet influence notamment l'allure des courbes de calibrage (A/C). Il varie suivant les éléments et le type de flamme.

SUMMARY

The concentration of the element to be analyzed is shown to affect the height of the zone of maximum atomic population in atomic absorption spectroscopy. This effect particularly influences the shape of the calibration curves. It varies according to the elements and the type of the flame; the cases of copper and manganese are discussed in detail.

ZUSAMMENFASSUNG

Bei der Atomabsorptionsspektroskopie beeinflusst die Konzentration des zu bestimmenden Elements die Höhe der Zone der maximalen Atomanhäufung. Dieser Effekt beeinflusst besonders die Gestalt der Eichkurven. Er variiert mit dem Element und dem Typ der Flamme. Der Einfluss von Kupfer und Mangan wird im einzelnen diskutiert.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR

PART I. CONSTRUCTION AND OPERATION OF ATOM RESERVOIR

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(Received October 25th, 1968)

Atomic populations are normally produced for the analytical techniques of atomic absorption and atomic fluorescence spectroscopy by nebulising an aqueous or organic solution of the preatomic species into a flame. In the flame plasma, the droplets of solution evaporate to form solid particles which then dissociate to form a gaseous dispersion of atoms. The atomisation process within the flame is, however, very inefficient. In addition, pneumatic nebulisers rarely exhibit a "spraying" efficiency of more than 15% with aqueous solutions and the remaining test solution runs to waste. The total consumption nebuliser–burner unit which is used for gas–oxidant mixtures of high burning velocity, such as H_2/O_2, C_2H_2/O_2, etc., is also inefficient in the sense that large droplets are produced and that in many instances evaporation of solvent, let alone gasification of the sample, is very incomplete. ROBINSON[1] has commented for example that by use of the formula,

$$\int \varepsilon_\nu \mathrm{d}\nu = \frac{\pi e^2}{mc} N \cdot f = 0.01 \text{ absorbance unit}$$

(ε_ν = atomic absorptivity at frequency ν; e = charge on electron; m = mass of electron; c = velocity of light; N is number of atoms in path; f is oscillator strength at frequency ν), it can be shown for copper that 10^8 atoms should produce an absorption of 0.01 unit whereas in practice the best report of sensitivity limit corresponds to 10^{15} atoms, *i.e.* the efficiency of atomisation is only 1 in 10^7 *or* 10^{-5}%.

Apart from their very low efficiency as atomisers, flames possess several other disadvantages. One of these is that there is very considerable absorption background in the flame plasma. This is very marked with carbonaceous fuels and becomes objectionable in long-path flames. Yet again, there exists a very considerable amount of emission from the primary and secondary (diffusion) zones of flames because of chemiluminescence reactions such as

$$2CO + O_2 \rightarrow 2CO_2 + h\nu$$

in the flame gases and because of thermal emission from the elements aspirated into the flame for examination. These emissions which are d.c. in nature can be rejected by modulating the absorption or fluorescence source and tuning the amplifier to the same modulating frequency, but the continuous radiation received by the detector adds considerably to the electronic noise level in the electronic circuit. Those elements which form refractory oxides, *e.g.* aluminium, beryllium, rare earths, zirconium, etc.,

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are also extremely difficult to atomise in flame media and although the advent of the strongly reducing hot cyanogen region[2] of the nitrous oxide–acetylene flame[3] has made their analysis possible, such flames are still inefficient and are unpleasant to use even in the separated flame mode[4]. Additionally, with some equipment, difficulties from monochromator drift arise particularly with very hot flames, and efficient exhaust systems have to be maintained to remove combustion products from the flame gases, particularly with fuel-rich flames where carbon soot and toxic products are released. Explosion hazards are always present with flames of high burning velocity and the presence of naked flames causes additional difficulties under many circumstances.

Despite these several fundamental and circumstantial disadvantages, all commercial equipment so far produced for atomic absorption and thermal emission spectroscopy relies exclusively on the use of flames for the production of free atoms for analytical purposes. The present communication describes a very simple and efficient device which dispenses with flames for the production of free atoms and which can readily be fitted or adapted for use with most commercial atomic absorption equipment. Furthermore, it is ideally suited to the newer and more sensitive technique of atomic fluorescence spectroscopy, the development of which has been delayed principally by the necessity to use a flame with its strong emissive background radiation and low atomisation efficiency.

Several devices have previously been described for the production of free atoms without the use of flames, but most of them are relatively complex and require expensive apparatus, though in most cases they are considerably more efficient than flames. GATEHOUSE AND WALSH[5] described the use of a hollow-cathode sputtering chamber for the direct atomic vaporisation of solid samples. A sample of the metal or alloy was shaped in the form of a hollow cathode and mounted in a suitable chamber, capable of being purged with a gas such as argon. An improved flow-through cathode sputtering chamber was subsequently described by WALSH[6]. Atomic vapour is produced within the hollow cathode and consequently can attenuate the signal from a conventional hollow-cathode lamp source in the usual way. Samples must be suitable for machining into the form of a cathode, although it has been shown by GOLEB AND BRODY[7] that solutions could be analysed by evaporating the solution evenly on the walls of a suitable cathode. The method is interesting, but at present appears to be beset by difficulties.

VIDALE[8] described a modified KING furnace method in which the sample is placed in a sealed quartz cell within a quartz tube which is itself placed within an electrically heated furnace at *ca.* 1100°C. The tube is purged with argon and evacuated before atomisation. Amounts down to 10^{-10} g were determined with a precision of *ca.* 20%. The method is, however, cumbersome and limited in application, though useful for specific problems.

NELSON AND KUEBLER[9] analysed solid samples such as wire, ribbon or powders by placing them on quartz or graphite strips supported in an enclosed silica chamber purged by an inert gas. The sample was vaporised by an intense flash (10 kw/cm^2) heating from a capacitor discharge lamp wound round the cell.

A spark-in-spray method has been described by ROBINSON[10]. The liquid sample is sprayed into an electrical discharge. The method is efficient in producing atoms of those metals which form refractory oxides in flames, but the spray becomes highly charged and strong electrical and magnetic fields upset the electronic circuitry of the detection system. The strong emission from the discharge is also very troublesome.

DAVID[11], BRECH[12], and HAGENAH *et al.*[13] have suggested the possibility of laser-shot evaporation, and recently the technique has been employed by MOSSOTTI, LAQUA AND HAGENAH[14]. Their experiments revealed that with some elements the number of free atoms outlasting the laser plume emission was sufficient to permit semi-quantitative atomic absorption at submicrogram levels, but there appears to be a considerable matrix effect. The small sampling area of the laser shot poses additional problems and, although the method scarcely requires sample preparation, it is highly dependent upon experimental parameters.

Undoubtedly, the two most promising methods are the L'VOV[15,16] adaptation of the KING furnace and the carbon tube method of MASSMANN[17,18]. The L'vov furnace utilises an electrically heated carbon tube lined with tantalum to prevent too rapid a diffusion of atomic vapour into the carbon walls of the tube. The sample in the form of a few microlitres of solution is placed on a carbon plug which fits into a hole in the tube and an electrical discharge is struck additionally to heat this plug, from an auxiliary electrode. Elements such as titanium and aluminium were determined in this way in the range 1–50 p.p.m. and sensitivities down to 10^{-8} and even $5 \cdot 10^{-11}$ g were obtained. NIKOLAEV[19] similarly obtained limits of $4 \cdot 10^{-9}$ g at 3075.9 Å and 10^{-12} g at 2138 Å for zinc. RAMIREZ-MUÑOZ[20] comments that the efficiency of the L'vov furnace is *ca.* 100%.

MASSMANN'S[17,18] device uses a heated carbon tube for atomic absorption or fluorescence and yields similar results, but his device is perhaps simpler to operate than that of L'VOV. The laser and carbon tube furnaces all require rapid response recorders and are restrictive in their application as well as being experimentally bulky and cumbersome. MOSSOTTI *et al.*[14] comment on the lack of adoption of the highly efficient VIDALE and L'VOV methods in terms of difficulty in sample prehandling, but it is also very pertinent to indicate that these devices are also physically cumbersome or expensive to operate so that the prospect of their attachment to an atomic absorption apparatus is unfavourable.

In the device described in this paper, the sample in liquid form is placed on a carbon filament supported between two electrodes in a small enclosed pyrex vessel with transparent silica windows. The chamber is purged with a small continuous flow of argon and the sample is vaporised by passage of *ca.* 100 A at 5 V through the filament, from a 10,000 VA stepdown transformer unit. The filament is heated to 2000–2500° within 5 sec when the switch on the transformer is closed, and the sample is vaporised. The entire unit is smaller than the average burner and nebuliser used in atomic absorption spectroscopy and, by placing a different glass cover over the same basic unit, it can be instantly adapted to atomic fluorescence spectroscopy. The carbon filament atom reservoir is described here for use in conjunction with a Techtron AA4 flame spectrometer both in absorption and fluorescence emission for silver and magnesium.

EXPERIMENTAL

Construction of filament atom reservoir

Two cylindrical stainless steel electrodes (diameter 9 mm, length 30 mm) are mounted on tungsten rods (diameter 3 mm, length 14 cm) sealed through a B55 Quickfit and Quartz pyrex cone as shown in Fig. 1. The lower ends of the tungsten rods protruding from the end of the sealed cone are connected to the leads from the 10,000 VA stepdown transformer. The upper ends of the stainless steel electrodes are sectioned so that the ends of the carbon filament electrode (diameter 1–2 mm, length 4 cm) can be firmly clamped to make good electrical connection. In the present assembly the effective length of the filament electrode is 2.2 cm, but this and the diameter of the filament and the current supplied to it may be altered to meet the temperature requirements of the element to be atomised within the cell. The temperature of the rod may readily be monitored for control purposes by means of an optical pyrometer.

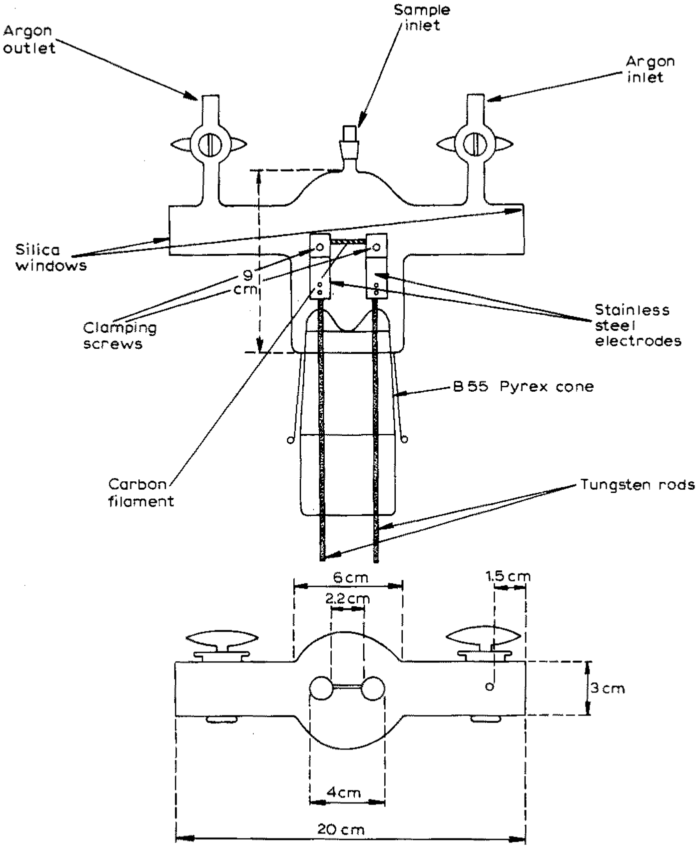

Fig. 1. Carbon filament atom reservoir for atomic absorption.

This assembly is mounted on the optical bar of the Techtron AA4 in the position normally occupied by the burner–nebuliser system used with conventional flame technology, in such a way that the longitudinal axis of the carbon filament is aligned with the optical axis and so that it lies slightly beneath the optical plane of the entrance slit of the monochromator, *i.e.* the filament is adjusted in vertical height so that it occupies approximately the same position as the primary cone of a conventional flame in atomic absorption measurements. The same assembly and positioning is used for atomic absorption or atomic fluorescence measurements. Only the dome placed over the filament need be changed in switching from one technique to the other.

The atomic absorption head and its approximate dimensions are also shown in Fig. 1. It is fabricated from pyrex glass and is built onto a B55/44 socket. Optical-quality silica end-windows are sealed onto the ends of the side arms to present an optical path through the device. A tap is sealed near the end of each side-arm to allow the passage of a stream of argon or other inert gas through the cell. A B12/21 socket with stopper is situated on the centre of the dome to allow samples of solutions to be deposited upon the filament for analysis. The a.a.s. head is placed on the electrode assembly so that the socket forms an air-tight seal over the B55 cone with some silicone grease and in such a way that the optical arms are aligned along the axis of the monochromator and optical bar. A hollow-cathode lamp is situated in the usual position for atomic absorption spectroscopy so that its beam of radiation passes through the device immediately above the heated filament and directly into the slit of the flame spectrometer. The unit must be rigidly clamped in position because small displacements can cause significant experimental variations as with the use of flames.

The atomic fluorescence head is virtually identical except that the side arms of the dome are shorter and are disposed at 90° instead of 180° (Fig. 2). This is to accommodate the normal right-angled excitation/fluorescence measurements conventionally made in all fluorescence studies. There is, however, no reason why this angle should not be altered to meet the instrumental requirements of an individual spectrometer. In setting up the unit for atomic fluorescence measurements, it is moved along the optical bar close to the slit and the a.f.s. head is placed so that one side-arm is situated as close as possible to the entrance slit of the monochromator, and the other points forwards, so that the source of excitation may be caused to irradiate the atomic vapour arising from the hot filament by pointing the intensely radiating source down the side-arm and away from the operator.

Conversion of the filament atom reservoir from atomic absorption to atomic fluorescence takes only as long as is necessary to lift one glass assembly off the B55 cone and replace it by the other, *i.e.* a matter of seconds.

In this communication the technique is illustrated for the atomic absorption and atomic fluorescence measurement of two test elements, silver and magnesium, as an illustration of its basic simplicity and uniquely high sensitivity, particularly in the fluorescence mode. In each instance, high-intensity hollow-cathode lamps of the type described by SULLIVAN AND WALSH[21] were used. These same sources and elements have recently been studied with flame technology and the same spectroscopic equipment in this laboratory[22,23]. A comparison of the results obtained by substitution of the proposed unit in place of a flame is therefore particularly instructive.

Reagents for analysis

Both silver and magnesium occur widely as trace elements in water. Because of this and the extremely high sensitivity of both atomic absorption and atomic fluorescence measurements, particularly the latter, when the proposed technique is used, the water used in these studies had to be distilled from a glass still and then deionised. Stock solutions containing 100 μg/ml of silver(I) and magnesium(II) were prepared. These solutions were not diluted with distilled–deionised water until immediately before use to minimise contamination and loss of material by adsorption on glassware.

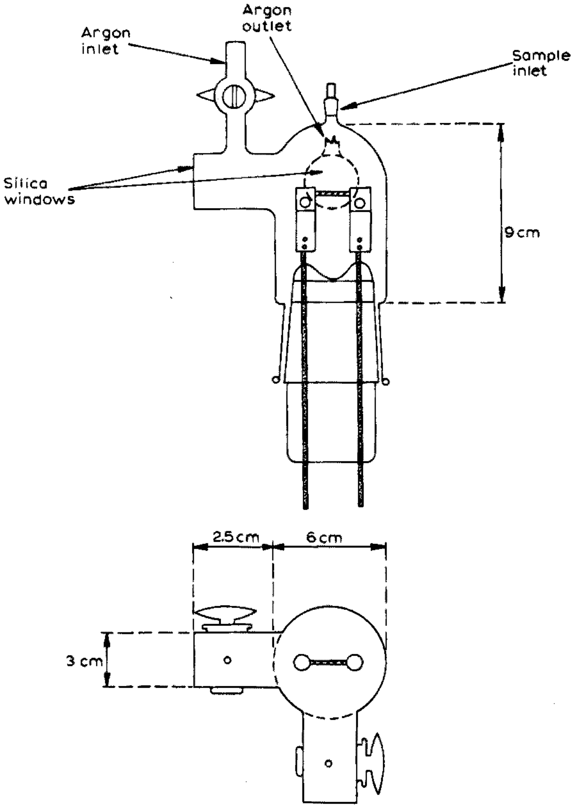

Fig. 2. Carbon filament atom reservoir for atomic fluorescence.

Apparatus

Varian-Techtron AA4 atomic absorption spectrometer fitted with A.S.L. high-intensity lamps for silver or magnesium and with burner–nebuliser system removed from optical bar.

Filament atom reservoir unit as described above clamped to the saddle that normally carried the burner unit.

Argon flow supply to the unit supplied *via* the flow-meter which normally monitors fuel-gas flow rates to the burner system from an argon cylinder through a 5-l reservoir vessel to smooth out fluctuations in flow rate arising at the reducing gauge on the cylinder.

Power supply for the atom-reservoir unit from the 240 V mains supply *via* 2 × 20 A gauged "Variac" transformers through the 10 V secondary O/P winding of a 10,000 VA stepdown transformer (Foster Transformers Ltd.). The circuit is shown in Fig. 3.

Carbon filaments (1–2 mm diameter, Morganite Ltd.).

"Agla" micrometer syringe pipette (Burroughs Wellcome), capacity 500 μl, fitted with a fine-bore hypodermic needle.

Sargent Model S.R. 204 strip-chart recorder, 1 mV 1 sec f.s.d.

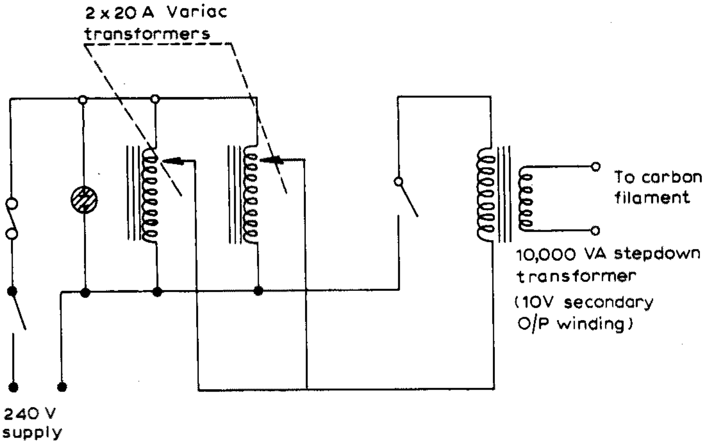

Fig. 3. Circuit diagram.

Gas and flow rate in the reservoir unit

An inert atmosphere is necessary within the atom-reservoir unit to prevent oxidation of the carbon filament with frequent necessity for replacement, fouling of the chamber and excessive radiative background, etc. Whilst any inert gas serves, argon is probably more suitable than nitrogen since there is no tendency for cyanogen emission to occur. In addition, it shows less quenching in a.f.s. measurements than does (diatomic) nitrogen. For this reason, argon was used as cell gas in these studies.

The unit described here is designed in such a way that it may be operated under static atmospheric conditions, or under flow conditions at reduced, standard or positive pressures. With the two elements tested here, it was found that at reduced pressure, under static conditions, atomisation was rapid, but tended to be irreproducible. Flow conditions under reduced pressure were not examined. At atmospheric pressure, atomic vapour came off slowly and on occasion two maxima of absorption were observed against a time plot. Reproducible results were most easily obtained under argon flow at a slightly positive pressure. Since the rate of diffusion of atomic vapour away from the hot carbon filament depends on the surrounding pressure of gas and its flow rate, experiments were initiated to study these effects. With this design of atom reservoir, an increase of pressure up to 8 p.s.i. on the Techtron fuel gauge (calibrated) increased the sensitivity, but above this level the atomic vapour was swept away too quickly and sensitivity decreased accordingly. It was found, however, that even with a 5-l smoothing chamber between the cylinder reducing gauge and the atom reservoir, increase of flow rate decreased the stability of gas flow. Figure 4 shows the effect of flow rate. A compromise flow rate of 3.8 l/min (*ca.* 4 p.s.i.) on the Techtron fuel gauge (calibrated) was chosen to yield a reasonable balance between sensitivity and precision.

The use of a flowing argon stream is also useful even at 0.1-p.s.i. pressure in that it disperses the water vapour which comes off initially before atomisation and which otherwise promotes fogging of the silica end windows and so loss of signal strength.

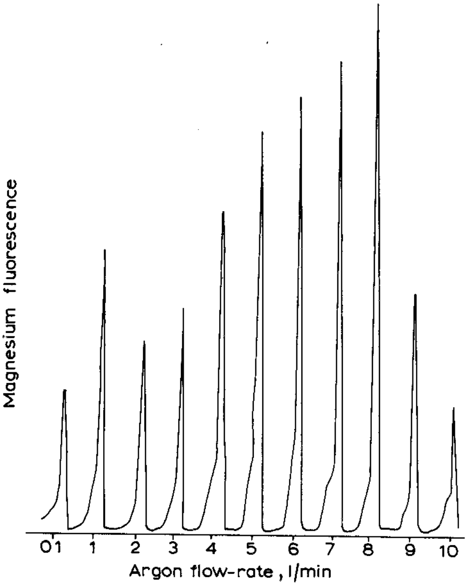

Fig. 4.

Determination of silver by atomic absorption spectroscopy with the filament atom reservoir

Light the high-intensity silver lamp with a primary cathode current of 2 mA and zero secondary current, *i.e.* using the conditions previously found to be most suitable[22]. Align the hollow-cathode lamp and peak the monochromator on the 3280.7 Å silver resonance line. Select a suitable slit width of 300 μ. Clamp the atom-reservoir unit in place with the carbon filament aligned along the axis and with the absorption cell-head in place. Sweep the cell out with a smoothed flow of *ca.* 4 l/min of argon. Adjust the lens between the hollow-cathode lamp and the reservoir unit, so that a diffuse image with maximal area is obtained in the space over the centre of the carbon filament, and similarly adjust the lens between the reservoir unit and the monochromator so that this image is focussed on its entrance slit.

When the hollow-cathode lamp has warmed up, switch the lamp to "operate", turn the amplifier gain to 4 (maximum = 20) and adjust the absorbance meter to zero absorbance. Set the Variacs to 50% with the switch off and set the recorder running. Throw the transformer switch for 5 sec to heat the carbon filament to 2000–2500°. There should be no deflection of the recorder trace unless the filament is contaminated with silver. If it is contaminated, the next throwing of the switch should show that the filament is now clean, *i.e.*, the filament is self purging and there should be no memory effect. If there is heavy contamination of a new or unused filament, the transformer switch should be left on for longer than 5 sec until the recorder trace has returned to the base-line. Switch off the recorder.

Allow the filament to cool for 2 min with the argon flowing and then remove the B 12 stopper on the central dome and deposit the necessary amount *e.g.* 5 μl of test solution on the centre of the filament by means of the hypodermic needle of the syringe pipette. Replace the stopper, check the argon flow rate, indicator setting, recorder zero, etc. which any inadvertent movement of the glass filament atom reservoir cell may have caused. By this time the solvent (water) will have been swept out of the cell. With the recorder running, switch the transformer main switch on for 5 sec (or longer if the absorption peak is incomplete) and observe the absorbance on the recorder chart. Allow the filament to cool for 2 min and then repeat with different amounts of silver and with the unknown sample solutions whose concentrations are to be determined.

A typical set of results is shown in Fig. 5 for the range $1\text{–}10 \cdot 10^{-9}$ g of silver. The coefficient of variation is 15% on these results.

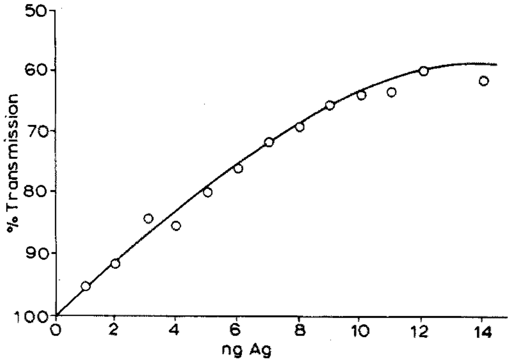

Fig. 5. Calibration curve for silver by atomic absorption spectroscopy with the proposed unit.

Determination of silver by atomic fluorescence spectroscopy with the filament atom reservoir

Light the high-intensity silver lamp with a primary cathode current of 20 mA and a secondary (booster) current of 400 mA. Place the fluorescence cell head on the reservoir unit as described previously, remove the focussing lenses and slide the reservoir assembly along the optical bar until the end-window is close up to the monochromator entrance slit. Situate the hollow-cathode lamp on a rigid support opposite the other optical window of the fluorescence head of the reservoir unit so that the light from the cathode illuminates the area above the filament. Flow argon through the reservoir unit at *ca.* 4 l/min and remove the stopper from the dome. Balance a glass rod (2–3 mm diameter, 8–9 cm long) on the centre of the carbon filament at the sample site. Peak the monochromator on the 3280.7 Å line by the reflection from the glass rod. Remove the rod and replace the B 12 stopper. Adjust the monochromator slit to 300 μ and set the Variacs to 50% with the transformer switch open. Set the amplifier gain at the desired level and adjust the indicator unit to zero % transmission.

At high amplifier-gain settings there is a correspondingly high background level caused by reflection from the walls of the cell but the signal is steady and (unlike flames) there is zero noise so that this does not interfere with the determinations except to reduce the possible range. Suitable screening of the cell could cut down reflective backgrounds to a very great extent.

Set the recorder running and throw the main switch of the transformer for 5 sec to heat the filament up to 2000–2500°. There should be no deflection of the recorder trace (*cf.* previous section on absorbance measurements). Switch off the recorder motor.

After the filament has cooled for 2 min, with the argon still flowing, remove the stopper and place the requisite amount of sample *e.g.* 5 μl on the centre of the carbon filament by means of the hypodermic needle of the syringe pipette. Replace the stopper and whilst the water vapour is being swept out, check the recorder zero, etc. Start the recorder and throw the switch on the transformer for 5 sec (or longer if the fluorescence peak is incomplete). The process may be repeated with other standards and unknown samples at 2-min intervals as described previously. Unless a filament is mistreated, there are no memory effects or "blank" signals between readings.

Two sets of results are shown in Fig. 6. Both show slight curvature. The first set of results (Fig. 6(a)) was obtained with an amplifier gain of 16 and covers the range $1–6 \cdot 10^{-9}$ g. The second set (Fig. 6(b)) was obtained with a gain setting of 18 (maximum = 20) and covers the range $1–9 \cdot 10^{-10}$ g. No effort was made here to probe the upper limit of the a.f.s. curves, but there is evidence that with high silver concentrations, self-absorption of fluorescence radiation occurs, as shown previously in a study of silver fluorescence in flame media[22].

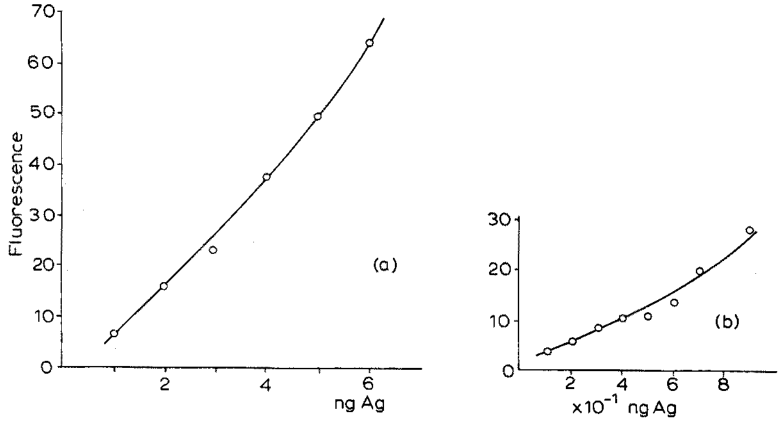

Fig. 6. Silver atomic fluorescence calibration curves: (a) 0–6 ng Ag; (b) 0–1 ng Ag.

Determination of magnesium by atomic absorption spectroscopy with the filament atom reservoir

For the determination of magnesium, follow the method described above for the atomic absorption determination of silver, but with magnesium test solution, a wavelength setting of 2852.1 Å, and a high-intensity magnesium hollow-cathode lamp with a 2 mA primary cathode current and no secondary current[23]. The amplifier gain setting should be varied to obtain 100% transmission.

Magnesium was determined in the range $1–5 \cdot 10^{-9}$ g with a coefficient of variation of 9% (Fig. 7(a)).

Determination of magnesium by atomic fluorescence spectroscopy with the filament atom reservoir

The method used for the atomic fluorescence determination of magnesium was identical to that described above for silver, but with magnesium test solutions and a magnesium high-intensity hollow-cathode lamp set at 20-mA primary and 400-mA secondary current and peaked on the 2852.1 Å line. In this instance an amplifier gain of only 12 was used. At this wavelength the background reflection from the unscreened glass cell was much higher, hence the lower amplifier gain, but the noise level remained zero.

Even at this low amplifier setting, magnesium could be determined down to $1 \cdot 10^{-15}$ g (Fig. 7(b)). At this low level the most imprecise result was only 30% different from the true result.

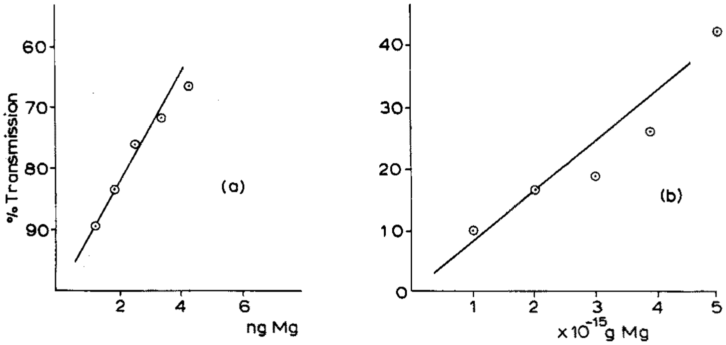

Fig. 7. Calibration curves for magnesium: (a) absorption method; (b) fluorescence method

DISCUSSION

Since we have recently described the atomic absorption and atomic fluorescence measurements of magnesium[23] and silver[22] with the same spectrometer and sources, but with conventional flames to produce atoms, a comparison with the carbon filament atom reservoir is instructive.

In terms of objective comparison the data for atomic absorption measurements are particularly reliable, since minor alterations in source intensity and detector sensitivity are without effect. It will be seen that a very considerable improvement in sensitivity has been obtained. Thus, in the flame work, calibration curves were obtained for 1–10 p.p.m. of silver; if it is assumed that it is possible to make measurements on as little as 1 ml of solution, which is a generous assumption, this corresponds to 10^{-6}–10^{-5} g of silver. With the atom reservoir in place of the flame, the range obtained was 10^{-9}–10^{-8} g, an improvement of three orders of magnitude. With magnesium, the flame range extended down to 0.4 p.p.m., *i.e.* $4 \cdot 10^{-7}$ g on the above basis of calculation, whereas with the atom reservoir, the smallest amount determined was 10^{-9} g, a similar *ca.* 1000-fold increase in sensitivity.

The fluorescence data are more difficult to compare because the intensity of the lamp for silver had decreased considerably during the intervening period. Nevertheless, the smallest amount of silver determined in the flame by fluorescence measurement[22] corresponded to 0.01 p.p.m., *i.e. ca.* 10^{-8} g whereas with the filament atom reservoir in the present study it corresponded to 10^{-10} g. On the basis of the increased atom population as shown by the absorption measurements, a figure of at least 10^{-11} g should have been realised. The fact that it was not obtained suggests serious deterioration of the hollow-cathode lamp over the intervening period of 18 months during which time it had been used fairly extensively. For magnesium, the minimum amount determined by flame fluorescence[23] was 0.01 p.p.m., *i.e.* 10^{-8} g, whereas with the filament atom reservoir cell in the present study it was 10^{-15} g, an increase in sensitivity of 7 orders of magnitude.

Sensitivities in atomic absorption are usually quoted in p.p.m. for 1% absorption. With these flameless techniques, which do not require large volumes of solution, it is, therefore, more logical to quote these in g corresponding to 1% absorption. Yet again sensitivities in thermal emission or atomic fluorescence measurements in flame media are variously quoted in terms of p.p.m. for 1% transmission or more logically as detection limits p.p.m. producing a signal/background noise ratio of 2:1 or 1:1 as the case may be. In the experiments with the filament atom reservoir techniques, so far, we have been unable to establish the existence of background noise because of the absence of a.c. or d.c. emission from a flame. Hence, in Table I sensitivities are quoted in g corresponding to 1% absorption and transmission for a.a.s. and a.f.s. respectively. Obviously these latter figures are susceptible to detector sensitivity, source intensity, etc. The relatively poor performance of silver in fluorescence has already been accounted for in terms of reduced source intensity.

TABLE I

SENSITIVITIES FOR Ag AND Mg BY THE FILAMENT ATOM RESERVOIR TECHNIQUE

	Absorption[a]	*Fluorescence*[b]
Ag at 3280.7 Å	10^{-10} g	$3 \cdot 10^{-11}$ g
Mg at 2852.1 Å	10^{-10} g	10^{-16} g

[a] For 1% absorption.
[b] For 1% transmittance at gains stated in text.

One of the most obvious advantages of the proposed method of atomisation is its simplicity and safety in operation. There are no dangers of explosion and no great dissipation of heat. The sample need only be very small indeed, so that most of the solution is available for other purposes. There are no special requirements for controlled laboratory atmospheres, special rooms where flames may safely be exposed, extensive exhaust systems or necessity to shield from draughts and dust, since the atoms are produced within a small vessel. Spectroscopic atomic studies in confined spaces where flames could not possibly be used are now also feasible. Heat effects and the possible deterioration of mirrors and optics of expensive monochromators due to the accidental entry of hot gases into the measuring equipment are completely eliminated. Samples may also be added very precisely from readily available and inexpensive microlitre syringes.

Apart from these obvious physical advantages and the extremely flexible nature of the cell housings that may be fitted onto the basic filament atom generating unit, there is no danger of electrocution because of the very low voltages employed. The carbon filaments are also self-purifying in use and the cell shows no measurable memory effects such as have been encountered with other non-flame methods. Sampling errors also do not arise, as in the laser-shot technique[14] and the same carbon filament may be used for many analyses without replacement. This is in marked contrast to our own limited experience of the L'vov and MASSMANN tube methods.

Spectroscopically, the low gains required for atomic absorption work with the filament atom reservoir unit are very significant. These arise because of the complete absence of an absorption background as in the conventional method with flames or even separated flames[4]. In atomic fluorescence, the advantage of the complete absence of an emissive flame background is even more significant because wide slit-widths and maximal gains can be used without risk since the only noise is that due to the electronic circuitry. In the present prototype fluorescence head designed for the reservoir unit, no precaution was employed to eliminate reflections within the cell. However, it is clear that such reflections could easily be minimised so that much higher gains could be used. No scale expansion facility was used in this work, though it could obviously be used to maximal benefit because of the complete absence of flame noise.

Whilst no work has as yet been done on interelement effects, it is reasonable to suppose that there will be the same freedom from these as reported by L'vov[15,16]. In addition, since oxygen is completely absent from the reservoir unit and even that added as water is removed before the atomisation occurs, it is reasonable to suppose that there will be little difficulty in producing atoms of elements such as aluminium, beryllium, titanium, zirconium, etc., which form refractory oxides in flame media. The only source of oxygen likely to be present is where the salt of the metal involves an oxygen-containing anion such as sulphate, nitrate or phosphate. Even then, this will only be present in small amounts and should readily be reduced by the hot carbon filament.

Further work is in progress on these and several other aspects of this new and simple method of producing atoms for atomic absorption and atomic fluorescence spectroscopy and will be reported at later dates.

We are grateful to the Science Research Council for financial support for this work.

SUMMARY

A highly efficient carbon filament atom reservoir is described for use in atomic absorption and atomic fluorescence spectroscopy. Atomisation of minute samples of aqueous solutions occurs on a 1–2 mm carbon filament electrically heated by the passage of *ca.* 100 A at 5 V in an inert atmosphere within a simple glass chamber. With the elements tested so far there are no memory effects and the carbon filament is self-purging and may be used repeatedly for the same or other analyses. The device operates with an inexpensive transformer unit and is so compact that it may easily be fitted in the place of the burner–nebuliser unit on any commercial atomic absorption equipment and operated with perfect safety without flame extractors or precautions against fire or electrocution hazards. Analyses are completed within 5 sec and may be repeated every 2 min. As little as 10^{-15} g of magnesium may be determined with a precision of better than 30%.

RÉSUMÉ

Un filament en carbone très efficace, jouant le rôle de réservoir d'atomes, est décrit pour son emploi en spectrophotométrie d'absorption atomique et de fluorescence atomique. L'atomisation de petits échantillons de solutions aqueuses se produit sur un filament de carbone de 1–2 mm, chauffé électriquement par le passage d'environ 100 A à 5 V; l'opération s'effectue dans une simple chambre à gaz contenant une atmosphère inerte. Avec les éléments testés jusqu'ici, il n'y a pas d'effets de mémoire et le filament de carbone se purge de lui-même et peut être employé à maintes reprises pour la même analyse ou pour d'autres analyses. L'appareil fonctionne avec une transformation peu coûteuse et est si petit que l'on peut facilement l'adapter à la place du brûleur–disperseur dans les équipements commerciaux d'absorption atomique; il opère avec une sécurité parfaite sans extracteurs de flammes, sans précautions contre le feu ou contre les risques d'électrocution. Les analyses sont terminées en 5 sec et peuvent être répétées toutes les 2 min. On peut déterminer des quantités aussi faibles que 10^{-15} g de magnésium avec une précision supérieure à 30%.

ZUSAMMENFASSUNG

Ein hochwirksamer Kohlenstoffglühfaden als Atomreservoir zur Verwendung bei der Atomabsorption und Atomfluoreszenzspektroskopie wird beschrieben. Die Atomisation genau dosierter Proben wässriger Lösung geschieht auf einem 1–2 mm starken Kohlenstoffdraht, der elektrisch geheizt wird mit etwa 100 A bei 5 V in einer inerten Atmosphäre innerhalb einer einfachen Gaskammer. Die untersuchten Elemente zeigten keinen Memoryeffekt, so dass der Kohlenstoffglühdraht sofort für weitere Analysen verwendet werden konnte. Die Anordnung ist so klein, dass sie in jedem komerziellen Gerät anstelle des Brenners angebracht werden kann. Eine Analyse dauert 5 sec, die folgende kann nach 2 Min durchgeführt werden. 10^{-15} g Magnesium konnten mit einer Genauigkeit von besser als 30% bestimmt werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF PHOSPHORUS, ARSENIC OR SILICON BY ATOMIC ABSORPTION SPECTROMETRY OF MOLYBDENUM HETEROPOLY ACIDS

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(Received September 14th, 1968)

Although atomic absorption spectroscopy has been successfully applied for the direct determination of trace amounts of many elements, this technique is not suitable for the determination of traces of phosphorus, arsenic and silicon either because their resonance lines lie in the vacuum ultraviolet region or because of the formation of refractory compounds that are not completely dissociated in the flame. These elements are most commonly determined spectrophotometrically by their reaction with molybdates in acidic solution with subsequent reduction of the resultant heteropoly acids to "molybdenum blue". ZAUGG AND KNOX[1] recently described an indirect procedure for the determination of inorganic phosphate by atomic absorption spectrometry. The phosphate was extracted as phosphomolybdate into 2-octanol and the molybdate stoichiometrically associated with the phosphate, was determined with an air–acetylene flame. The method, however, is subject to interferences from both arsenic and silicon. Later KIRKBRIGHT, SMITH AND WEST[2] reported procedures for the sequential determination of phosphorus and silicon in a nitrous oxide–acetylene flame. Although the determination of phosphorus is almost specific, because of the selectivity of isobutyl acetate towards the extraction of phosphomolybdic acid[3], both arsenic and germanium interfered in the determination of silicon owing to the extraction of their respective heteropoly molybdic acids into butanol. Our investigation along these lines showed that, in the absence of phosphomolybdic acid, arsenomolybdic acid can be selectively extracted into a solvent mixture containing ethyl acetate, butanol and isoamyl acetate. In addition, it was also found that silicomolybdic acid can be selectively separated from considerable amounts of phosphomolybdic and arsenomolybdic acids by extracting into methyl isobutyl ketone in the presence of citrate. On the basis of these observations and reported facts, a procedure has been developed for the simultaneous determination of phosphorus, arsenic and silicon by atomic absorption spectrometry. The heteropoly acids were selectively extracted into an organic phase and the amount of molybdenum present in each of these phases was determined with a nitrous oxide–acetylene flame. The method is rapid, simple, accurate and completely free from interferences from several extraneous ions. Details of these investigations and other aspects of the procedure are described below.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer (Model 303) atomic absorption spectrometer fitted with a HETCO total consumption burner and a tri-flame 5-cm slot burner head (Jarrel-Ash Co., Waltham, Massachusetts) was used for absorption measurements. A Perkin-Elmer molybdenum hollow-cathode lamp was used as radiation source. A Leeds and Northrup pH meter was used for pH adjustments. Table I lists the instrumental conditions employed for the determination of molybdenum.

TABLE I

INSTRUMENTAL CONDITIONS

Wavelength:	3132 Å
Slit:	2 Å (0.3 mm)
Lamp current:	40 mA
Nitrous oxide:	15 psi
Acetylene:	Adjusted to give a rose red inner cone about 1–2 cm in height above the burner head during aspiration of the organic phase

Reagents

Reagent-grade chemicals were used throughout and all solutions were stored in polyethylene bottles to avoid silicon contamination.

Molybdate solution. Dissolve 10 g of ammonium molybdate tetrahydrate in 100 ml of water.

Standard phosphorus solution (25 µg P/ml). Dissolve 0.1098 g of potassium dihydrogen phosphate in distilled water and dilute to 1 l.

Standard arsenic solution (100 µg As/ml). Dissolve 0.4165 g of disodium hydrogen arsenate heptahydrate in water and dilute to 1 l.

Standard silicon solution (100 µg Si/ml). Fuse 0.1070 g of pure, dry precipitated silica with 1 g of anhydrous sodium carbonate in a platinum crucible. Cool the melt, extract with water and dilute to 500 ml.

Standard working solutions were prepared by appropriate dilution of the stock solutions.

Nitric acid (assay about 70%): 10% solution in distilled water.

Citrate solution. Dissolve 100 g of citric acid in about 800 ml of distilled water, adjust to pH 3.2 with sodium hydroxide and dilute to 1 liter.

Wash solution. Prepare 1% nitric acid solution and equilibrate it with a solvent mixture containing 1 part ethyl acetate and 1 part butanol.

Solvents for extraction: iso-butyl acetate, iso-amyl acetate, 1:1 mixture of butanol ethyl acetate, methyl-iso-butyl ketone.

Procedure

Transfer 10 ml of sample or an aliquot containing not more than 10 µg of each of phosphorus and silicon and 20 µg of arsenic into a separatory funnel and dilute to 10 ml with distilled water. Add 1 ml of molybdate solution and 2 ml of dilute nitric acid or sufficient acid to bring the pH to about 0.7 and mix well. Allow the contents of the funnel to stand for about 20 minutes for the complete formation of phosphomolybdic acid, arsenomolybdic acid and silicomolybdic acid.

Determination of phosphorus

Add 10 ml of iso-butyl acetate and shake the funnel for one minute. After the separation of phases, carefully transfer the lower aqueous phase (A) into another separatory funnel for the subsequent determination of arsenic and/or silicon. Determine the absorption due to molybdenum in the iso-butyl acetate extract under conditions listed in Table I, using a blank prepared in a similar way to set the zero of the instrument.

Determination of arsenic

To the aqueous phase (A) or, in the absence of phosphorus, to the sample treated as given under *procedure*, add 5 ml of 1:1 ethyl acetate–butanol mixture and shake for 1 min. Add 5 ml of isoamyl acetate and extract once again for about 30 sec. Allow the phases to separate and drain the aqueous phase (B) into another funnel for the determination of silicon. Wash the organic phase twice by shaking it vigorously for 1 min with 10-ml portions of wash solution to remove the free molybdate reagent. Determine the absorption due to molybdenum in the organic phase as described for phosphorus.

Determination of silicon

To the aqueous phase (A or B) or to the sample add 2 ml of citrate solution, mix well and let stand for 2 min. Extract the silicomolybdic acid with 10 ml of methyl isobutyl ketone by inverting the funnel for about 30 sec, and determine the molybdenum absorption as before against a solvent blank.

The concentrations of phosphorus, arsenic and silicon were determined by means of calibration curves prepared from standard solutions containing 1–10 μg of phosphorus, 2–20 μg of arsenic and 1–10 μg of silicon and treated as above.

RESULTS AND DISCUSSION

Extraction of phosphomolybdic acid

The study of the extraction of phosphomolybdic acid was confined to isobutyl acetate, as it has been established to be highly selective and gives virtually 100% efficiency in a single extraction[3].

A systematic investigation was next undertaken to determine the optimum conditions for the extraction of phosphomolybdic acid into isobutyl acetate. In order to establish the optimum pH for the quantitative extraction of phosphomolybdic acid, 10-ml samples containing 2.5 μg of phosphorus were treated with 1 ml of molybdate solution and the pH was adjusted with dilute nitric acid. After allowing the samples to stand for 20 min, the absorption due to molybdenum was determined as described under procedure. Figure 1 shows the effect of pH on the extraction of phosphomolybdic acid. It was evident that the amount extracted increased as the pH decreased and became quantitative over the range 0.6–1.0. No attempt was made to determine the lower pH limit for quantitative extraction, as the sample was found to be well buffered in this pH range. It was also confirmed that shaking for 1 min was sufficient for quantitative separation in a single extraction. No interference was

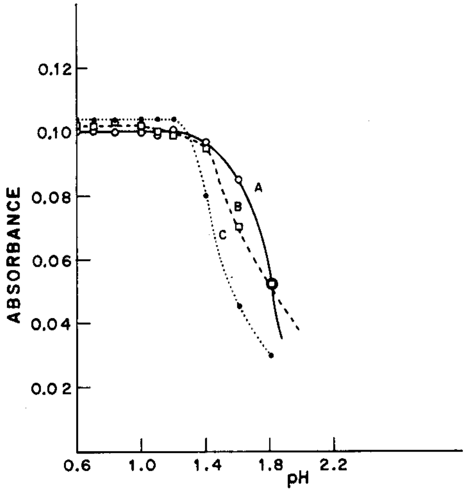

Fig. 1. Effect of pH. (A) Arsenic; (B) phosphorus; (C) silicon.

evident in the presence of 50 μg of arsenic or silicon or germanium.

Extraction of arsenomolybdic acid

Unlike phosphomolybdic acid, arsenomolybdic acid cannot be selectively extracted from other heteropoly acids, particularly in the presence of phosphomolybdic acid, except that a few solvents are known that can selectively extract arsenomolybdic acid from silicomolybdic acid. DESESA AND ROGERS[4] have demonstrated that arsenomolybdic acid can be separated from silicomolybdic acid by extracting with isoamyl acetate from solutions containing ethanol. The approach was studied for possible use but repeated determinations of molybdenum in the organic phase by atomic absorption spectrometry showed that the results were not reproducible. The method finally adopted was that described by KLEIN AND VORHES[5] which was slightly modified to permit measurements by atomic absorption spectroscopy. Extraction was accomplished with 1:1 butanol–ethyl acetate mixture, isoamyl acetate being used instead of chloroform for the separation. In addition to being as effective as chloroform for the selective extraction of arsenomolybdic acid, isoamyl acetate proved to be most suitable for spraying into the nitrous oxide–acetylene flame. However, a considerable amount of free molybdic acid was found to pass into the organic phase and it was necessary to wash the organic phase with a dilute acid solution. Two washes with 10 ml of 1% nitric acid solution were found to be sufficient to remove most of the molybdate from the organic phase. Because ethyl acetate and butanol are slightly soluble in water, the nitric acid solution was equilibrated with 1:1 butanol–ethyl acetate mixture before it was used for washing purposes.

The optimum pH for the extraction of arsenomolybdic acid was established; 10 ml of sample containing 5 μg of arsenic were treated with molybdate solution and nitric acid as described for phosphorus. After about 15 min, the solutions were shaken with 5 ml of 1:1 butanol–ethyl acetate mixture for 1 min, then 5 ml of isoamyl acetate were added and extracted once again by shaking for 30 sec. The organic phase was washed twice with the wash liquid and the absorption due to molybdenum was measured against blanks for each pH. The results are shown in Fig. 1 from which it is evident that maximum extraction takes place between pH 0.6–1.2. It was also confirmed by another experiment that as much as 30 µg of arsenic can be quantitatively extracted in a single extraction. By this procedure no interference was caused by the presence of 50 µg of silicon or germanium, but phosphate must be absent or separated by prior extraction with isobutyl acetate.

Extraction of silicomolybdic acid

It has been reported that citric acid effectively destroys both phosphomolybdic acid and arsenomolybdic acid but does not affect silicomolybdic acid[3]. This suggested that a selective method for the determination of silicon could be developed without involving separation of arsenic and phosphorus. Preliminary studies indicated that silicomolybdic acid could be readily extracted into methyl isobutyl ketone. Also, it was found that the addition of 2 ml of 10% citric acid with the pH raised to about 3.2 with sodium hydroxide solution completely prevented the extraction of free molybdic acid into the organic phase. However, a slight absorption due to molybdenum in the blank, which was reproducible, was always obtained perhaps from silicon present as impurity in the reagents used.

For 2.5 µg of silicon, the optimum pH for the extraction of silicomolybdic acid was determined as described for phosphorus and arsenic. The complex was extracted with 10 ml of methyl isobutyl ketone. The absorption caused by molybdenum in the organic phase, measured against blanks for each pH, is shown in Fig. 1, from which it is evident that maximum extraction takes place over the pH range 0.6–1.2. The procedure thus developed showed no interference in the presence of 50 µg of phosphorus or arsenic, as their complexes with molybdenum were readily destroyed by the presence of citric acid. However, germanium must be absent as it interfered by giving high results.

Simultaneous determination of phosphorus, arsenic and silicon

When the optimum conditions for the selective extraction of phosphomolybdic acid, arsenomolybdic acid and silicomolybdic acid had been established, a scheme was evolved for the separation and analysis of mixtures. It may be seen from Fig. 1 that the quantitative extraction of each of these heteropolyacids can be accomplished over a range of pH conditions. Because the sample was found to be well buffered between pH 0.6 and 1.0, the slight loss of acid after the extraction of phosphomolybdic acid and/or arsenomolybdic acid should not affect the quantitative extraction of silicomolybdic acid, particularly if the initial extraction was begun at the lower end of the pH range. As may be seen from Fig. 1, the extraction of silicomolybdic acid will not be affected even if the pH should rise to 1.2 at the end of these extractions. The addition of 2 ml of a 10% nitric acid solution to the sample yielded a pH of *ca.* 0.7 which proved suitable for the analysis of phosphorus, arsenic and silicon mixtures. The samples were analyzed by the recommended procedure and the results are shown in Table II. It was obvious that the extractions were selective and the determinations accurate.

Interference studies

The effect of the presence of a number of foreign ions listed in Table III was

TABLE II

DETERMINATION OF PHOSPHORUS, ARSENIC AND SILICON IN THE PRESENCE OF EACH OTHER

Phosphorus present (μg)	*Phosphorus found (μg)*	*Arsenic present (μg)*	*Arsenic found (μg)*	*Silicon present (μg)*	*Silicon found (μg)*
1.0	1.0	2.5	2.0	8	8.3
8.0	7.6	15.0	14.1	5	5.1
3.5	3.0	10.0	10.0	7.5	7.5
5.0	5.0	6.0	6.0	10.0	9.5
2.0	2.2	7.5	7.0	1.0	1.0
1.5	1.5	5.0	5.0	2.0	2.3

next examined. Separate analyses were made for phosphorus, arsenic and silicon in the presence of 200 μg of each of the interferents. In these investigations the concentrations of phosphorus and silicon were 2.5 μg and that of arsenic 5 μg. With the exception of titanium(IV) and zirconium(IV), which led to low recovery for phosphorus, none of the ions listed interfered.

The non-interfering effect of tungstate and the interfering effect of titanium on phosphorus determination was in contrast to the observation made by KIRKBRIGHT, SMITH AND WEST[2]. These authors noticed no interfering effect in the presence of titanium(IV), but the results were low in the presence of tungstate. Their experimental conditions under which phosphomolybdic acid was extracted into isobutyl acetate were entirely different from those described here, and this probably explains the interference that was noted.

TABLE III

INTERFERENCE STUDIES

Group I	Li^+, Na^+, K^+, Cs^+, Cu^{2+}, Ag^+
Group II	Be^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Hg_2^{2+}
Group III	$B_4O_7^{2-}$, Al^{3+}, Ce^{4+}
Group IV	Ti^{4+}, Zr^{4+}, Sn^{4+}, Pb^{2+}
Group V	VO_3^-, Sb^{5+}, Bi^{3+}
Group VI	SO_3^{2-}, SO_4^{2-}, Cr^{3+}, SeO_3^{2-}, TeO_3^{2-}, WO_4^{2-}, UO_4^{2-}
Group VII	F^-, Cl^-, Br^-, I^-, Mn^{2+}
Group VIII	Fe^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}

Conclusion

The results of this investigation indicate that phosphorus, arsenic and silicon can be selectively extracted as their heteropoly-molybdo acids and determined by the measurement of molybdenum by atomic absorption spectroscopy. Although phosphorus and silicon can be selectively extracted and determined in the presence of each other as well as arsenic, phosphorus must be absent or must be removed by extraction with isobutyl acetate before arsenic can be satisfactorily determined. Germanium did not affect the determination of phosphorus or arsenic, but interfered in the determination of silicon. Although it was not established experimentally, the method can be made quite specific for silicon if germanium is first removed by distillation as the chloride from dilute hydrochloric acid solution. The sensitivities established for the organic extract by the proposed procedure were 0.01 p.p.m. for phosphorus and silicon and 0.025 for arsenic for 1% absorption.

This investigation was supported by U.S. Public Health Service Research Grant No. AP 00128, National Center for Air Pollution Control, Bureau of State Services.

SUMMARY

A method is described for the determination of trace amounts of phosphorus, arsenic or silicon by atomic absorption spectrometry. The heteropoly-molybdo acids of phosphorus, arsenic and silicon were formed and selectively separated by means of solvent extraction, and the molybdenum present in the organic phase was determined by atomic absorption spectroscopy with a nitrous oxide–acetylene flame. The method is rapid, simple and accurate and is essentially free from interferences.

RÉSUMÉ

On propose une méthode pour le dosage de traces de phosphore, d'arsenic ou de silice par spectrométrie par absorption atomique. On précipite les hétéropolyacides molybdiques du phosphore, de l'arsenic et du silicium; on procède ensuite à une extraction dans un solvant. Le molybdène présent dans la phase organique est dosé par absorption atomique à l'aide d'une flamme oxyde nitreux–acétylène. La méthode est rapide, simple, précise et essentiellement exempte d'interférences.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren Phosphor, Arsen oder Silicium in der Atomabsorptionsspektrometrie beschrieben. Die Heteropolymolybdo-Säuren des Phosphors, Arsens und Siliciums werden gebildet und selektiv mittels Flüssigextraktion abgetrennt und das in der organischen Phase enthaltene Molybdän mit der Atomabsorptionsspektroskopie unter Verwendung einer Stickstoffoxyd–Acetylen-Flamme bestimmt. Die Methode ist schnell, einfach und genau und im wesentlichen frei von Störungen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF NANOGRAM AMOUNTS OF CHROMIUM IN URINE BY X-RAY FLUORESCENCE SPECTROSCOPY*

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(Received October 25th, 1968)

Chromium has been recognized as an essential trace element[1] in glucose metabolism. Because chromium is normally present in biological materials at concentrations of 10–100 p.p.b., sensitive and specific methods are required for its determination. A review of the analytical chemistry of chromium[2,3] points out the difficulty of obtaining good analytical data at these low levels.

Practically all separation procedures suggested in the literature require that chromium be hexavalent, a state that is less stable than the tervalent state. The tervalent state forms a stable chelate on boiling with an excess of 8-quinolinol[4–7]; the chelate is readily extracted into chloroform. While all other oxine chelates, except cobalt(III), are readily decomposed by 3 *M* hydrochloric acid, the chromium(III) chelate is unaffected and provides a ready means for separation of chromium from other oxinates. This preconcentration method is used in combination with the X-ray milliprobe to determine nanogram amounts of chromium in urine.

Although it is known that for small samples X-ray fluorescence spectroscopy with curved crystal optics is about an order of magnitude more sensitive than flat crystal optics, only a few applications for the actual determination of submicrogram amounts have been published[8,9]. The reasons for this limited applicability are twofold. First, the sample must be confined to the area of focus, generally 2–4 mm in diameter. Second, the element must be nearly free of dilution by any reagent. The latter restriction requires the removal of excess of reagent after separation has been accomplished.

EXPERIMENTAL

Reagents

All chemicals were of reagent-grade purity. Water, nitric acid, sulfuric acid, hydrochloric acid, acetic acid, ammonia and chloroform were redistilled with all-glass stills and stored in new glassware to ensure that there was no contact with chromic acid. The 8-quinolinol (oxine) was used in solid form.

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* Publication authorized by the Director, U.S. Geological Survey.
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Radioactive chromium-51 was obtained from commercial sources. One nanogram of chromium gave 10,000 counts/min when measured with a scintillation counter.

Apparatus

X-ray measurements were made with a spectrometer modified for use with a curved LiF (200) crystal bent to a 14-in radius and ground to a 7-in radius. A 0.050-in diameter conical aperture was used to define the sample area. Other parameters were a helium path, a flow proportional counter operating at 1450 V, a tungsten target at 60 kV, 50 mA and a line pulse set at 8 V with a base level of 3.5 V and 10 V window. A brass sample carrier insert was used for the X-ray measurements. All the data were obtained from the Cr Kα line.

Procedure

Add 25 ml of urine, 2 ml of concentrated sulfuric acid, 2 ml of concentrated nitric acid and 0.1 ng of radioactive chromium to a 50-ml Kjeldahl flask. Heat gently to distil off water until charring is excessive. Cool and add 2 ml of nitric acid. Heat to fumes of sulfuric acid. Cool and add 2 ml of nitric acid. Heat again to complete the digestion. Cool, dilute with 10 ml of distilled water and neutralize with a saturated solution of ammonia, adjusting to pH 4.

Add 0.5 g of solid oxine. Heat the flask in boiling water for 5 min and cool. Add 5 ml of chloroform, and shake the flask gently to establish the liquid–liquid equilibrium of the chromium oxinate. After separation of the two phases, withdraw and discard the aqueous layer. Transfer the chloroform layer to a centrifugal cone (15-ml volume) with ground-glass stopper. Rinse the Kjeldahl flask with 5 ml of 3 *M* hydrochloric acid, transfer to the cone, stopper and shake for 10 sec. After separation, withdraw and discard the hydrochloric acid layer. Make two more extractions with 3 *M* hydrochloric acid to remove excess of oxine from the chloroform layer. The last washing should be colorless. Wash the chloroform with 10 ml of 5% ammonia solution and then with 5 ml of distilled water.

Evaporate the chloroform to dryness and dissolve in 20 μl of chloroform, rotating the cone to allow contact with the walls. Draw the chloroform into a 50-μl syringe. Deliver the solution in 5-μl increments to the smooth polished surface of a 1/8-in brass rod previously heated to 45°. Allow each small volume to dry before delivering the next increment. Rinse the cone with another 20 μl of chloroform and transfer to the top of the brass rod. Determine chromium with the milliprobe.

RESULTS

Effect of various parameters on the formation and extraction of chromium oxinate

Figure 1 shows the influence of hydrogen ion concentration of the aqueous phase on the formation of the chromium chelate. The percentage of chromium extracted is plotted as a function of the pH before the addition of oxine. The curve indicates an optimum between pH 3 and 5 in which practically all the chromium is extracted. At higher acidity chelation is hindered and the sigmoidal curve that theory predicts[10] is seen at pH 1–3. The formation of the chelate decreases at a pH higher than 6 because chromium(III) forms an unreactive hydroxide. The optimum chelation occurs at a pH which is slightly more acidic than that required for the hydrolysis of chromium(III) chloride. Once formed, less than 1% of the chromium chelate is extracted from chloroform by aqueous solutions from pH 11 to 3 *M* hydrochloric acid. The same behaviour is observed within the range pH 2–6, when the experiments are repeated with chromium concentrations from 0.1 ng to 100 μg. Thus, the chelate extraction is independent of the chromium concentration.

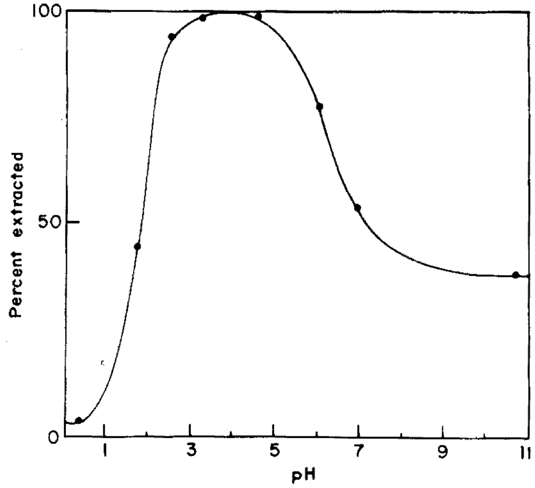

Fig. 1. Influence of pH on the formation of chromium oxinate. Amount of Cr: 10 ng; further conditions: see text.

A number of other parameters were varied to determine their effect on the oxinate extraction procedure. No influence was observed by varying the aqueous phase between 5 ml and 30 ml, the oxine between 0.2 and 1.0 g, the chloroform between 2 and 20 ml, or the amount of 3 *M* hydrochloric acid between 3 and 10 ml. The heating period for samples resulting from urine digestion must be at least 5 min for quantitative formation of the chelate and no variation was noted in heating periods of 10-min duration.

Influence of other ions

In the presence of 200 mg of NaCl, KCl, $MgCl_2$, $CaCl_2$, KNO_3, $NaClO_4$, $(NH_4)_2SO_4$ or KH_2PO_4, a slight influence was observed on the chelation of 10 ng of Cr. The yield was decreased to 90–95%. $ZnCl_2$, $FeCl_3$, $CuSO_4$ and $(NH_4)_2MoO_4$ react with oxine and seriously interfere at higher concentrations but when present at concentrations of 10 mg or less did not affect the extraction of 10 ng of chromium. High concentrations of oxinate-forming ions are not to be expected in biological materials and would be entirely removed by the three acid washings.

Loss of chromium

Experiments proved that the volatility of the chelate is negligible even at the nanogram level. No appreciable loss of chromium was detected during evaporation of chloroform or during the heating periods in the cone. No losses were detected from the brass support media even when heated at 100° for a period of 30 min. The low volatility of the chromium chelate was checked by gas chromatography.

The yields of the transfer process were about the same for chromium concentrations ranging from 0.1 ng to 100 μg. The first 20 μl transferred about two-thirds of the chromium present. The second transfer increased the yield to 80%. The consistency of the results indicates little or no absorption of the chelate by the walls of the glass vessel. The inherent errors of the transfer process were checked by adding a small amount of radioactive chromium at the beginning of the analysis and measuring its activity then and at the end of the transfer.

Sensitivity

Carrying a blank through the procedure is mandatory. The results of five blank determinations were 6, 8, 4, 7 and 10 ng. While the contamination probably originates with the oxine, the inconsistency of the results indicates that an additional external source of impurity is possible and this uncertainty is the factor that limits the determination to 15 ng.

The mean of seven determinations made on one urine sample was 17 ng per 25-ml aliquot with a standard deviation of 5 ng. These values correspond to 0.7 p.p.b. ±0.2 p.p.b. The mean recovery of the entire procedure was 74±7%. A summary of counting rates and statistics is given in Table I.

TABLE I

SUMMARY OF COUNTING STATISTICS

Cr (ng)	*10^2 counts/100 sec*	*Relative S.D. (10^2 counts/100 sec)*
0	52	1
10	71	2
20	91	3
40	130	3

The authors feel that sensitivity can be improved in several ways. The X-ray spectrometer used in this study is semifocusing in design and a crystal bent and ground specifically for the Cr Kα wavelength should substantially improve intensities. Confining the sample to a rod of smaller diameter[11] equal to the effective diameter of the aperture should further improve intensities. The method should be of considerable interest to those engaged in trace element investigations.

The authors are indebted to Professor CARL L. ROLLINSON of the University of Maryland for assistance with the radioactivity measurements and to the Division of Biochemistry, Walter Reed Army Institute of Research for permission to use the counting equipment.

SUMMARY

Nanogram amounts of chromium can be extracted as oxinate into chloroform. By treatment of the chloroform layer with 3 *M* hydrochloric acid, oxinates of other elements and excess of reagent are removed, leaving a chloroform solution of the chromium chelate only. This solution is concentrated and transferred to the top of a small brass rod acting as sample holder. The intensity of the X-ray fluorescence of the Cr Kα line is measured with curved crystal optics. Chromium amounts greater than 5 ng can be detected. The application of the procedure to the analysis of the chromium content of urine is demonstrated.

RÉSUMÉ

Des quantités de l'ordre du nanogramme de chrome peuvent être extraites sous forme d'oxinate dans le chloroforme. En traitant la couche chloroformique avec de l'acide chlorhydrique 3 *M*, les oxinates des autres éléments et l'excès du réactif sont éliminés, laissant une solution chloroformique du chélate de chrome uniquement. Cette solution est concentrée et transférée au sommet d'une petite baguette en laiton jouant le rôle de porte-échantillon. L'intensité de la fluorescence de RX de la ligne Kα du chrome est mesurée avec des optiques en cristaux incurvés. Des quantités de chrome plus grandes que 5 ng peuvent être détectées. On démontre l'application du procédé pour l'analyse de la teneur en chrome de l'urine.

ZUSAMMENFASSUNG

Nanogramm Mengen von Chrom können als Oxinat mit $CHCl_3$ extrahiert werden. Der Reagensüberschuss und Oxinate anderer Elemente können durch Behandlung des $CHCl_3$ mit 3 *M* HCl entfernt werden, so dass eine Lösung des Chromchelates allein in $CHCl_3$ verbleibt. Diese Lösung wird konzentriert und auf einen Messingstab als Probenhalter überführt. Die Intensität der Röntgenfluoreszenz der Chromlinie Kα wird gemessen, wobei Optik mit gebogenen Kristallen verwendet wird. Chrommengen grösser als 5 Nanogramm können bestimmt werden. Die Anwendung der Methode zur Bestimmung des Chromgehalts von Harn wird gezeigt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE SOLVENT EXTRACTION OF ZINC(II) WITH ALIPHATIC MONOCARBOXYLIC ACIDS

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(Received October 29th, 1968)

Little work has been done on the extraction of zinc(II) from aqueous media into an immiscible organic medium with the aid of an aliphatic monocarboxylic acid. Most of the previously reported investigations involve the exchange extraction of zinc. BLUMBERG AND MELZER[1] state that aqueous zinc can be extracted into kerosine containing an α-halo-substituted aliphatic monocarboxylic acid in a pH-controlled reaction. GINDIN *et al.*[2] studied the extraction into kerosine using a 7–9-carbon aliphatic monocarboxylic acid mixture. GINDIN *et al.*[3] investigated zinc in conjunction with a study of soap distributions between aqueous and kerosine phases, the soaps being metallic salts of 7–9-carbon aliphatic acid mixtures.

The purpose of this present study was to investigate the extraction of small amounts of zinc(II) from aqueous media into organic phases containing aliphatic monocarboxylic acids. The acids used included those from formic through decanoic. Several different solvents were employed and the enhancement of extraction by adducting agents was observed.

EXPERIMENTAL PROCEDURES

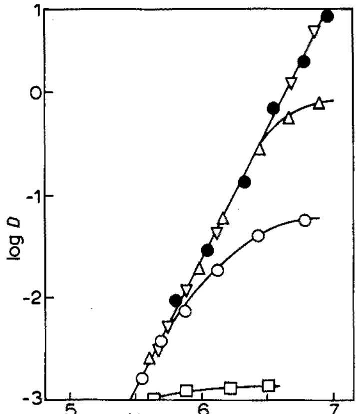
Zinc-65, as obtained in the chloride form from The International Chemical and Nuclear Corporation, was converted to the perchlorate by three successive evaporations with perchloric acid. All reagents of less than reagent grade were purified by distillation or crystallization procedures. All water was triply distilled from alkaline permanganate solution.

In each determination, a 20-ml sample bottle contained 8 ml of an aqueous phase and 8 ml of an immiscible organic phase. These two-phased systems were equilibrated by tumbling them on a rotating bar for at least 24 h at 27.0 ± 0.5°, this being sufficient time for equilibrium to be reached. Each aqueous phase consisted of a 0.1 *M* sodium perchlorate solution containing a known amount of zinc-65 labelled zinc perchlorate. In the case of the lower carboxylic acids, the aqueous phase also contained a known amount of the acid. The organic phase consisted either of a pure higher carboxylic acid or a known concentration of a higher carboxylic acid in an organic solvent. In certain cases, the organic phase also contained a known amount of adducting agent. The pH values of the aqueous phases were adjusted by the addition of sodium hydroxide and perchloric acid solutions.

After equilibration, each sample was centrifuged, its pH was measured, and the two phases were sampled. Radioactivity measurements were carried out by well-scintillation counting and the distribution coefficient of the total zinc D was calculated by dividing the organic-phase activity by that of the aqueous phase.

RESULTS

Figure 1 presents data for the extraction of 10^{-7} M zinc into benzene with 0.1 M normal aliphatic monocarboxylic acids ranging from hexanoic acid through



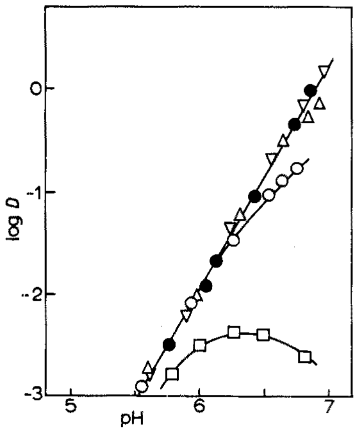
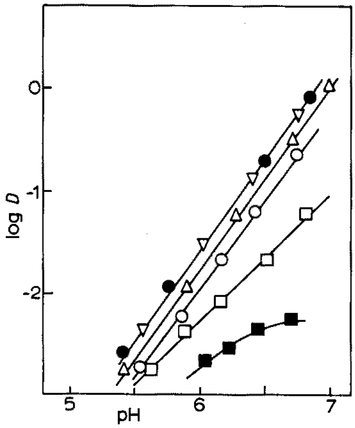


Fig. 1. Extraction of zinc(II) into benzene containing 0.1 M carboxylic acids. (□) Hexanoic acid, (○) heptanoic acid, (△) octanoic acid, (▽) nonanoic acid, (●) decanoic acid.

Fig. 2. Extraction of zinc(II) into chloroform containing 0.1 M carboxylic acids. (□) Hexanoic acid, (○) heptanoic acid, (△) octanoic acid, (▽) nonanoic acid, (●) decanoic acid.



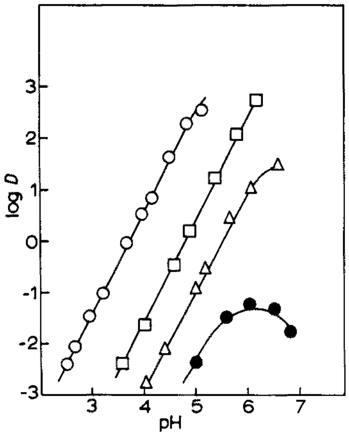
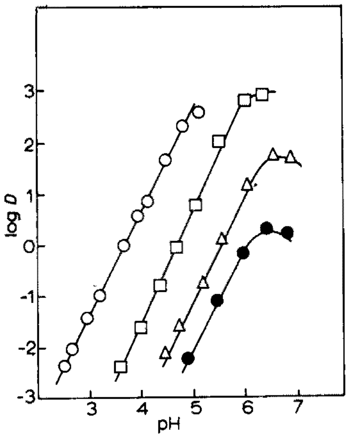


Fig. 3. Extraction of zinc(II) into 4-methyl-2-pentanone containing 0.1 M carboxylic acids. (■) Pentanoic acid, (□) hexanoic acid, (○) heptanoic acid, (△) octanoic acid, (▽) nonanoic acid, (●) decanoic acid.

Fig. 4. Extraction of zinc(II) into benzene containing hexanoic acid at various concentrations. (○) Pure acid, (□) 3.0 M, (△) 1.0 M, (●) 0.3 M.

decanoic acid. No appreciable extraction was observed when 0.1 *M* formic acid through pentanoic acid was employed. Figure 2 shows the results when similar experiments were conducted with chloroform as the organic solvent, and Fig. 3 shows the results when 4-methyl-2-pentanone was employed. In the case of chloroform, no appreciable extraction was observed when 0.1 *M* formic through butanoic acid was present.

Since the hexanoic-acid systems appeared to represent intermediate situations in the acid series, it was deemed reasonable to make more detailed investigations on them. Figures 4, 5, and 6 show the data obtained when 10^{-7} *M* solutions of zinc were



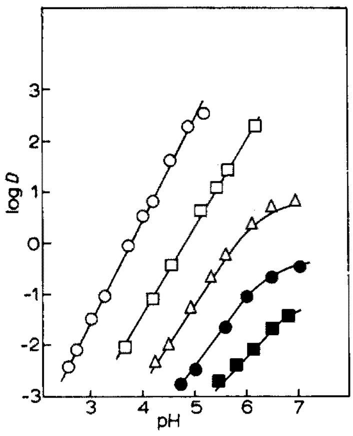
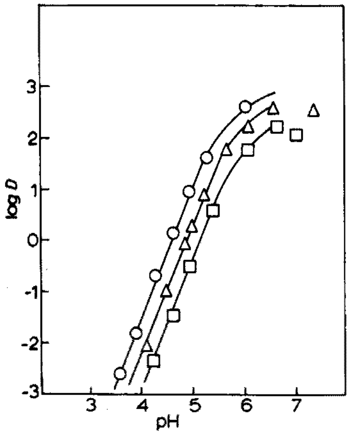


Fig. 5. Extraction of zinc(II) into chloroform containing hexanoic acid at various concentrations. (○) Pure acid, (□) 3.0 *M*, (△) 1.0 *M*, (●) 0.3 *M*.

Fig. 6. Extraction of zinc(II) into 4-methyl-2-pentanone containing hexanoic acid at various concentrations. (○) Pure acid, (□) 3.0 *M*, (△) 1.0 *M*, (●) 0.3 *M*, (■) 0.1 *M*.



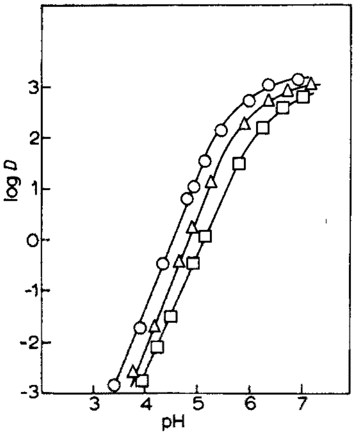
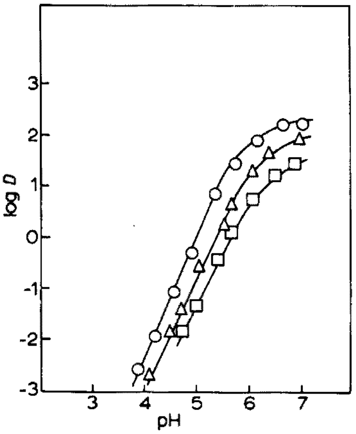


Fig. 7. Extraction of zinc(II) into benzene containing 1.0 *M* hexanoic acid and various amounts of 1-aminobutane. (○) 1.0 *M*, (△) 0.3 *M*, (□) 0.1 *M*.

Fig. 8. Extraction of zinc(II) into chloroform containing 1.0 *M* hexanoic acid and various amounts of 1-aminobutane. (○) 1.0 *M*, (△) 0.3 *M*, (□) 0.1 *M*.

extracted with benzene, chloroform, and 4-methyl-2-pentanone containing various concentrations of hexanoic acid.

To ascertain the effects of an adducting agent on zinc carboxylate extractions, 1-aminobutane was chosen as a representative substance. Figures 7, 8, and 9 present the results realized when 10^{-7} *M* aqueous solutions of zinc were extracted into benzene, chloroform, and 4-methyl-2-pentanone containing 1.0 *M* hexanoic acid and various concentrations of 1-aminobutane.



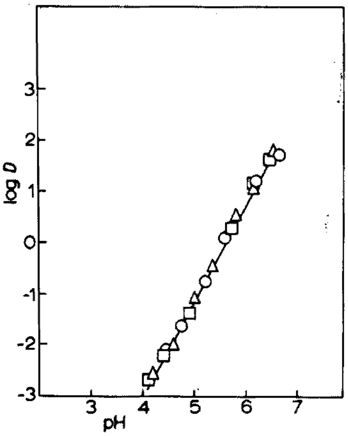


Fig. 9. Extraction of zinc(II) into 4-methyl-2-pentanone containing 1.0 *M* hexanoic acid and various amounts of 1-aminobutane. (○) 1.0 *M*, (△) 0.3 *M*, (□) 0.1 *M*.

Fig. 10. Extraction of various concentrations of zinc(II) into chloroform containing 1.0 *M* hexanoic acid. (△) 10^{-3} *M*, (□) 10^{-5} *M*, (○) 10^{-7} *M*.

Polymerization of the zinc-containing species in the organic or the aqueous phase can often be detected by observing the influence of the zinc concentration on the extraction. Figure 10 presents data for the extraction of zinc at various aqueous concentrations into chloroform containing 1.0 *M* hexanoic acid. No concentration dependence is indicated. Similar results were seen in benzene and chloroform and also when 1-aminobutane was employed in conjunction with hexanoic acid.

INTERPRETATION

The foregoing results indicate that the extraction of 10^{-3}–10^{-7} *M* zinc into benzene, chloroform, and 4-methyl-2-pentanone with 1–10-carbon aliphatic monocarboxylic acids is enhanced by increasing acid molecular weight, increasing acid concentration, the presence and increasing concentration of 1-aminobutane, and increasing pH, and is unaffected by zinc concentration. In general, extractions into benzene and chloroform seem to be fairly similar, but the 4-methyl-2-pentanone curves show somewhat less extraction under comparable conditions.

From curve-fitting procedures it is discovered that the following equation fits the data for the rising portions of the benzene–hexanoic acid curves as given in Fig. 4

$$D = 10^{-10.3}[\mathrm{H}]^{-2}[\mathrm{H_2R_2}]_{\mathrm{o}}^{\frac{3}{2}}$$

where D is the distribution coefficient as previously defined, [H] is the aqueous hydrogen-ion activity, and $[H_2R_2]_o$ is the concentration of the hexanoic-acid dimer in the benzene phase. These latter concentrations were calculated with a dimerization constant of $10^{2.2}$ and a partition constant of $10^{0.5}$ as determined by SAWHNEY[4]. Assuming the predominant species in the organic phase to be ZnR_2HR (where R is the hexanoate anion and HR is hexanoic acid) and in the aqueous phase to be Zn^{2+}, and substituting appropriate constants, the equation becomes[5]

$$D = K_{21}P_{21}K^{-2}P^{-3}C^{-\frac{3}{2}}[H]^{-2}[H_2R_2]_o^{\frac{3}{2}}$$

where K_{21} is the aqueous association constant of ZnR_2HR, P_{21} the distribution coefficient of ZnR_2HR, K the aqueous association constant of HR ($10^{4.9}$, see ref. 6), P the partition coefficient of HR, and C the dimerization constant of HR. Upon substituting the values for K, P, and C, the product $K_{21}P_{21}$ was found to be $10^{4.3}$.

A similar treatment applies to the chloroform data which are shown in Fig. 5. The equation turns out to be

$$D = 10^{10.6}[H]^{-2}[H_2R_2]_o^{\frac{3}{2}}$$

which indicates the same predominating species as in the benzene case. If a dimerization constant[4] of $10^{1.6}$ and a partition constant[4] of $10^{0.9}$ are used, the product $K_{21}P_{21}$ again equals $10^{4.3}$.

The data for the hexanoic acid extractions into 4-methyl-2-pentanone in Fig. 6 are found to correspond to the following equation when the rising portions of the curves are treated

$$D^{-1} = 10^{11.0}[H]^2[HR]_o^{-3} + 10^{6.2}[H][HR]_o^{-2}$$

where $[HR]_o$ is the concentration of the hexanoic acid in the organic phase, where there is little tendency toward dimerization[4]. This relation may be satisfied by postulating the predominant organic species to be ZnR_2HR and the predominant aqueous species to be Zn^{2+} and ZnR^+. This leads to the following expression[5]

$$D^{-1} = K_{21}^{-1}P_{21}^{-1}K^2P^3[H]^2[HR]_o^{-3} + K_{21}^{-1}P_{21}^{-1}KP^2C_{10}[H][HR]_o^{-2}$$

Substitution of $K = 10^{4.9}$ and $P = 10^{1.6}$ (see refs. 4 and 6) leads to values of the product $K_{21}P_{21}$ of $10^{3.6}$ and C_{10} of $10^{1.6}$, this latter being the association constant for the aqueous species ZnR^+. This value is not too far out of line with other values for monocarboxylatozinc complexes, the value for the formate being $10^{0.6}$, for the acetate $10^{1.0}$, for the propionate $10^{1.0}$, and for the butanoate $10^{1.0}$ (see ref. 6). This difference may be at least partially assignable to the solubility of 4-methyl-2-pentanone in water.

In Figs. 1 and 2, the rising portions of the curves for acids above hexanoic all have a slope of about 2.0. This leads to the conclusion that in these the most important aqueous species is Zn^{2+} and, in analogy with the hexanoic-acid system, the predominant organic species is ZnR_2HR. As the molecular weight of HR falls, this species would be expected to become less organophilic and thus decreased extraction would be expected.

In Fig. 3 the slopes of the rising portions of the curves go from about 1.0 to about 2.0 as the molecular weight of the acid increases. It is reasonable to think of this in terms of the predominating aqueous species changing from ZnR^+ in the case of pentanoic acid to Zn^{2+} in the case of decanoic acid. This follows when it is realized that the concentration of the R^- anion in the aqueous phase drops as one goes from pentanoic to decanoic acid because of the rise of the constant P.

The failure of formates, acetates, propionates, and butanoates to undergo appreciable extraction is readily assignable to the hydrophilicity of practically all possible extracting species.

When a plot of log D against the logarithm of the concentration of 1-aminobutane at constant pH is made for the data on the rising slopes of the curves in Fig. 7, a slope of about 1.3 is obtained, indicating the presence of about one molecule of the 1-aminobutane (B) in the major extracting species. A likely possibility is ZnR_2HRB or ZnR_2B. Since the slope is greater than 1.0, there is probably also present some species containing two molecules of the 1-aminobutane such as ZnR_2B_2 or ZnR_2HRB_2. Since no HR concentration dependence studies were made in the presence of B, no differentiations between these species are possible. Similar conclusions apply to both Figs. 8 and 9. In all instances the effect of adduct formation is seen to be an enhancement of extraction.

SUMMARY

Extractions of 10^{-3}–10^{-7} M zinc from aqueous 0.1 M sodium perchlorate solutions into organic media (benzene, chloroform, 4-methyl-2-pentanone) with the aid of 1–10-carbon aliphatic monocarboxylic acids and 1-aminobutane have been studied. Extraction is increased by increases in acid molecular weight, acid concentration, pH, and 1-aminobutane concentration. The extractions are independent of zinc concentration. Detailed studies on the hexanoic-acid systems have led to identifications of possible aqueous and organic species and to the calculation of some equilibrium constants.

RÉSUMÉ

Les auteurs ont étudié les extractions du zinc en concentration 10^{-3}–10^{-7} M, contenu dans des solutions aqueuses 0.1 M de perchlorate de sodium, dans des milieux organiques (benzène, chloroforme, 4-méthyl-2-pentanone) au moyen de 5 acides aliphatiques monocarboxyliques contenant 1 à 10 atomes de carbone et du 1-amino-butane. L'extraction est augmentée quand le poids moléculaire de l'acide, la concentration de l'acide, le pH et la concentration du 1-amino-butane augmentent. Les extractions sont indépendantes de la concentration en zinc. Des études détaillées des systèmes de l'acide hexanoïque ont conduit à l'identification d'espèces possibles en milieux aqueux et organique et au calcul de quelques constantes d'équilibre.

ZUSAMMENFASSUNG

Die Extraktion von 10^{-3} bis 10^{-7} M Zink aus wässriger 0.1 M Natriumperchloratlösung mit organischen Lösungsmitteln (Benzol, Chloroform, 4-Methyl-2-pentanon) mit Hilfe von aliphatischen Monocarbonsäuren mit 1–10 Kohlenstoffatomen und 1-Aminobutan wurde untersucht. Die Extraktion steigt bei Zunahme des Molekulargewichts der Säure, der Säurekonzentration, des pH-Werts und der Konzentration an 1-Aminobutan. Die Extraktionen sind unabhängig von der Zink-konzentration. Detaillierte Untersuchungen mit Hexansäuren führten zur Identifikation von möglichen wässrigen organischen Spezies und zur Berechnung einiger Gleichgewichtskonstanten.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE PARTITION AND DIMERIZATION OF OCTANOIC ACID IN SEVERAL ORGANIC–AQUEOUS SYSTEMS

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(Received October 29th, 1968)

In the past several years aliphatic carboxylic acids have been employed as reagents for extracting metal ions from aqueous solutions into organic media[1]. In order to apply proper theoretical interpretations to these extraction systems, the association, partition, and dimerization constants of the acids must be known[2]. Even though the association constants for many of these acids are available, there are very few published results of partition and dimerization constants. This paper reports the measurement of partition and dimerization constants for octanoic acid in five different organic–aqueous systems involving the organic solvents hexane, benzene, chloroform, 1-hexanol, and 4-methyl-2-pentanone.

QUANTITATIVE RELATIONS

The distribution d of octanoic acid between an organic and an aqueous phase may be defined as $d=[\mathrm{HA}]_{\mathrm{to}}[\mathrm{HA}]_{\mathrm{ta}}^{-1}$ where $[\mathrm{HA}]_{\mathrm{to}}$ is the total concentration of all forms of the acid in the organic phase and $[\mathrm{HA}]_{\mathrm{ta}}$ is the total concentration of all forms of the acid in the aqueous phase. The partition constant P and the dimerization constant D may be defined by the relations $P=[\mathrm{HA}]_{\mathrm{o}}[\mathrm{HA}]^{-1}$ and $D=[\mathrm{H_2A_2}]_{\mathrm{o}}[\mathrm{HA}]_{\mathrm{o}}^{-2}$ where $[\mathrm{HA}]_{\mathrm{o}}$ is the concentration of the acid monomer in the organic phase, $[\mathrm{H_2A_2}]_{\mathrm{o}}$ is the concentration of the acid dimer in the organic phase, and $[\mathrm{HA}]$ is the concentration of the acid monomer in the aqueous phase. The acid association constant K is defined by $K=[\mathrm{HA}][\mathrm{H}]^{-1}[\mathrm{A}]^{-1}$ where $[\mathrm{H}]$ is the aqueous hydrogen ion activity and $[\mathrm{A}]$ is the aqueous hexanoate concentration.

If it is assumed that the species present in an organic–aqueous system are the dimer, the monomer, and the hexanoate ion, then the distribution

$$d=(2[\mathrm{H_2A_2}]_{\mathrm{o}}+[\mathrm{HA}]_{\mathrm{o}})([\mathrm{HA}]+[\mathrm{A}])^{-1}$$

Upon substitution of K, D, and P one arrives at

$$d(1+K^{-1}[\mathrm{H}]^{-1})=P+2DP^2[\mathrm{HA}]_{\mathrm{ta}}(1+K^{-1}[\mathrm{H}]^{-1})^{-1}$$

Since the value of K for octanoic acid[3] is well known to be $10^{4.9}$, the expression $(1+K^{-1}[\mathrm{H}]^{-1})$ has a value smaller than 1.01 if the pH is held below 2.90. In such cases the relation simplifies to $d=P+2DP^2[\mathrm{HA}]_{\mathrm{ta}}$. Using this relation, a plot of d against $[\mathrm{HA}]_{\mathrm{ta}}$ should give a straight line with an intercept P and a slope of $2DP^2$. Thus P and D can be measured by ascertaining d as a function of $[\mathrm{HA}]_{\mathrm{ta}}$ and by subjecting the data to a linear least-squares analysis with a proper computer program, as has been done in this work.

PREVIOUS WORK

GOODMAN[4] has measured the distribution of $10^{-5.0}$–$10^{-1.5}$ M carbon-14 labelled octanoic acid between heptane and an aqueous phosphate buffer solution at a constant pH of 7.45 and an ionic strength of 0.16. The values of P and D were found to be 4.26 and 5800.

KHOL'KIN AND GINDIN[5] studied the distribution of the acid between decane and water by a titration method. No pH measurements were made. In order to determine P and D, equilibrium pH values must be known. Assuming that the decane–water system was neutral before the addition of the octanoic acid, then $[H]=[A]+[OH]$ where [OH] is the aqueous hydroxide ion activity. Rearrangement and substitution of $W=[H][OH]$ yields $[A]=[H]-W[H]^{-1}$. Since $[HA]_{ta}=[HA]+[A]$, substitution of K and [H] gives

$$[HA]_{ta}=K[H]^2+[H]-KW+W[H]^{-1}$$

This equation may be solved graphically to obtain an equilibrium pH value for any value of $[HA]_{ta}$. Then by plotting $d(1+K^{-1}[H]^{-1})$ against $[HA]_{ta}(1+K^{-1}[H]^{-1})^{-1}$, P and D values of 1.59±0.67 and 20470±17300 were obtained by computer least-squares analysis with the error limits being at the 95% confidence level. A similar treatment of data for the petroleum ether–aqueous system as investigated by GROSSFELD AND MIERMEISTER[6] yields a P of 45±2 and a D of 646±394. BODANSKY[7] gives only two points for the olive oil–water system; these indicate a P of around 200 and a very small D. It is to be recognized that the validity of these P and D values hinges strongly upon the assumption of system neutrality prior to the addition of the octanoic acid.

BROUGHTON[8] measured the freezing-point depression of octanoic acid in cyclohexane in the range $10^{-1.5}$–$10^{-0.8}$ M and calculated D in the range $10^{2.4}$–$10^{2.8}$. SARKADI AND DE BOER[9] spectrophotometrically investigated the association of octanoic acid in a high molecular-weight paraffin finding D values ranging from 131 at 46° to 0.4 at 179°.

EXPERIMENTAL PROCEDURES

Carbon-14 labelled sodium octanoate as obtained from a commercial supplier was found to be contaminated with about 2% of an impurity. This impurity could be removed by converting the sodium octanoate to the acid, then performing several successive extractions of a 1-hexanol solution of the acid with water at a pH of about 2.00. All other chemicals were reagent grade. The scintillation cocktail employed for counting the solutions consisted of 7 g of 2,5-diphenyloxazole and 0.3 g of 1,4-bis-2-(4-methyl-5-phenyloxazolyl)-benzene made up to 1 l with 1,4-dioxane. All determinations of pH were made with a Beckman Research pH Meter and Beckman Microelectrodes which were standardized with a Coleman buffer solution of pH 2.00.

Two basic equilibration procedures were employed. In the first procedure, used for systems with high d values, 8.00 ml of the organic phase containing labelled octanoic acid and 110.00 ml of aqueous 0.1 M sodium perchlorate solution were introduced into a 125-ml Erlenmeyer flask. Each phase had been presaturated with the opposite phase in order to minimize volume changes and the aqueous phase was adjusted to a pH of 2.50. The systems were stirred for 4 h on a combined magnetic stirrer and water bath regulated at 25°. After phase separation, the organic phase was sampled by withdrawing 200 μl, and then 100 ml of the aqueous phase was removed. This 100 ml of aqueous phase was then equilibrated with 8.00 ml of presaturated pure organic phase. After phase separation, 200 μl of this second organic phase was withdrawn. In each instance, the 200-μl sample was placed into 15 ml of the scintillation cocktail, and the pipette was rinsed twice with 1,4-dioxane, the rinsings also being added to the cocktail.

In the second procedure, used for systems with relatively low *d* values, 8.00 ml of the presaturated organic phase containing labelled octanoic acid and 8.00 ml of presaturated aqueous 0.1 *M* sodium perchlorate were stirred together for 4 h at 25°. After phase separation, the aqueous phase was sampled by withdrawing 200 μl and adding it to a prepared scintillation medium. Then the pipette was rinsed twice with 0.1 *M* sodium perchlorate at pH 2.50, and the rinsings were also added to the scintillation medium consisting of 15 ml of the scintillation cocktail, 200 μl of presaturated organic phase, and 400 μl of 1,4-dioxane. Then 200 μl was removed from the organic phase and added to another prepared scintillation medium. Two pipette rinsings of 200 μl of 1,4-dioxane were also added to the medium. The scintillation medium in this case consisted of 15 ml of the scintillation cocktail, 200 μl of the presaturated aqueous phase, and 400 μl of 0.1 *M* sodium perchlorate solution. The above procedure with regard to scintillation media was used in order that all scintillation counting samples would have practically the same composition, thus bypassing the need for quenching corrections.

CALCULATIONS

Since two different methods were employed in the extractions, two different data treatment methods were called for. In the case of the single extractions (8.00 ml organic, 8 ml aqueous), the ratio of organic to aqueous activities gives the *d* value directly.

In the case of double extractions (8.00 ml organic, 110.00 ml aqueous), calculations were straightforward for systems in which *d* was not dependent on acid concentration. However, in systems in which *d* varied with octanoic acid concentration, *d* values were calculated by a successive approximation method either coupled with values of *d* from regions where *d* is independent of concentration or coupled with values of *d* ascertained by single extractions where *d* is low enough to be so evaluated.

The distribution values *d* obtained for octanoic acid are given in Table I. With the values of *d* obtained at lower acid concentrations (where the systems should be more nearly ideal), the data were subjected to a least-squares analysis based on the equation $d = P + 2DP^2[\mathrm{HA}]_{\mathrm{t\,a}}$ to obtain values of *P* and *D*. These values are reported in Table I along with error limits at the 95% confidence level. The data not used in the least-squares analyses are superscripted with an a. The unused data were omitted either because they deviated by at least two standard deviations or because they obviously departed from a straight line at the higher acid concentrations.

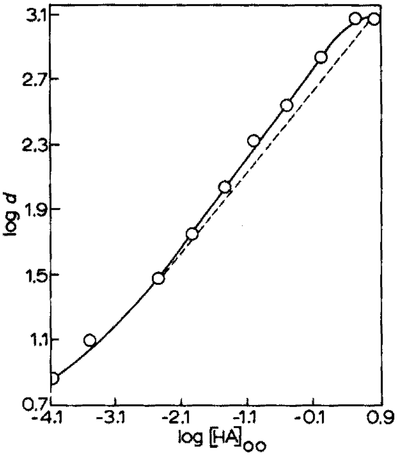
Figures 1–4 present plots of the experimental values of log *d* against log $[\mathrm{HR}]_{\mathrm{oo}}$, this latter symbol signifying the original concentration of octanoic acid in an organic phase placed in contact with an aqueous phase of equal volume. The

TABLE I

DISTRIBUTION VALUES OF OCTANOIC ACID

System	*Data expressed as* $d(\log [HA]_{ta})$
Benzene	$d(\log [\mathrm{HA}]_{ta})$ 44.6 (−5.71), 53.0 (−5.22), 38.1 (−4.48)[a], 74.6 (−4.84), 149 (−4.17), 260 (−3.88), 370 (−3.58), 715 (−3.34), 1090 (−3.04)[a], 1240 (−2.60)[a], $P = 47 \pm 6$, $D = 320 \pm 86$
Hexane	$d(\log [\mathrm{HA}]_{ta})$ 7.0 (−4.95), 12.4 (−4.62), 10.5 (−4.01)[a], 29.8 (−3.95), 56.1 (−3.70), 109 (−3.52)[a], 212 (−3.35)[a], 359 (−3.09)[a], 688 (−2.85)[a], 1239 (−2.60)[a], $P = 4.6 \pm 0.4$, $D = 5940 \pm 1890$
Chloroform	$d(\log [\mathrm{HA}]_{ta})$ 168 (−6.29), 183 (−5.82), 204 (−5.33), 249 (−4.76)[a], 425 (−4.63), 685 (−4.35), 1250 (−4.06), 1208 (−3.61)[a], 1910 (−3.28)[a], 2145 (−2.86)[a], $P = 148 \pm 15$, $D = 286 \pm 18$
Hexanol	$d(\log [\mathrm{HA}]_{ta})$ 1872 (−7.31), 1874 (−6.80), 1740 (−6.24), 1690 (−5.77)[a], 1843 (−4.78), 1820 (−4.23), 1803 (−3.73), 1604 (−3.12)[a], 1205 (−2.55)[a], $P = 1830 \pm 85$, $D = -0.02 \pm 0.12$
MIBK	$d(\log [\mathrm{HA}]_{ta})$ 1165 (−7.11), 1183 (−6.61), 1177 (−6.07), 1119 (−5.57), 1136 (−5.05), 1122 (−4.57), 1055 (−4.00)[a], 1126 (−3.59), 1188 (−3.08), 1079 (−2.57)[a], 992 (−2.51)[a], 960 (−2.45)[a], $P = 1150 \pm 47$, $D = 0.01 \pm 0.04$
Neat acid	$d(\log [\mathrm{HA}]_{ta})$ 1156 (−2.27)

[a] Data not used in least-squares analysis.



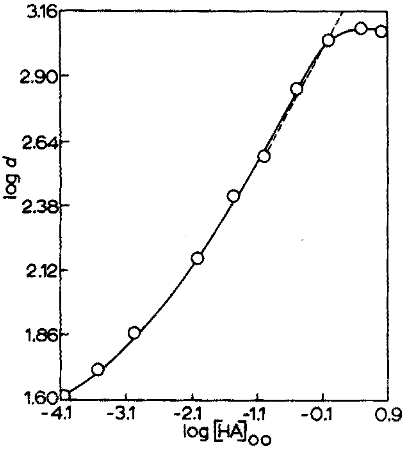
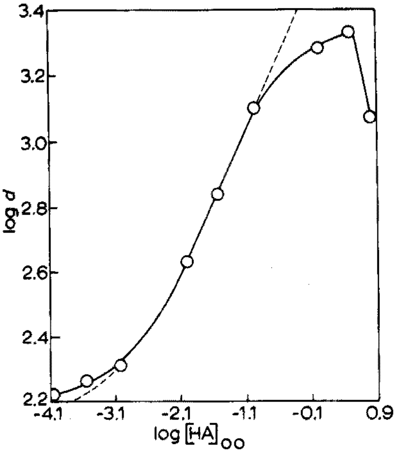


Fig. 1. Plot of log d against log $[\mathrm{HA}]_{oo}$ for the hexane–0.1 M sodium perchlorate system.

Fig. 2. Plot of log d against log $[\mathrm{HA}]_{oo}$ for the benzene–0.1 M sodium perchlorate system.

highest concentration point on each plot represents the pure acid. The dotted lines in Figs. 1–4 represent curves obtained using the calculated values of P and D. In the cases of Figs. 2 and 4, the experimental and theoretical curves fit very well, but in Figs. 1 and 3, a somewhat better fit over the entire range of data is obtained when a P value of 4.58 and a D value of 6430 are used for the hexane system, and a P value of 155 and a D value of 260 for the chloroform system.



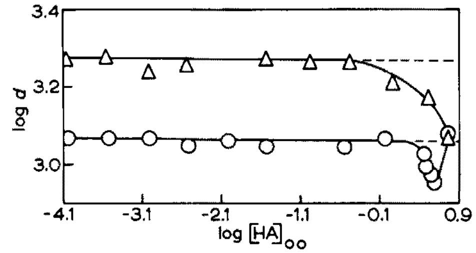


Fig. 3. Plot of log d against log $[HA]_{oo}$ for the chloroform–0.1 M sodium perchlorate system.

Fig. 4. Plots of log d against log $[HA]_{oo}$ for the 1-hexanol–0.1 M sodium perchlorate system (△) and for the 4-methyl-2-pentanone–0.1 M sodium perchlorate system (○).

REMARKS

The five systems investigated are representative of three groups of organic solvents found in most extraction work. Representative of the group capable of strong hydrogen bonding with octanoic acid are 1-hexanol and 4-methyl-2-pentanone. No dimerization occurs at acid concentrations up to about $10^{-0.5}$ M, but at higher concentrations acid–acid association begins to compete with solvent–acid association. The relatively high values of P in these systems indicate the existence of strong solvent–acid association in competition with water–acid association. The authors are unable to explain the strange high-concentration dip in the 4-methyl-2-pentanone curve.

Hexane and heptane as investigated by GOODMAN[4] represent the group of solvents in which the acid tends to dimerize considerably. There is a marked breaking of the dimer only as the octanoic acid concentration undergoes considerable decrease. Chloroform and benzene represent solvents with intermediate D and P values. In the systems studied, it is to be noted that as the P value falls, the D value rises, these trends reflecting strong organic solvent–acid associations for high P values and strong acid–acid associations for high D values. In all cases, water–acid association seems to be the weakest type of association.

SUMMARY

The partition and dimerization constants of octanoic acid between five organic solvents and 0.1 M sodium perchlorate solution have been measured over the organic concentration range of $10^{-4.1}$–$10^{0.9}$ M with carbon-14 labelled acid. The partition and dimerization constants for the five organic solvent systems were determined to be 1830 ± 85 and negligible for 1-hexanol, 1150 ± 47 and negligible for 4-methyl-2-pentanone, 148 ± 15 and 286 ± 18 for chloroform, 47 ± 6 and 320 ± 86 for benzene, and 4.6 ± 0.4 and 5940 ± 1890 for hexane.

RÉSUMÉ

Les constantes de partage et de dimérisation de l'acide octanoïque réparti entre 5 solvants organiques et une solution 0.1 M de perchlorate de sodium ont été mesurées; les concentrations dans les solvants organiques étaient comprises dans un domaine s'étendant de $10^{-4.1}$ à $10^{0.9}$ M avec un acide marqué au carbone 14. Les constantes de partage et de dimérisation pour les 5 systèmes de solvants organiques ont été déterminées; les résultats sont: 1830 ±85 et négligeable pour le 1-hexanol, 1150 ±47 et négligeable pour la 4-méthyl-2-pentanone, 148 ±15 et 286 ±18 pour le chloroforme, 47 ±6 et 320 ±86 pour le benzène, 4.6 ±0.4 et 5940 ±1890 pour l'hexane.

ZUSAMMENFASSUNG

Die Verteilungs- und Dimerisationskonstanten von Oktansäure zwischen 5 organischen Lösungsmitteln und 0.1 M Natriumperchloratlösung wurden gemessen bei Konzentrationen des organischen Stoffes von $10^{-4.1}$ bis $10^{0.9}$ M unter Verwendung von C-14 markierter Säure. Die Verteilungs- und Dimerisations-Konstanten für die 5 organischen Lösungsmittelsysteme wurden bestimmt zu: 1830±85 und vernachlässigbar für 1-Hexanol; 1150±47 und vernachlässigbar für 4-Methyl-2-pentanon; 148±15 und 286±18 für Chloroform; 47±6 und 320±86 für Benzol; 4.6±0.4 und 5940±1890 für Hexan.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE EXTRACTION OF URANIUM(VI) AND COBALT(II) FROM HYDROCHLORIC ACID SOLUTIONS BY CYCLOHEXYL- AND BENZYL ALKYLAMINES

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(Received October 9th, 1968)

The extractions of uranium(VI) and cobalt(II) from hydrochloric acid solutions by long-chain aliphatic amines have been described in previous papers[1]. The author has also investigated the extraction of uranium(VI) from sulphuric and nitric acid solutions by cyclohexyl- and benzylalkylamines[2]. In the present paper, the extraction of uranium(VI) and cobalt(II) from hydrochloric acid solutions by these amines is described.

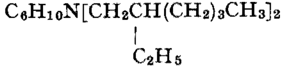
EXPERIMENTAL

Reagents

The amines listed in Table I were of high purity, and were used without further purification. They were diluted with various organic solvents, and were not pre-equili-

TABLE I

CYCLOHEXYL- AND BENZYLALKYLAMINES[a] USED AS EXTRACTANTS

Amine	*Abbreviation*	*Structure*
N-Cyclohexyl-*n*-octyl	COA	$C_6H_{10}NH(CH_2)_7CH_3$
N-Cyclohexyl-*n*-dodecyl	CDA	$C_6H_{10}NH(CH_2)_{11}CH_3$
N-Cyclohexyl-2-ethylhexyl	CEHA	 $C_6H_{10}NHCH_2\underset{C_2H_5}{\underset{\vert}{CH}}(CH_2)_3CH_3$
N-Cyclohexyl-di-(*n*-dodecyl)	CDDA	$C_6H_{10}N[(CH_2)_{11}CH_3]_2$
N-Cyclohexyl-di-(2-ethylhexyl)	CDEHA	 $C_6H_{10}N[CH_2\underset{C_2H_5}{\underset{\vert}{CH}}(CH_2)_3CH_3]_2$
N-Benzyl-*n*-dodecyl	BDA	$C_6H_5CH_2NH(CH_2)_{11}CH_3$
N-Benzyl-2-ethylhexyl	BEHA	 $C_6H_5CH_2NHCH_2\underset{C_2H_5}{\underset{\vert}{CH}}(CH_2)_3CH_3$
N-Benzyl-di-(*n*-octyl)	BDOA	$C_6H_5CH_2N[(CH_2)_7CH_3]_2$
N-Benzyl-di-(*n*-dodecyl)	BDDA	$C_6H_5CH_2N[(CH_2)_{11}CH_3]_2$
N-Benzyl-di-(2-ethylhexyl)	BDEHA	 $C_6H_5CH_2N[CH_2\underset{C_2H_5}{\underset{\vert}{CH}}(CH_2)_3CH_3]_2$
N,N-Dibenzyl-*n*-dodecyl	DBDA	$(C_6H_5CH_2)_2N(CH_2)_{11}CH_3$

[a] All amines were obtained from the Yoshitomi Pharmaceutical Industries, Ltd., and BDA, BDDA and DBDA from the Kao Soap Co., Ltd.

brated with hydrochloric acid solutions. The uranyl or cobalt chloride solutions were prepared by dissolving uranyl chloride dihydrate or cobalt chloride hexahydrate in hydrochloric acid solution of the required concentration. The other chemicals were of analytical-reagent grade.

Extraction and analytical procedures

The procedure for obtaining partition coefficients (the ratio of the equilibrium concentration of uranium or cobalt in the organic phase to that in the aqueous phase $[U]_{org}/[U]_{aq}$ or $[Co]_{org}/[Co]_{aq}$) was as described in the extraction of thorium nitrate solutions with long-chain aliphatic amines[3]: the amine solution in the organic solvent (20 ml) and uranyl or cobalt chloride solution (20 ml) containing hydrochloric acid were shaken for 10 min, and then uranium or cobalt was stripped from the organic phase with 1 *M* hydrochloric acid.

Uranium(VI) and cobalt(II) were determined by titration with EDTA and xylenol orange as indicator[4]: for uranium, an excess of EDTA and ascorbic acid were added to form the uranium(VI)–EDTA complex in boiling solution, and the free EDTA was back-titrated with thorium nitrate solution at pH 2–3; for cobalt, the aqueous solution, adjusted to pH 5.1–5.3 with hexamethylenetetramine, was titrated with EDTA.

RESULTS AND DISCUSSION

Extraction efficiency of various systems

The extractions of uranyl and cobalt chloride solutions containing hydrochloric acid at constant concentration (5 g/l as UO_2Cl_2 in 10 *M* hydrochloric acid and 1 g/l as $CoCl_2$ in 8 *M* hydrochloric acid, respectively) with 0.1 *M* solution of amines in benzene or chloroform at 20° gave the results shown in Table II. These show that cyclohexyl- and benzylalkyl tertiary amines are more efficient extractants for uranium and cobalt than secondary amines. The efficiency is increased with the chain length of the alkyl

TABLE II

EXTRACTION OF URANIUM(VI) FROM 10 *M* HYDROCHLORIC ACID SOLUTION AND OF COBALT(II) FROM 8 *M* HYDROCHLORIC ACID SOLUTION BY 0.1 *M* SOLUTIONS OF CYCLOHEXYL- AND BENZYLALKYL-AMINES

Amine	*Partition coefficient*			
	Uranium		*Cobalt*	
	Benzene	*Chloroform*	*Benzene*	*Chloroform*
COA	15.0	0.262	—	—
CDA	16.4	0.273	4.85	0.031
CEHA	6.10	0.220	0.441	0.004
CDDA	17.7	0.877	7.46	0.042
CDEHA	—[a]	0.843	3.21	0.005
BDA	—[a]	0.444	—[a]	0.056
BEHA	6.51	0.364	1.16	0.026
BDOA	25.0	1.14	—	—
BDDA	29.8	1.61	15.9	0.075
BDEHA	—[a]	1.41	5.55	0.052
DBDA	—[a]	1.09	—	—

[a] Third phase was formed.

group and is reduced when the alkyl chain is branched; a benzyl group is essential for promoting the extraction efficiency. It also appears that the extraction efficiency of cyclohexyl- and benzylalkylamines for uranium(VI) is greater than that for cobalt-(II). Further, it can be inferred that the uranium extraction of cyclohexyl- and benzylalkylamines is influenced by the organic solvent used as diluent. This point is clarified by some representative results for various CDDA–organic solvent systems in the extraction of uranyl chloride solutions (5 g/l) containing 4 *M* hydrochloric acid or a mixture of 0.1 *M* hydrochloric acid and 4 *M* lithium chloride at 20° (Table III). From this it can be seen that the extraction efficiency of CDDA for uranium is reduced with halogen-substituted hydrocarbons; in particular, chloroform is a very poor extractant. Similar effects are also observed in the extractions of aqueous solutions containing 1 g/l of cobalt chloride in 0.2 *M* hydrochloric acid in the presence of 7.8 *M* lithium chloride with 0.1 *M* solutions of cyclohexylalkylamines in various organic solvents at 20° (Table IV). These results are basically in agreement with those obtained in the extraction of cobalt by aliphatic amines[1].

TABLE III

EXTRACTION OF URANIUM(VI) FROM DIFFERENT SOLUTIONS WITH 0.1 *M* CDDA IN VARIOUS ORGANIC SOLVENTS

Diluent	*Partition coefficient*	
	4 M HCl	*0.1 M HCl + 4 M LiCl*
Carbon tetrachloride	5.37	5.32
Benzene	13.5	7.25
Toluene	12.5	10.1
Chloroform	0.042	0.040
Chlorobenzene	11.6	1.80
o-Dichlorobenzene	9.55	4.22
1,2-Dichloroethane	6.58	6.32
Nitrobenzene	29.7	4.35

TABLE IV

EXTRACTION OF COBALT(II) FROM 0.2 *M* HYDROCHLORIC ACID SOLUTION IN THE PRESENCE OF 7.8 *M* LITHIUM CHLORIDE WITH 0.1 *M* SOLUTIONS OF CYCLOHEXYLALKYLAMINES IN VARIOUS SOLVENTS

Diluent	*Partition coefficient*			
	CDA	*CEHA*	*CDDA*	*CDEHA*
n-Hexane	0.629	0.520	7.66	5.29
Benzene	5.00	1.10	11.2	3.52
Chloroform	0.019	0.004	0.030	0.007
Chlorobenzene	0.542	0.466	6.77	5.32
o-Dichlorobenzene	0.434	0.366	6.59	4.35
Nitrobenzene	2.19	1.93	11.9	6.28

The extraction of uranium with 0.1 *M* solutions of CDDA, BDDA, CEHA and BEHA in benzene or chloroform at 20° was also examined at varying hydrochloric acid concentrations (Figs. 1 and 2). For the tertiary amine, the partition coefficient rises with the acidity of the aqueous phase at low acidities, then passes through a maximum at an initial hydrochloric acid concentration of *ca.* 7–8 *M*, and then falls at higher acidities. The initial aqueous acidities for the maximum partition coefficient are not greatly influenced by varying the amine concentration; this is shown in Fig. 3 for CDDA. In the extraction of cobalt chloride solutions at 1 g/l with 0.1 *M* solutions of CDDA, CDEHA, BDDA and BDEHA in benzene at 20°, a maximum appears at an initial acidity of 7 *M* (Fig. 4). For the shapes of these curves, the following interpretation is suggested: at low acidities, the increase in the partition coefficient is attributed to the salting-out effect of hydrochloric acid or to the formation of a uranyl or cobalt chloride–hydrochloric acid complex, while at higher acidities the decrease in the partition coefficient arises either from the competition between uranium or cobalt and hydrochloric acid for association with the amine, or from the formation of less readily extractable complexes. In contrast, as shown in Figs. 1 and 2, although the partition coefficients with the secondary amines in benzene and with the various amines in chloroform increase with aqueous acidity in the region of hydrochloric acid concentrations illustrated, it is assumed that the decrease in the partition coefficient caused by the hydrochloric acid competition for association with amine appears at higher acidities for secondary amines than for tertiary amines.

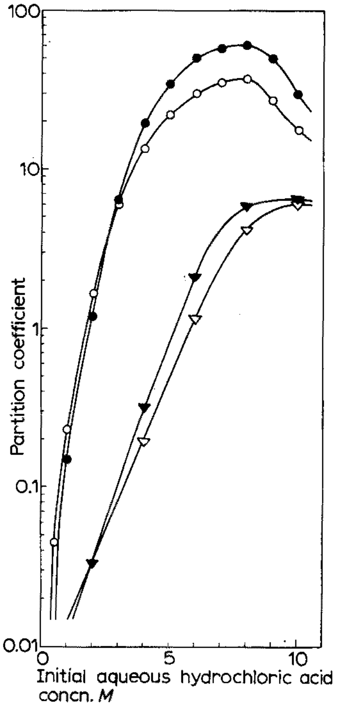


Fig. 1. Extraction of uranium(VI) from hydrochloric acid solutions with 0.1 *M* solutions of various amines in benzene (○ CDDA, ▽ CEHA, ● BDDA, ▼ BEHA).

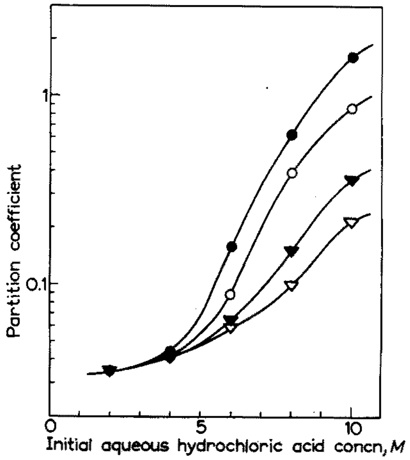
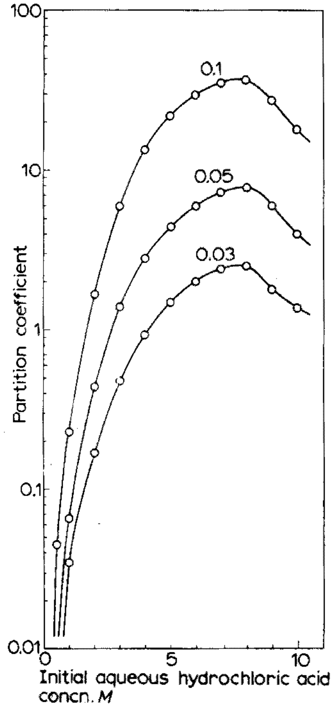


Fig. 2. Extraction of uranium(VI) from hydrochloric acid solutions with 0.1 *M* solutions of various amines in chloroform (○ CDDA, ▽ CEHA, ● BDDA, ▼ BEHA).



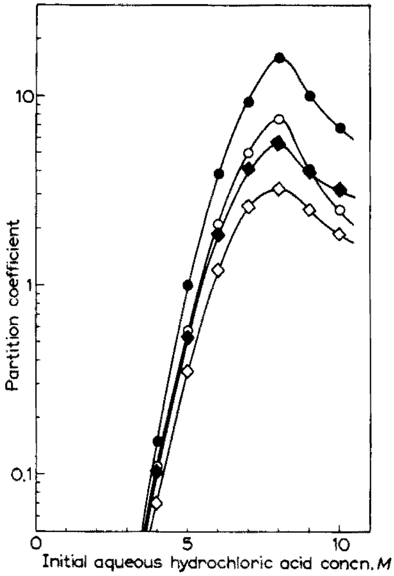


Fig. 3. Extraction of uranium(VI) from hydrochloric acid solutions with solutions of CDDA in benzene (numbers on curves are amine concentrations, M).

Fig. 4. Extraction of cobalt(II) from hydrochloric acid solutions with 0.1 M solutions of various amines in benzene (○ CDDA, ◇ CDEHA, ● BDDA, ◆ BDEHA).

Extraction in the presence of lithium chloride

The results for the extraction of uranyl chloride solutions (5 g/l) containing 0.1 M hydrochloric acid and lithium chloride at various concentrations, with 0.03 M CDDA in benzene at 20° are compared with those for similar extractions from hydrochloric acid solutions of different acidities in Fig. 5 (a). It can be seen that the partition coefficient in the presence of hydrochloric acid passes through a maximum; when part of the hydrochloric acid in the aqueous phase is replaced by lithium chloride, the partition coefficient rises with the total chloride concentration. The replacement of hydrochloric acid in the aqueous phase by lithium chloride checks the decrease in the partition coefficient, probably because of the removal of hydrochloric acid which competes for association with the amine. Furthermore, in the distribution of chloride ion between mixed 0.1 M hydrochloric acid and lithium chloride solutions at various concentrations, in the absence of uranium, and benzene solutions of 0.1 M CDDA, the chloride concentration of the organic phase was not influenced by the presence of lithium chloride. It is thus expected that the lithium chloride, which is virtually unextractable by amine, itself acts as a salting-out agent. Similar results were also obtained in the extraction of cobalt chloride solutions (1 g/l) containing 0.2 M hydrochlorid acid and lithium chloride at various concentrations by 0.1 M CDDA or BDDA in benzene (Fig. 5 (b)).

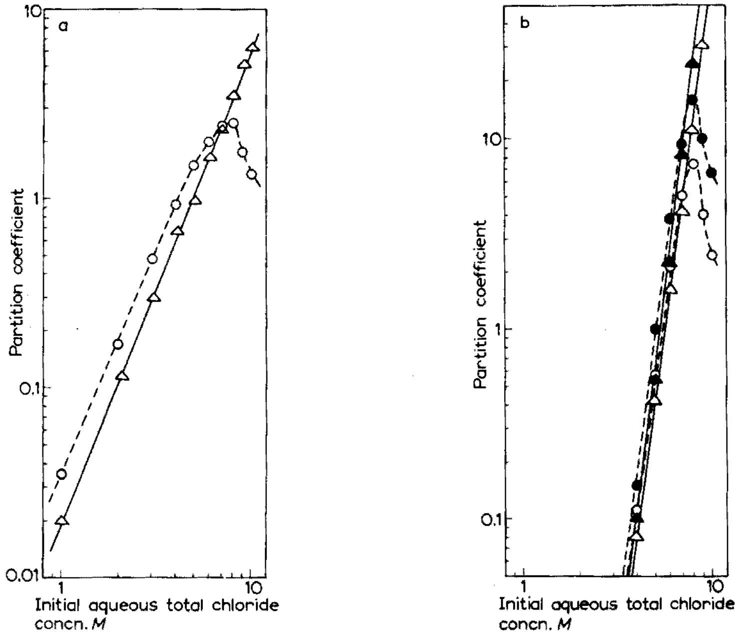


Fig. 5. Salting-out effect of both hydrochloric acid and lithium chloride in the extraction of uranium-(VI) with 0.03 M CDDA in benzene, and of cobalt(II) with 0.1 M CDDA or BDDA in benzene. △ CDDA and ▲ BDDA in the presence of hydrochloric acid at constant concentration (0.1 and 0.2 M HCl for uranium and cobalt, respectively) and lithium chloride; ○ CDDA and ● BDDA in the presence of hydrochloric acid only. (a) Uranium, (b) cobalt.

Dependence on concentrations of amine and uranium or cobalt

If it is assumed that the increase in the partition coefficient with cyclohexyl- and benzylalkylamines at low aqueous acidities is governed by a solvating reaction similar to that in the extraction of uranium(VI) or cobalt(II) by tri-*n*-octylamine (TOA)[5], *viz.*

$$UO_2Cl_2\,(a) + n\,R_2R'NHCl\,(o) \rightleftharpoons (R_2R'NH)_nUO_2Cl_{n+2}\,(o) \qquad (1)$$

where R is an alkyl group, and (a) and (o) represent aqueous and organic phases respectively, the following relationship would be expected:

$$\log E_a{}^\circ = \log K + n \log (C_A - nC_U) \qquad (2)$$

in which $E_a{}^\circ$ is the partition coefficient, K the equilibrium constant, C_A the total amine concentration and C_U the uranium concentration of the organic phase. From a log–log plot of $E_a{}^\circ$ *vs.* $(C_A - n\,C_U)$ in 2 and 4 M acidities (Fig. 6), it was found that eqn. (2) is satisfied for $n = 2$, the slopes of the lines being 2.0 and 1.7 for CDDA, and 1.65 and 2.0 for BDDA in 2 and 4 M hydrochloric acid, respectively. This suggests that each uranium ion is associated with two amine molecules. It is thus inferred that $n = 2$ in eqn. (1), *i.e.*

$$UO_2Cl_2\,(a) + 2R_2R'NHCl\,(o) \rightleftharpoons (R_2R'NH)_2UO_2Cl_4\,(o) \qquad (3)$$

In the extraction of cobalt, the slope of a log–log plot of $E_a{}^\circ$ *vs.* $(C_A - nC_{Co})$, where C_{Co} is the cobalt concentration of the organic phase, is 1.6 and 1.75 for CDDA, and

1.8 and 1.85 for BDDA in 8 *M* hydrochloric acid and 0.2 *M* hydrochloric acid in the presence of 7.8 *M* lithium chloride, respectively, by using $n = 2$. From this it is considered that the following equilibrium expression, similar to the case of uranium, is valid for the extraction of cobalt:

$$CoCl_2\,(a) + 2R_2R'NHCl\,(o) \rightleftharpoons (R_2R'NH)_2CoCl_4\,(o) \qquad (4)$$

Furthermore, the uranium concentration of the organic phase as a function of initial aqueous uranium concentration at 8 *M* hydrochloric acid or 0.1 *M* hydrochloric acid in the presence of 8 *M* lithium chloride, with 0.1 *M* CDDA in benzene at 20°, approaches a limiting value (~0.05 *M*) as shown in Fig. 7. This supports the association number of amine for uranium obtained from the solvent dependency. In these extractions, when the mole ratio of the increase in the chloride concentration of the organic phase to the concentration of uranium extracted into the organic phase, was plotted at different aqueous uranium concentrations, a value of nearly two was obtained, based on the extraction of uranyl chloride. Similar results were also obtained in the extraction of cobalt from 8 *M* hydrochloric acid solution or 0.2 *M* hydrochloric acid solution in the presence of 7.8 *M* lithium chloride with 0.1 *M* solution of CDDA or BDDA in benzene (Table V).

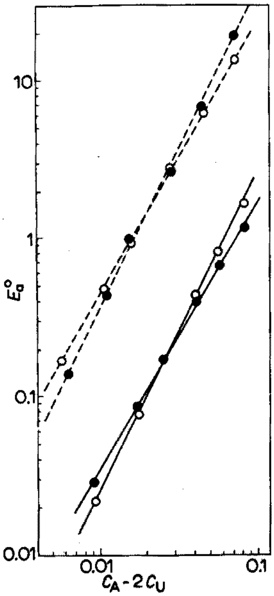


Fig. 6. Solvent dependence of partition coefficient for the extraction of uranium(VI) from hydrochloric acid solutions with CDDA or BDDA (○ CDDA, ● BDDA; continuous and broken lines represent the values for 2 and 4 *M* hydrochloric acid, respectively).

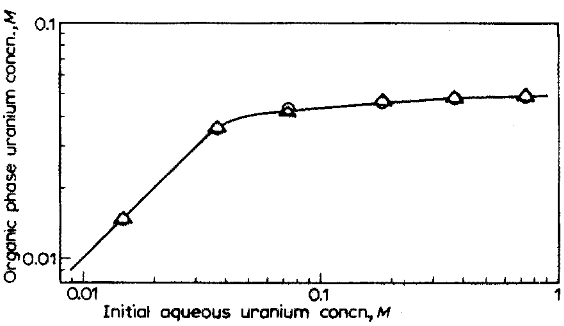


Fig. 7. Variation in uranium concentration of organic phase with initial aqueous uranium concentration for the extraction of uranium(VI) from hydrochloric acid solutions with 0.1 *M* CDDA in benzene (0.8 *M* hydrochloric acid, 0.1 *M* hydrochloric acid plus 8 *M* lithium chloride).

TABLE V

VARIATION IN COBALT CONCENTRATION OF ORGANIC PHASE WITH INITIAL AQUEOUS COBALT CONCENTRATION FOR THE EXTRACTION OF COBALT(II) FROM DIFFERENT SOLUTIONS WITH 0.1 *M* CDDA OR BDDA IN BENZENE

Initial aqueous cobalt concn. (M)	*Cobalt concentration of organic phase (M)*			
	CDDA		*BDDA*	
	8 M HCl	*0.2 M HCl + 7.8 M LiCl*	*8 M HCl*	*0.2 M HCl + 7.8 M LiCl*
0.0078	0.0068	0.0072	0.0074	0.0074
0.019	0.015	0.017	0.018	0.018
0.038	0.028	0.031	0.031	0.033
0.096	0.039	0.041	0.041	0.042
0.19	0.042	0.045	0.043	0.045
0.48	0.045	0.048	0.046	0.048
0.96	0.049	0.050	0.050	0.050

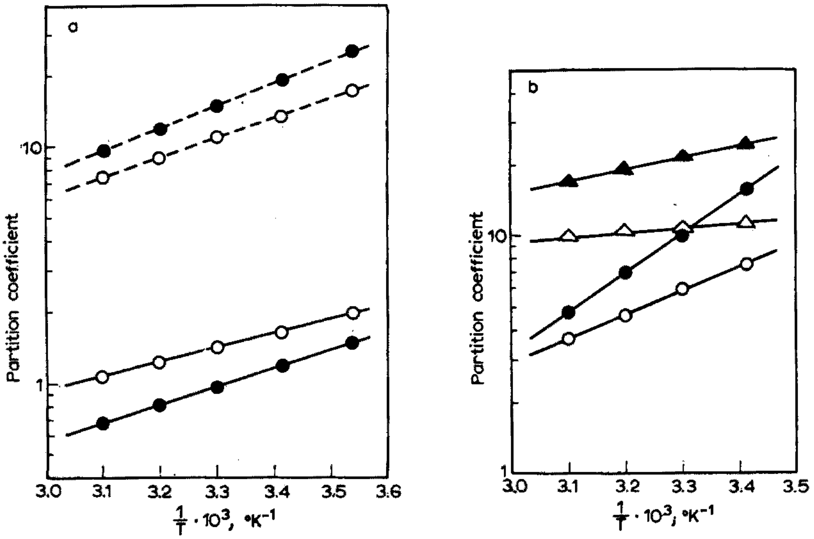


Fig. 8. Temperature dependence of partition coefficient for the extraction of uranium(VI) and cobalt(II) from hydrochloric acid solutions with 0.1 *M* CDDA or BDDA in benzene. The logarithm of the partition coefficient is plotted against the reciprocal of the absolute temperature.
(a) Uranium (○ CDDA, ● BDDA; continuous and broken lines represent the values of 2 and 4 *M* hydrochloric acid, respectively);
(b) cobalt (○ CDDA and ● BDDA in 8 *M* hydrochloric acid; △ CDDA and ▲ BDDA in 0.2 *M* hydrochloric acid plus 7.8 *M* lithium chloride).

Temperature effect

The extraction of uranyl chloride solutions (5 g/l) containing 2 or 4 *M* hydrochloric acid with 0.1 *M* solution of CDDA and BDDA in benzene was carried out at temperatures between 10 and 50°. The extraction of cobalt chloride (1 g/l) in 8 *M* hydrochloric acid or a mixture of 0.2 *M* hydrochloric acid and 7.8 *M* lithium chloride was studied similarly. The results (Fig. 8) show that the partition coefficients decrease with rising temperature. The heats of reaction (change in enthalpy) (in kcal/mol) for eqns. (3) and (4) were estimated: for uranium, these were found to be 3.3 and 3.9 with

CDDA, and 3.9 and 4.4 with BDDA in 2 and 4 M HCl, respectively; for cobalt, 4.6 and 1.0 with CDDA, and 7.7 and 2.3 with BDDA in 8 M HCl and 0.2 M HCl+7.8 M LiCl, respectively. As the values are close to those for the energy of hydrogen bonds, it is postulated that the nature of the bonding in the organic phase is similar to that for hydrogen bonds.

The author wishes to thank Miss S. HAMANO and Mr. K. NAKAJIMA for experimental assistance, and the Yoshitomi Pharmaceutical Industries, Ltd. and Kao Soap Co., Ltd. for samples of various amines. He would also like to thank Professor M. L. GOOD of Louisiana State University in New Orleans, for interest in this study.

SUMMARY

The partition of uranium(VI) and cobalt(II) between hydrochloric acid solutions and solutions of cyclohexyl- and benzylalkylamines in benzene has been investigated at different conditions. The effects of amine structure and organic solvent on the extractions have also been examined. It is found that cyclohexyl- and benzylalkyl tertiary amines are more efficient extractants for uranium and cobalt than secondary amines; a benzyl group is essential for promoting the extraction efficiency; the efficiency is reduced when the alkyl chain is branched and is strongly influenced by the kind of organic solvent used as diluent.

RÉSUMÉ

On examine le partage de l'uranium(VI) et du cobalt(II) entre des solutions d'acide chlorhydrique et des solutions de cyclohexyl- et benzylalkylamines dans le benzène, dans différentes conditions. On examine également l'influence de la structure de l'amine et du solvant organique sur les extractions. On constate que les amines tertiaires cyclohexyl- et benzylalcoyle sont de meilleurs réactifs d'extraction pour l'uranium et le cobalt que les amines secondaires. Le groupe benzyle est essentiel pour élever le rendement d'extraction, ce rendement diminue lorsqu'une chaine alcoyle est branchée et est fortement influencé par la nature du solvant organique utilisé comme diluant.

ZUSAMMENFASSUNG

Die Verteilung von Uran(VI) und Cobalt(II) zwischen salzsauren Lösungen und Lösungen von Cyclohexyl- und Benzyl-Alkylaminen in Benzol wurde unter verschiedenen Bedingungen untersucht. Der Einfluss der Aminstruktur und des organischen Lösungsmittels auf die Extraktionen wurden ebenfalls geprüft. Es wurde gefunden, dass tertiäre Cyclohexyl- und Benzyl-Alkylamine wirksamere Extraktionsmittel für Uran und Cobalt sind als sekundäre Amine. Eine Benzylgruppe ist wesentlich für die Verbesserung der Extraktion. Die Wirksamkeit der Extraktion wird verringert, wenn die Alkylkette verzweigt ist und wird stark beeinflusst durch die Art des organischen Lösungsmittels.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DISTRIBUTION COEFFICIENTS AND THE CATION-EXCHANGE BEHAVIOUR OF ELEMENTS IN HYDROCHLORIC ACID–ETHANOL MIXTURES

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(Received November 4th, 1968)

KEMBER *et al.*[1] probably were the first to employ addition of water-miscible non-aqueous solvents to promote metal–halide complex formation for the selective elution of transition metal ions from cation-exchange resins, while the first systematic survey of cation-exchange distribution coefficients in partly organic solvents has been carried out by FRITZ AND RETTIG[2], who have investigated the exchange behaviour of 14 elements in hydrochloric acid–acetone media. A more comprehensive survey has been undertaken recently by KORKISCH AND AHLUWALIA[3], who determined distribution coefficients for 20 elements in hydrochloric acid containing methanol, ethanol, *n*-propanol, isopropanol, methyl glycol, acetic acid, tetrahydrofuran and acetone as organic solvents. The concentration of hydrochloric acid in these systematic investigations[2,3] has been limited to an upper value of 1.0 and 1.2 M, respectively, and attention has been focussed mainly on elements with differences in their tendencies to form chloride complexes which promised spectacular increases in selectivities. Generally, the effect of increasing amounts of the organic solvent is a reduction of the concentration of water molecules around the cations, a decrease in the forces binding the coordinated hydration shell, and a decrease in the size of the outer hydration cloud. One consequence of this is that metal chloride anions are formed at lower concentrations of hydrochloric acid while, generally, the differences in tendencies to chloride-complex formation are enhanced. Although several investigations of the ion-exchange behaviour of small numbers of elements with negligible tendencies to chloride-complex formation have been carried out in partly non-aqueous media[4–11], another consequence of the underlying physicochemical aspects often does not seem to have been fully appreciated. Because the forces binding the hydration cloud depend on the charge density of the cation, they will decrease with an increase in volume for elements in a periodic group. Selective destruction of the hydration cloud will therefore start at a lower organic solvent concentration for the larger cation. As a result, the larger cation (unhydrated size) will enter the resin relatively more easily and differences between distribution coefficients of elements of the same periodic group will be enhanced, provided that other effects are absent. Since the distribution coefficients are measured against H_3O^+, the most strongly hydrated of the cations, they have higher values in partly organic solvents than in aqueous solutions, provided that the effect of chloride-complex formation is negligible. Favourable conditions for separations of elements with negligible tendencies to chloride-complex formation therefore require partly non-aqueous solutions with concentrations of hydrochloric acid which are higher than those at which separations in aqueous solutions are carried out. The range of these concentrations has not been covered in the studies mentioned above[2,3]. Furthermore, only a limited number of elements has been investigated. This paper therefore presents distribution coefficients for 45 elements covering the acid concentration range from 0.1 to 3.0 *M* hydrochloric acid in water–ethanol mixtures, and discusses some of their exchange properties and possibilities for separations.

EXPERIMENTAL

Reagents and apparatus

The resin used was the AG50W-X8 sulphonated polystyrene cation exchanger (100–200 or 200–400 mesh particle size; Bio-Rad Laboratories, Richmond, California). Borosilicate glass tubes of 20 mm i.d. with fused-in glass sinters of No. 2 porosity and a burette tap at the bottom and a B19 ground-glass joint at the top, were used as columns.

Analytical-reagent grade chemicals were used whenever possible. Chlorides of the platinum metals, and of gold, germanium, gallium and indium, and scandium and gadolinium oxides were obtained from Fluka A.G., Buchs, Switzerland. Standard chloride solutions of V(V), Mo(VI), W(VI), As(III) and Se(IV) were prepared by

TABLE I

CATION-EXCHANGE DISTRIBUTION COEFFICIENTS IN 0.10 *M* HCl

Element	*Percentage ethanol*						
	0	*20*	*40*	*60*	*80*	*90*	*95*
Ga(III)	$\sim 10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	6730	153
Sn(IV)	$\sim 10^4$	ppt.	ppt.	ppt.	43.1	3.5	1.1
Fe(III)	9000	$>10^4$	$>10^4$	$>10^4$	$>10^4$	3340	176
U(VI)	758	1300	3200	$>10^4$	$>10^4$	4960	3330
Mn(II)	1360	1580	3020	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Co(II)	1270	1450	2840	6500	$>10^4$	$>10^4$	$>10^4$
Ni(II)	1230	1470	2950	10^4	$>10^4$	$>10^4$	$>10^4$
Fe(II)	1220	1410	2830	6400	$>10^4$	9800	1010
Zn(II)	1030	1200	2150	2250	876	47.5	5.7
Cu(II)	1010	1200	2190	4410	4280	1250	430
Mg(II)	860	990	$>10^3$	$>10^3$	$>10^3$	$>10^4$	$>10^4$
In(III)	806	210	193	153	83	29.2	6.3
Cd(II)	410	367	332	317	123	81	20.8
Mo(VI)	10.9	35.0	43.0	39.8	36.1	38.8	40.9
Rh(III)	4.2	3.1	2.2	1.5	0.9	0.6	<0.5
Tl(III)	2.1	2.4	2.7	1.9	2.2	2.6	2.4
Hg(II)	1.6	1.1	0.8	0.6	<0.5	<0.5	<0.5
Pd(II)	1.6	0.8	1.0	0.8	0.9	0.7	0.5
Pt(IV)	1.4	1.5	1.6	2.1	2.7	3.1	3.4
As(V)	1.4	~ 2	~ 5	~ 3	<1	<1	<1
Ir(IV)	1.4	1.5	1.4	1.3	1.0	1.1	0.9
W(VI)[a]	1.1	1.3	1.7	1.8	8.1	3.0	—
Se(IV)	1.1	1.3	1.0	1.5	1.7	1.0	0.8
Au(III)	0.8	1.1	0.9	1.2	1.3	0.8	1.0
Ge(III)	0.5	0.6	0.4	0.5	1.7	1.8	1.7
Mo(VI)[a]	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

[a] H_2O_2 present.

TABLE II

CATION-EXCHANGE DISTRIBUTION COEFFICIENTS IN 0.20 *M* HCl

Element	*Percentage ethanol*						
	0	*20*	*40*	*60*	*80*	*90*	*95*
Fe(III)	3400	3600	5100	6000	1410	31.7	15.7
Ga(III)	3040	8680	$>10^4$	$>10^4$	3860	446	6.9
Mn(II)	510	690	1240	2280	5280	5410	4260
Co(II)	460	625	1120	2160	5010	$>10^4$	9330
Ni(II)	450	610	1110	2140	4960	8380	6320
Fe(II)	430	580	1020	2010	4370	1460	249
Cu(II)	380	424	706	1060	1040	308	69
Zn(II)	361	368	489	299	48.3	5.2	1.7
Mg(II)	350	361	369	1510	1990	6400	5100
U(VI)	252	284	469	847	1270	1430	1133
In(III)	110	53	48.8	38.1	17.9	6.0	2.9
Cd(II)	84	118	88	34.8	13.7	2.7	0.6
Sn(IV)	45	3400	1610	18.1	3.6	0.7	0.5
V(V)	7.0	19.7	39.1	84.0	202	ppt.	ppt.
V(V)[a]	6.5	6.6	9.0	57	488	529	336
Mo(VI)	4.5	17.7	25.9	25.7	23.1	12.6	7.4
Mo(VI)[a]	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

[a] H_2O_2 present.

TABLE III

CATION-EXCHANGE DISTRIBUTION COEFFICIENTS IN 0.50 *M* HCl

Element	*Percentage ethanol*					
	0	*20*	*40*	*60*	*80*	*90*
Ga(III)	260	633	1470	4650	428	3.5
Fe(III)	225	226	304	361	153	6.6
Mn(II)	84	90	162	285	608	730
Mg(II)	74	78	126	234	601	1140
Cr(III)	73	93	118	170	279	421
Co(II)	72	93	159	305	671	1830
Ni(II)	70	96	165	315	689	880
Fe(II)	66	69	131	252	408	136
Cu(II)	65	88	119	176	195	35.9
U(VI)	58	67	111	182	264	220
Zn(II)	64	64	48.3	17.8	4.1	1.5
Cs(I)	44.2	63	108	229	852	—
V(IV)	44.1	53	84	157	286	508
Be(II)	42.3	47.3	69	114	170	—
Ti(IV)	39.1	121	265	634	1700	ppt.
Rb(I)	33.2	42.8	73	165	571	—
K(I)	29.1	47.3	89	201	838	—
Na(I)	13.5	19.1	34.1	79	254	—
Li(I)	8.1	10.8	17.1	28.8	50	—
In(III)	7.6	7.8	8.5	7.2	4.2	2.4
Cd(II)	6.5	6.0	4.6	1.4	<0.5	<0.5
Sn(IV)	6.2	5.9	3.6	2.2	1.3	0.6
V(V)	5.0	19.5	42.6	86	143	142
V(V)[a]	2.1	4.7	23.9	59	129	140
Mo(VI)	<0.5	7.6	11.0	12.8	11.0	7.3
Mo(VI)[a]	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Bi(III)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

[a] H_2O_2 present.

passing aqueous solutions of the ammonium or sodium salts through a cation-exchange column and adding the required amount of standard hydrochloric acid to the eluate. Solutions of tungsten(VI) thus prepared were stable only in the presence of hydrogen peroxide.

Distribution coefficients

The coefficients were determined using 5 meq (related to exchange) amounts of the elements in 250 ml of solution and 2.500 g of AG50W-X8 resin in the hydrogen form which had been dried at 60° in a vacuum pistol with phosphorus pentoxide as drying agent. In the cases of W(VI), Mo(VI) and V(V), marked with a subscript a in the Tables, the solutions also contained 2.5 ml of 30% hydrogen peroxide. After equilibration for 24 h at 25° in a mechanical shaker, the resin was separated from the aqueous phase by filtration and the amounts of the elements in the resin and in solution were determined by appropriate analytical methods. From the results, weight

TABLE IV

CATION-EXCHANGE DISTRIBUTION COEFFICIENTS IN 1.00 *M* HCl

Element	*Percentage ethanol*				
	0	*20*	*40*	*60*	*80*
Gd(III)	183	259	498	1460	$\sim 10^4$
Yb(III)	153	178	331	841	4340
Ba(II)	128	193	615	1920	5140
Sc(III)	120	345	925	3680	$>10^4$
Al(III)	61	74	124	251	502
Sr(II)	60	76	162	543	3490
Ga(III)	42.6	102	204	347	5.8
Ca(II)	41.3	55	106	310	1570
Fe(III)	33.5	31.9	39.4	47.3	6.9
Cr(III)	26.7	35.9	53	83	114
Ni(II)	21.9	19.7	41.8	82	182
Co(II)	21.3	27.6	38.2	78	175
Mn(II)	20.2	28.2	42.4	78	157
Mg(II)	20.1	19.3	33.0	71	166
Fe(II)	19.8	25.8	46.9	81	184
U(VI)	19.2	22.1	34.2	58	70
Cs(I)	19.1	27.0	44.1	96	358
Cu(II)	17.5	17.8	21.9	23.2	24.7
Zn(II)	16.0	9.7	5.3	3.5	2.4
Rb(I)	15.4	21.4	36.8	81	326
K(I)	13.9	20.0	39.3	94	609
Be(II)	13.3	13.5	19.0	31.6	50.5
Ti(IV)	11.9	18.2	57	181	496
V(IV)	7.2	15.4	22.6	38.8	76
Na(I)	6.9	9.7	16.6	36.5	138
Li(I)	3.8	5.1	7.8	13.1	28.8
In(III)	1.8	1.81	1.9	1.3	0.7
Sn(IV)	1.6	1.4	0.8	<0.5	<0.5
Cd(II)	1.6	0.5	0.2	<0.2	<0.2
V(V)	1.1	4.7	10.3	23.1	43.0
Mo(VI)	0.8	4.2	6.9	7.3	5.8
Bi(III)	0.8	0.6	<0.5	<0.5	<0.5
Hg(II)	<0.5	<0.5	<0.5	<0.5	<0.5
Ge(IV)	<0.5	<0.5	<0.5	<0.5	<0.5

equilibrium distribution coefficients

$$D = \frac{\text{amount of element in resin}}{\text{amount of element in solution}} \times \frac{\text{ml of solution}}{\text{g of dry resin}}$$

were calculated. The distribution coefficients in 0.10, 0.20, 0.50, 1.00, 2.00 and 3.00 M hydrochloric acid are presented in Tables I–VI, respectively. Coefficients for solutions containing no ethanol have been included for the sake of completeness. Coefficients for elements like the platinum metals and gold which show only very slight absorption in 0.1 M hydrochloric acid were not determined at all higher concentrations, while coefficients for elements which showed very strong absorption at high acid concentration over the whole range of ethanol concentrations were not determined at the lowest acid concentrations.

Elution curves

Three multicomponent elution curves (Figs. 1, 2 and 3) demonstrate how the

TABLE V

DISTRIBUTION COEFFICIENTS IN 2.0 M HCl

Element	*Percentage ethanol*					
	0	*20*	*40*	*60*	*70*	*80*
Zr(IV)	489	925	2720	6400	$>10^4$	$>10^4$
Th(IV)	239	298	672	3170	$>10^4$	$>10^4$
La(III)	48.1	68	143	474	1200	$\sim 10^4$
Gd(III)	36.2	49.8	116	313	610	1280
Ba(II)	36.0	74	197	951	3260	—
Y(III)	29.7	32.4	72	196	490	1800
Sc(III)	28.8	57	140	470	1140	—
Yb(III)	27.4	36.2	59	151	298	—
Sr(II)	17.8	22.3	49.3	192	542	—
Al(III)	12.5	12.7	16.9	44.8	69	118
Ca(II)	12.2	16.3	31.7	90	202	—
Cs(I)	10.4	10.4	17.1	32.6	60	—
Rb(I)	8.1	10.0	16.4	39.6	77	—
Cr(III)	7.9	7.5	12.3	27.2	33.3	—
Ga(III)	7.8	13.5	20.9	6.3	1.5	<0.5
K(I)	7.4	10.0	21.0	54	118	—
Ni(II)	7.2	7.4	11.7	23.1	31.5	47.3
U(VI)	7.0	7.2	10.4	15.6	16.1	15.4
Co(II)	6.7	8.9	15.4	30.4	44.7	—
Mg(II)	6.2	7.2	12.1	23.8	36.2	55
Mn(II)	6.0	7.7	10.6	18.4	26.2	—
Be(II)	5.2	5.6	7.0	10.8	14.9	—
Fe(III)	5.2	5.0	6.2	5.0	3.1	0.6
V(IV)	5.0	5.8	7.6	13.3	16.4	17.8
Cu(II)	4.2	4.2	4.8	5.1	2.8	0.9
Fe(II)	4.1	4.3	6.9	8.5	6.3	1.8
Na(I)	3.8	5.5	8.9	24.5	57	—
Ti(IV)	3.7	3.8	9.8	41.9	88	123
V(V)	<0.5	2.9	5.2	10.3	13.4	—
In(III), Sn(IV) Bi(III), Hg(II) Ge(IV), Mo(VI)[a]	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

[a] H_2O_2 present.

information presented in the Tables can be applied to develop analytical separation procedures.

Fe(III), U(VI), Ca(II), La(III). A solution containing about 1 millimole of each element in 25 ml of 0.2 *M* hydrochloric acid was passed through a column (length 10 cm, diameter 19 mm) of 30 ml (10 g) of AG50W-X8 resin (200–400 mesh, hydrogen form), the cations being absorbed in the top resin layer. The elements were then eluted using the following elution sequence: 250 ml of 1.50 *M* hydrochloric acid in 75% ethanol for iron(III), 300 ml of 3.00 *M* hydrochloric acid in 60% ethanol for uranium-(VI), 250 ml of 3.00 *M* hydrochloric acid in 30% methanol for calcium(II) and 300 ml of 4.0 *M* hydrochloric acid for lanthanum. Before eluents were changed, the solution was allowed to drain to the level of the resin bed. The maximum flow rate attainable with a solution head of 25–30 cm in the column was maintained throughout. This amounted to about 1–1.2 ml/min for the solutions containing a large percentage of ethanol and hydrochloric acid and about 2.5–3.0 ml/min for pure aqueous solutions. Aliquots of 25 ml were taken with an automatic fractionator, and the amounts of elements in the fractions were determined by appropriate analytical procedures. The experimental elution curve is presented in Fig. 1.

TABLE VI

DISTRIBUTION COEFFICIENTS IN 3.0 *M* HCl

Element	*Percentage ethanol*				
	0	*20*	*40*	*60*	*70*
Th(IV)	114	142	363	2360	—
Zr(IV)	61	152	343	2800	ppt.
La(III)	18.8	32.6	72	239	948
Ba(II)	18.5	42.6	143	1340	—
Gd(III)	15.3	22.8	51	178	495
Sc(III)	14.9	30.9	76	281	—
Y(III)	13.6	17.7	32.6	128	288
Yb(III)	12.2	15.2	25.2	76	—
Sr(III)	10.0	13.1	29.8	162	—
Ca(II)	7.3	8.4	17.2	69	—
Cs(I)	5.9	5.7	9.3	19.9	—
Rb(I)	5.3	6.5	10.6	28.7	—
K(I)	4.9	7.1	14.3	40.4	—
Cr(III)	4.8	3.9	4.9	11.4	—
Al(III)	4.7	4.3	7.3	13.2	—
Mg(II)	4.3	3.7	5.9	12.3	—
Co(II)	4.2	3.8	6.2	11.8	—
Mn(II)	3.9	3.5	5.5	8.6	—
Fe(III)	3.6	1.8	2.4	2.2	—
V(IV)	3.5	4.3	5.6	7.4	—
U(VI)	3.5	3.5	5.5	6.3	—
Fe(II)	2.9	3.0	4.1	4.3	—
Na(I)	2.7	3.8	6.8	20.5	—
Ti(IV)	2.4	3.1	5.3	22.1(6.8[a])	—
Ni(II)	2.0	2.1	4.5	6.7	—

[a] H_2O_2 present.

Cd(II), Zn(II), Fe(III), Ca(II), Ba(II). A solution containing 0.5 millimole of each element in 25 ml of 0.1 *M* hydrochloric acid containing 40% ethanol was passed through a pre-equilibrated column of the size and type mentioned above. For the elution of the elements, the following sequence was used: 200 ml of 0.50 *M* hydro-

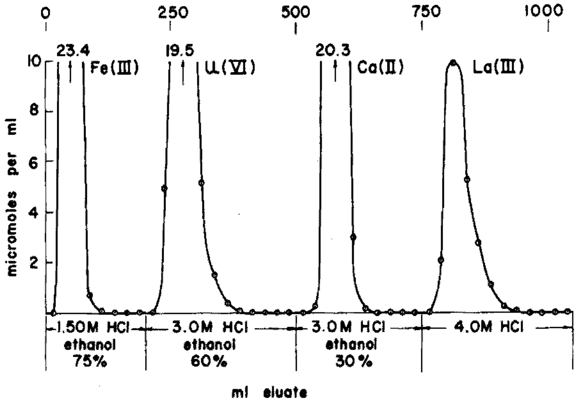

Fig. 1. Elution curve for Fe(III)–U(VI)–Ca(II)–La(III) mixture.

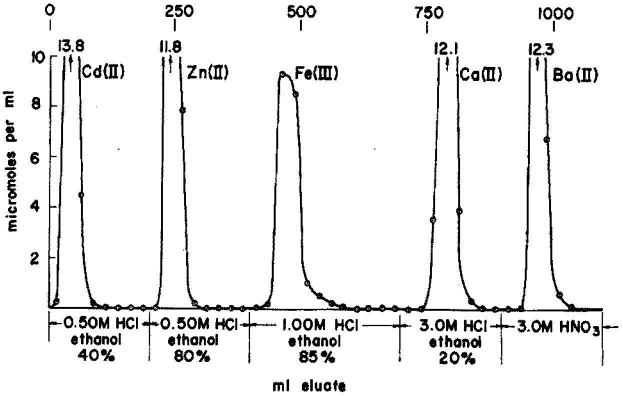

Fig. 2. Elution curve for Cd(II)–Zn(II)–Fe(III)–Ca(II)–Ba(II) mixture.

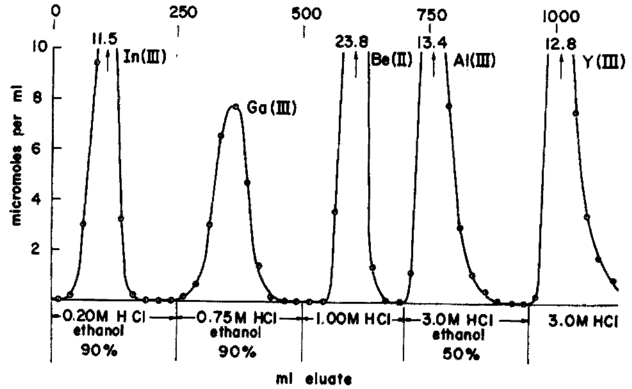

Fig. 3. Elution curve for In(III)–Ga(III)–Be(II)–Al(III)–Y(III) mixture.

chloric acid in 40% ethanol for cadmium(II), 200 ml of 0.5 *M* hydrochloric acid in 80% ethanol for zinc(II); 300 ml of 1.00 *M* hydrochloric acid in 85% ethanol for iron-(III); 200 ml of 3.0 *M* hydrochloric acid in 20% ethanol for calcium(II); and 200 ml of 3.0 *M* nitric acid for barium(II). The flow rates were as described above. The experimental elution curve is presented in Fig. 2.

In(III), Ga(III), Be(II), Al(III), Y(III). A solution containing about 0.7 millimoles of In(III) and Ga(III) and 1 millimole of Be(II), Al(III) and Y(III) in 0.1 *M* hydrochloric acid containing 40% ethanol was passed through a column as described above. The elution sequence was: 250 ml of 0.20 *M* hydrochloric acid in 90% ethanol for indium(III); 250 ml of 0.75 *M* hydrochloric acid in 90% ethanol for gallium(III); 250 ml of 1.00 *M* hydrochloric acid for beryllium(II); 250 ml of 3.0 *M* hydrochloric acid in 50% ethanol for aluminium(III) and 350 ml of 3.0 *M* hydrochloric acid for yttrium-(III). The experimental curve is presented in Fig. 3.

RESULTS AND DISCUSSION

Cation-exchange distribution coefficients in the region from 0.10 to 3.00 *M* hydrochloric acid generally decrease with increasing hydrochloric acid concentration. They increase with increasing concentration of alcohol until the hydration field around the cation is weakened enough so that the water dipoles in the co-ordination shell can be replaced by chloride anions. This causes a sudden decrease in the value of the distribution coefficients. In cases where the tendency to chloride-complex formation is fairly strong, only a slight increase of the coefficients at low alcohol concentration or no increase at all occurs, and the decrease takes place at lower ethanol concentrations. Exchange rates in dilute acid concentrations (< 0.5 *N*) are fast and comparable to those for cation exchange in aqueous solutions. At high acid and alcohol concentrations, the exchange rates seem to be somewhat slower than in aqueous acid and the use of resin of small particle size and slow flow rates often improves chromatographic separations of the strongly absorbed ions, such as Al(III), Ca(II), Sr(II) and Ba(II), considerably.

Alkali metals

Coefficients increase with increasing ethanol concentrations. Those for sodium increase faster than those for lithium and good separations can be obtained by eluting lithium with 1.0 *M* hydrochloric acid in 70% ethanol, while sodium is retained by the column. Separation of the other alkalies from each other is less favourable than in aqueous hydrochloric acid.

Alkaline earths

An excellent separation of calcium from Mg, Al, Fe, Ti and many other elements is possible in 3 *M* hydrochloric acid containing 60% ethanol[12], and barium can be separated from strontium, calcium and many other elements in 3 *M* hydrochloric acid containing 20% ethanol[13]. The separation factors are comparable to those obtained with organic complexing agents. The separation factors of the Mg–Be and Sr–Ca pairs increase only slightly with increase in ethanol concentration and the advantage gained is more than neutralized by the slower exchange rates in solutions containing high concentrations of both hydrochloric acid and ethanol.

Al(III), Ga(III), In(III) and Tl(III)

Tendencies to chloride-complex formation increase with increasing atomic weights and good separations are possible by using the following elution sequence: 0.10 *M* hydrochloric acid containing bromine for thallium(III), 0.20 *M* hydrochloric acid in 90% ethanol for indium(III), 0.75 *M* hydrochloric acid in 90% ethanol for gallium(III) and 3.0 *M* hydrochloric acid for Al(III). Furthermore, aluminium(III) can be separated from Fe(III), Be(II) and U(IV) by eluting these elements with 2 *M* hydrochloric acid in 70% ethanol, and indium(III) can be separated from Cu(II), Co(II), Ni(II), Fe(III) and many other elements by elution with 0.20 *M* hydrochloric acid in 90% ethanol.

Cr(III)

The distribution coefficients are composites of coefficients of different ionic species existing in solution and the composite values depend on the history of the solutions. Different bands, due to the species $[CrCl_3(H_2O)_3]^\circ$ green, $[CrCl_2(H_2O)_4]^+$ green, $[CrCl(H_2O)_5]^{2+}$ dirty blue violet, and $[Cr(H_2O)_6]^{3+}$ red violet, can be observed during column work. The uncharged species passes through the column without absorption, but its presence can be avoided by boiling the solutions in very dilute hydrochloric acid. Coefficients for the other species were estimated from column work to be about 50, 400 and >2000, respectively, in 1.0 *M* hydrochloric acid containing 80% ethanol and 5, 60 and 400 in 2.0 *M* hydrochloric acid containing 60% ethanol. Because the rates of aquo- and chloride-complex formation in ethanolic hydrochloric acid are even slower than in the corresponding aqueous solutions, almost quantitative separation of the different chromium species can be obtained by chromatographic elution, but separation of chromium from most other elements, except Th(IV), Zr(IV), Ba(II) and some rare earths which are strongly absorbed, is prevented by the fact that the different chromium species are eluted under widely different conditions.

V(V), Mo(VI) and W(VI)

Molybdenum(VI) and tungsten(VI) can easily be eluted with 0.1 or 0.2 *M* hydrochloric acid at ethanol concentrations up to 95% and thus be separated from many other elements, provided that hydrogen peroxide also is present. Tungsten(VI) precipitates in the absence of peroxide and molybdenum(VI) shows no agreement between batch distribution coefficients and column behaviour. This apparently is due to the presence of several ionic species with slow conversion reaction rates. Vanadium(V) shows no agreement between distribution coefficients and elution curves in the absence or presence of peroxide. Even with a *D* value of >100 (0.2 *M* hydrochloric acid in 80% ethanol) some vanadium appears in the eluate not far behind the elution front while the bulk remains absorbed at the top of the column and appears in the eluate gradually. This is ascribed to the simultaneous presence of several cationic species such as VO^{3+}, VO_2^+ and their peroxide complexes, and a small amount of neutral species. Effective elution of vanadium(V) can be obtained with 0.01 *M* or more dilute aqueous hydrochloric acid containing a small amount of hydrogen peroxide because only neutral or anionic species are present above pH 2. Alternatively, 0.25 *M* aqueous sulphuric acid or 0.5 *M* aqueous hydrochloric acid containing a small amount of hydrogen peroxide can be used.

Au(III), Pt(IV), Pd(II), Rh(III), Ir(IV), Hg(II) and Ge(IV)

These elements are only very weakly, or not at all, absorbed from all concentrations of hydrochloric acid and ethanol. They can be eluted with aqueous 0.1 *M* hydrochloric acid and thus be separated from most other elements of the periodic table, yet residual traces of rhodium(III) and palladium(II) are retained tenaciously by the resin. Considerably reduced tailing and quantitative elution can be obtained with 0.1 *M* hydrochloric acid in 90 or 95% ethanol as eluent. Rhodium(III) shows two elution peaks on elution with 0.1 *M* hydrochloric acid in 40% ethanol, a large one appearing with the elution front and a small one corresponding to a distribution coefficient of about 10, while only the first elution peak appears in 0.1 *M* hydrochloric acid in 95% ethanol. The two peaks are ascribed to the presence of two different rhodium(III) complexes, probably $[RhCl_3(H_2O)_3]^{\circ}$, not absorbed, and $[RhCl_2(H_2O)_4]^+$, weakly absorbed, which have slow complex conversion rates.

Zn(II), Cd(II) and Sn(IV)

These elements are only very weakly absorbed from 0.2 *M* hydrochloric acid in 90% ethanol and can easily be separated from Cu(II), Co(II), Ni(II), Mn(II), Fe(III), U(VI) and many others by elution with this reagent.

Fe(III)

Iron(III) can be eluted with 1.0 *M* hydrochloric acid in 85% ethanol while Mg(II), Ca(II), Al(III), Ti(IV), Mn(II), Co(II), Ni(II) and many other elements are retained by the column.

Zr(IV), Th(IV), Sc(III), Y(III), La(II) and the rare earths

These elements are strongly absorbed from 3 *M* hydrochloric acid containing 50 or 60% of ethanol. Most other elements, including Al(III), Fe(III) and Ti(IV), in the presence of water can be eluted and separated quite easily. The separation factor D_{Sc}/D_{Al} in 3 *M* hydrochloric acid containing 60% ethanol is about 21, compared with 3.2 in aqueous 3 *M* hydrochloric acid, while the respective values for D_Y/D_{Al} are 10 and 2.9. The coefficients for scandium(III) increase faster with increasing ethanol concentration than those for yttrium(III). Exchange rates are slower in ethanol solutions than in aqueous hydrochloric acid and resin of small particle size and slow flow rates improve separations of these elements from aluminium(III), etc., considerably.

Cu(II), Co(II), Ni(II), Mn(II) and V(IV)

The last four elements show the normal behaviour of divalent elements with small or negligible tendencies to chloride-complex formation, and the coefficients increase with increasing ethanol concentrations, while those for copper(II) do not increase as strongly and decrease at the highest concentration. Thus copper(II) can be separated from the other elements by elution with 1.50 *M* hydrochloric acid in 80% ethanol. The alkalies, alkaline earths, Al(III), Ti(IV), Zr(IV), Hf(IV), Th(IV), Sc(III), Y(III), La(III) and the rare earths are retained together with Co(II), etc.

General

The system offers many attractive possibilities for separations. Its advantages over the acetone system are the higher boiling point of ethanol and the facts that ethanol does not polymerize in acid solution and that the vapours are less of a health hazard. Its disadvantages are that it promotes chloride-complex formation less strongly and that solutions containing high concentrations of hydrochloric acid in high percentages of ethanol have relatively high viscosities. Exchange rates for elements which require these kind of eluents often are slow in aqueous solutions. In ethanolic solutions they are even slower and resin of a fine particle size leads to considerably improved separations. High viscosities in such cases limit the maximum flow rates attainable without the application of external pressures.

SUMMARY

Cation-exchange equilibrium distribution coefficients with Bio-Rad AG50W-X8, a sulfonated polystyrene resin, are presented for 45 elements in hydrochloric acid–ethanol media. The acid concentration range 0.1–3.0 *M* and the ethanol concentration range 0–95% are covered. The elements are arbitrarily arranged in tables according to their coefficients in aqueous hydrochloric acid. Possibilities for separations inherent in the system are demonstrated by elution curves for the multicomponent systems Fe(III)–U(VI)–Ca(II)–La(III); Cd(II)–Zn(II)–Fe(III)–Ca(II)–Ba(II); and In(III)–Ga(III)–Be(II)–Al(III)–Y(III). Some aspects in the elution behaviour of various elements are discussed.

RÉSUMÉ

Les coefficients de distribution, à l'équilibre, lors d'un échange cationique sur une résine Bio-Rad AG50-X8 au polystyrène sulfoné sont présentés pour 45 éléments dans des milieux acide chlorhydrique–éthanol. Les concentrations de l'acide vont de 0.1 à 3.0 *M*, celles de l'éthanol de 0 à 95%. Les éléments sont classés arbitrairement dans des tables selon leurs coefficients dans les solutions aqueuses d'acide chlorhydrique. Les possibilités de séparation inhérentes au système sont démontrées au moyen des courbes d'élution pour des systèmes à multicomposants Fe(III)–U(VI)–Ca(II)–La(III); Cd(II)–Zn(II)–Fe(III)–Ca(II)–Ba(II); et In(III)–Ga(III)–Be(II)–Al(III)–Y(III). On discute quelques aspects du pouvoir d'élution de divers éléments.

ZUSAMMENFASSUNG

Verteilungskoeffizienten an Kationenaustauschern mit Bio-Rad AG50-X8 und mit sulfoniertem Polystyrolharz werden für 45 Elemente in einem Medium aus Salzsäure und Äthanol angegeben. Die Säurekonzentration lag zwischen 0.1 und 3.0 *M* und die des Äthanols zwischen 0 und 95%. Mögliche Trennungen in diesem System werden demonstriert durch Elutionskurven der Systeme Fe(III)–U(VI)–Ca(II)–La(III); Cd(II)–Zn(II)–Fe(III)–Ca(II)–Ba(II) und In(III)–Ga(III)–Be(II)–Al(III)–Y(III). Einige Aspekte im Elutionsverhalten zahlreicher Elemente werden diskutiert.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SOURCES OF ERROR IN THE USE OF ARSONIUM REAGENTS

PART II. THE ULTRAVIOLET SPECTRA OF TETRAPHENYL- AND TRIPHENYLMETHYLARSONIUM SALTS AND TRIPHENYLARSINE OXIDE

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(Received October 1st, 1968)

Arsonium salts have characteristic ultraviolet absorption spectra resembling that of benzene. The positions of the peak maxima and the values of the molar absorptivities at these maxima have been reported several times[1-6] and these data have been used in the determination of arsonium salts[7-11]. However, the published data are sometimes incorrect or presented in a manner which may lead to errors. The errors can arise either directly or indirectly from the fact that the absorption spectra peaks are very narrow. The peak maxima must be located to within ±1 Å for accurate absorbance measurements and small shifts of the maxima which would usually be thought negligible can cause significant errors. These shifts can arise from solvent and structural effects and the presence of impurities.

EXPERIMENTAL

Unless otherwise stated, all compounds were synthesized and examined by the methods described previously[12].

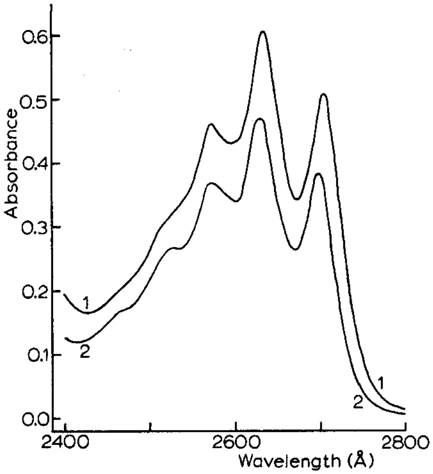
Ultraviolet absorption spectra of solutions were measured in 1.000-cm silica cells in a Beckman DU or Cary 14 spectrophotometer. The Beckman DU was fitted with a stabilized power pack, photomultiplier and cell compartment temperature control plates; the compartment temperature was held at 23°±2°. The wavelength scale and setting of each spectrophotometer was checked by measuring the absorption spectra of benzene and toluene vapors in 1-cm cells and correcting the recorded maxima wavelength positions from standard published data[13,14]. The maxima could be located to within ±0.5 Å and the published data are considerably more accurate than that, so the corrected wavelength values should be accurate to within ±1 Å. Measurements in the Cary 14 were made at a slow scan of 0.5 Å/sec, a chart-speed of 2 in/min and under automatic slit-width control (about 0.05 mm); measurements in the Beckman DU were made at 1 Å intervals and with a 0.1-mm slit width (±20% variation did not alter the absorbance values). Care was taken to minimize backlash when settings were made; all adjustments were made slowly and controls were always adjusted in the same direction to make the final setting.

Infrared absorption spectra were measured on a Perkin-Elmer 137 spectrophotometer. Samples were mulled in #9 white oil (Standard Oil Co., Chevron brand) and examined between rock-salt plates at a fast scan.

RESULTS AND DISCUSSION

Measurement of spectra

The arsonium salts and triphenylarsine oxide have benzene-like absorption spectra in the 2400–2800 Å region. Examples of such spectra are given in Fig. 1. The absorption peaks are rather sharp and the spectrophotometer wavelength settings must be precise and accurate to ± 1 Å to locate the maxima wavelengths. This can be seen clearly from a trace of an absorption peak of aqueous tetraphenylarsonium chloride, recorded at a slow scan so as to give an extended wavelength scale (see Fig. 2). An error of 2 Å in the maximum wavelength causes a −0.86% error in the absorbance, of 5 Å a −4.3% error and of 10 Å a −15.4% error. The errors are systematic, not random.



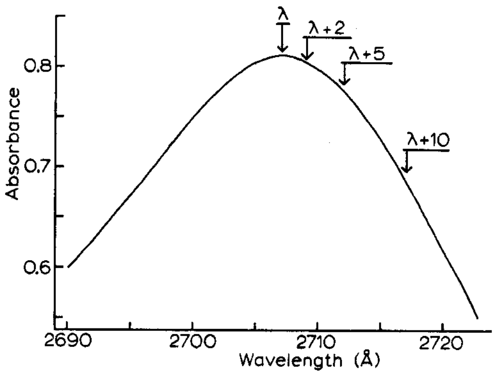


Fig. 1. Absorption spectra of (1) tetraphenylarsonium chloride, (2) triphenylarsine oxide, concentrations 8.0 mg/100 ml in water.

Fig. 2. Absorption peak of aqueous tetraphenylarsonium chloride, measured at slow scan, to show the effect on absorbance measurement of small λ_{max} errors.

Most of the published works on arsonium salt spectra either state or imply that the spectra vary little with changes in structure or solvent. In context this is true, but because the peaks are so sharp, a shift of only 2 Å can be significant. (Most published values are reported with a nominal uncertainty of ± 10 Å.) Hence structural and solvent shifts of maxima positions can be important even though they are small and should not be neglected in the measurement of absorbance.

The values of the wavelengths of maximum absorbance of a variety of tetraphenylarsonium (TPA) and triphenylmethylarsonium (TPMA) salts were measured in water. No significant differences were found in the wavelengths within each of the two sets of results for chloride, bromide, iodide, sulfate, nitrate and perchlorate. Values agreed within ± 1 Å, hence the accompanying anions had no significant effect on arsonium salt absorption spectra. This agrees with a previous report[9].

The values of the maximum wavelengths were measured for TPA and TPMA chlorides and triphenylarsine oxide in a variety of solvents; the results are shown in

TABLE I

ABSORPTION MAXIMA POSITIONS (λ) AND MOLAR ABSORPTIVITIES (ε) OF TETRAPHENYLARSONIUM SALTS IN VARIOUS SOLVENTS

Salt	*Solvent*	λ_1 *(Å)*	ε_1	λ_2 *(Å)*	ε_2	λ_3 *(Å)*	ε_3	*Reference*
TPA.Cl	H_2O	*2590*	*2550*	*2650*	*2780*	—	—	Popov and Humphrey[3]
TPA.Cl	H_2O	2578	2518	2640	3348	2707	2786	This work
TPA.Br	H_2O	2578	2560	2640	3388	2707	2823	This work
TPA.Cl	MeCN	—	—	*2640*	*3230*	*2710*	*3160*	Cole and Pflaum[7]
$TPA.ClO_4$	MeCN	*2580*	*2580*	*2640*	*3420*	*2710*	*2840*	Going and Pflaum[8]
TPA.Cl	MeCN	*2590*	*2660*	*2650*	*2830*	—	—	Popov and Humphrey[3]
TPA.Cl	MeCN	2583	—	2643	—	2712	—	This work
$TPA.NO_3$	EtOH	*2570*	*2480*	*2630*	*3300*	*2700*	*2770*	Armstrong *et al.*[5]
TPA.Br	EtOH	2600	—	*2660*	—	*2730*	—	Rao *et al.*[1]
TPA.Cl	EtOH	2583	—	2644	—	2713	—	This work
TPA.Cl	$CHCl_3$	2588	—	2650	—	2718	—	This work

TABLE II

ABSORPTION MAXIMA POSITIONS (λ) AND MOLAR ABSORPTIVITIES (ε) OF TRIPHENYLMETHYLARSONIUM SALTS AND TRIPHENYLARSINE OXIDE IN VARIOUS SOLVENTS

Salt	*Solvent*	λ_1 *(Å)*	ε_1	λ_2 *(Å)*	ε_2	λ_3 *(Å)*	ε_3	*Reference*
TPMA.Cl	H_2O	2572	1770	2633	2333	2701	1925	This work
TPMA.Br	H_2O	2572	1730	2633	2317	2701	1915	This work
TPMA.Cl	MeCN	2575	—	2636	—	2703	—	This work
TPMA.I	EtOH	*2570*	*1830*	*2630*	*2380*	*2700*	*1970*	Armstrong *et al.*[5]
TPMA.I	EtOH	*2580*	*1890*	*2640*	*2440*	*2710*	*2060*	Mann *et al.*[4]
TPMA.Cl	EtOH	2577	—	2637	—	2705	—	This work
TPMA.Cl	$CHCl_3$	2581	—	2644	—	2711	—	This work
$(C_6H_5)_3AsO$	H_2O	2570	—	2640	—	2696	—	This work
$(C_6H_5)_3AsO$	MeCN	2569	—	2627	—	2694	—	This work
$(C_6H_5)_3AsO$	EtOH	*2580*	*1400*	*2630*	*1720*	*2700*	*1370*	Jaffé[6]
$(C_6H_6)_3AsO$	EtOH	2575	—	2631	—	2698	—	This work
$(C_6H_5)_3AsO$	$CHCl_3$	2575		2636	—	2703	—	This work

Tables I and II, along with published data. It is clear that change of solvent does shift the values by small but significant amounts, hence spectrophotometric results for different solvents are not interchangeable.

The molar absorptivities (ε) were measured for TPA and TPMA chlorides and bromides in water. Standard assayed solutions of each salt were weighed out and diluted to known volumes. (The assayed concentrations of the standard solutions were accurate to within $\pm 0.2\%$ and the final diluted concentrations were in the range $0.5–25 \cdot 10^{-5}$ *M*.) The absorbance of each solution was measured on a Beckman DU spectrophotometer. A new solution was made up for each measurement and the sample cell was removed each time from its holder, rinsed, filled, wiped clean with lens tissue and replaced in the holder for measurement with respect to a matched cell filled with water. Thus the results include all errors, equally weighted, arising from the making of the solution and the handling and positioning of the cell. (For discussions of the importance of these errors, see Caster[15], Loomeijer and Zijlstra[16] and Ketelaar *et al.*[17].) The results are shown in Table III. The molar absorptivity values for TPA chloride and bromide are just significantly different at the 0.01 probability level, by Student's *t* test. The TPMA chloride and bromide values are not significantly different at the 0.01 level. The discrepancies between these values and the literature values given in Tables I and II are probably largely due to imprecise measurement and setting of λ values by previous workers.

TABLE III

ABSORPTION MAXIMA POSITIONS (λ), MOLAR ABSORPTIVITIES (ε) AND ESTIMATED STANDARD DEVIATIONS ($\hat{s}$) OF ARSONIUM SALTS IN AQUEOUS SOLUTION

Salt	λ *(Å)*	ε	$\pm\hat{s}$	*Number of measurements*
TPA.Cl	2578	2518	31	20
	2640	3348	29	20
	2707	2786	27	20
TPA.Br	2578	2560	14	10
	2640	3388	15	10
	2707	2823	16	10
TPMA.Cl	2572	1770	19	16
	2633	2333	21	16
	2701	1925	19	15
TPMA.Br	2572	1730	7	5
	2633	2317	14	5
	2701	1915	8	5

Coprecipitation of impurities

Triphenylarsine oxide is slightly soluble in water and does not give precipitates with perchlorates, iodides or any of the other anions which precipitate insoluble arsonium salts. However, it can coprecipitate with these arsonium salts and so act as a contaminant which can cause large spectrophotometric errors.

An aqueous solution, about 0.01 *M* in TPA chloride and half-saturated with triphenylarsine oxide, was precipitated with an excess of potassium perchlorate solution. The white precipitate was washed with water and air-dried. The product proved to be TPA perchlorate contaminated with triphenylarsine oxide. The product turned brown at 335° and melted at 358°–360°; pure TPA perchlorate does not brown until the melting point at 358°–360°. The ultraviolet absorption spectrum of a saturated aqueous solution of the product showed maxima at 2577, 2634, 2702 Å (compare with pure TPA perchlorate maxima at 2580, 2640, 2708 Å and triphenylarsine oxide maxima at 2570, 2630, 2696 Å) and the absorbance of the solution was about twice as great as that of a saturated TPA perchlorate solution at any selected wavelength. The infrared absorption spectrum of the product showed no evidence of the characteristic triphenylarsine oxide absorption peak at 880 cm^{-1} [18–20] so that the oxide concentration must have been low.

This coprecipitation of triphenylarsine oxide with arsonium salts is important because the standard method of synthesis of arsonium salts[21,22] is by Grignard condensation with triphenylarsine oxide followed by isolation of the arsonium salt by precipitation from the hydrolyzed reaction mixture. When TPA iodide and perchlorate were prepared directly by precipitation from the hydrolyzed reaction mixture they were found to be contaminated with triphenylarsine oxide. The arsine oxide could not be detected by infrared absorption analysis but could be detected by its causing a small shift (2–10 Å) of the maximum absorbance wavelengths to lower wavelengths and a slight broadening of the peaks.

When the contaminated TPA iodide was converted to chloride (by treatment with silver oxide and neutralization with hydrochloric acid) the chloride was also contaminated. The contaminant was isolated by precipitating the TPA chloride from absolute ethanol by slowly adding 15 volumes of diethyl ether[22]; the mother liquor was filtered and evaporated at room temperature to yield triphenylarsine oxide (identified by its ultraviolet and infrared absorption spectra and melting point).

The contamination of the TPA perchlorate was not recognized at first. The melting point, arsenic content and infrared absorption did not indicate the presence of impurity and the shift of the maximum absorbance wavelengths was so small (8–13 Å lower) that it was at first ignored. However, the small amount of triphenylarsine oxide contaminant caused serious error when an attempt was made to measure the solubility of TPA perchlorate in water. Triphenylarsine oxide is more soluble than TPA perchlorate (although not very soluble) and so the saturated solution had more the properties of a solution of the oxide than of the perchlorate. In particular, the ultraviolet absorbance and arsenic content were much higher than expected. A sample of 1571 g of the saturated solution, evaporated at 40° on a rotary vacuum evaporator, gave 0.7646 g of white crystalline solid, m.p. 205°–206° (TPA perchlorate, m.p. 353°–357°; triphenylarsine oxide, m.p. 189°–190°). The properties of the residue agreed closely with those of triphenylarsine oxide for the thermogravimetric curve and ultraviolet and infrared absorption spectra.

Purification of arsonium salts

The standard synthesis of TPA chloride proceeds via a precipitation of the insoluble TPA hydrogen dichloride from the hydrolyzed Grignard reaction mixture[21]. The hydrogen dichloride salt is neutralized with sodium carbonate[22] and the evaporated product is digested with ethanol and filtered to remove sodium chloride. TPA chloride is then isolated by precipitation from the ethanolic solution with ether. It is now clear that this procedure serves not only to isolate the TPA chloride from the neutralized intermediate mixture but also to remove triphenylarsine oxide and other like impurities. This is an important step because triphenylarsine oxide is not easily detected as an impurity in low concentrations; many of its properties are similar to those of the arsonium salts.

Care should be taken to check the purity of samples of arsonium salts before they are used for precise work. This can be done by careful examination of the ultraviolet absorption spectra for any small shifts (>2 Å) in the absorbance maxima positions. A better way would be to recrystallize the samples from ethanol by precipitation with ether and examine the ultraviolet absorption spectrum of the soluble fraction in the mother-liquor.

There is some evidence that many previous workers have not paid sufficient attention to the purity of their arsonium reagents. Most workers have used commercial reagents without further purification[9,10,23–28]. Two workers reported the presence of water-insoluble material in the arsonium reagents[27,28]. This material was most likely triphenylarsine oxide; if so, then it could not be effectively removed by simply filtering the aqueous solution because the oxide is somewhat soluble in water.

SUMMARY

Arsonium salts have characteristic ultraviolet absorbance spectra with several sharp absorbance peaks in the 2400–2800 Å region. When they are estimated or identified by their absorption spectra, care must be taken to measure the peak maximum positions to within ±1 Å in order to obtain reliable wavelength or absorbance values. The peak positions can be significantly shifted by change of solvent or the presence of coprecipitated impurities, especially triphenylarsine oxide.

RÉSUMÉ

Les sels d'arsonium ont des spectres d'absorption caractéristiques dans l'ultraviolet avec plusieurs pics d'absorption nets dans la région 2400–2800 Å. Quand on veut les doser ou les identifier au moyen de leurs spectres d'absorption, il faut faire attention de mesurer les positions des maxima des pics avec une précision de ±1 Å de façon à obtenir des longueurs d'ondes et des valeurs d'absorption exactes. Les positions des pics peuvent être déplacées d'une façon importante quand on change de solvant ou en présence d'impuretés qui coprécipitent, en particulier l'oxyde de triphénylarsine.

ZUSAMMENFASSUNG

Arsonium-Salze besitzen charakteristische UV-Spektren mit zahlreichen scharfen Absorptionsmaxima im Bereich von 2400–2800 Å. Wenn diese Salze durch ihre Absorptionsspektren bestimmt oder identifiziert werden, so muss man dafür sorgen, dass die Maxima mit einer Genauigkeit von ±1 Å gemessen werden, um zuverlässige Wellenlängen oder Absorptionswert ezu erhalten. Die Lage der Maxima kann bedeutend verschoben werden durch Wechsel des Lösungsmittels oder durch Gegenwart von mitgefällten Verunreinigungen, besonders von Triphenylarsinoxid.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE SEPARATION AND DETERMINATION OF COBALT(II) AND COBALT(III)

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(Received October 31st, 1968)

The determination of cobalt either alone or in combination with other metals has received considerable attention and there are numerous papers devoted to this subject; indeed, it is a formidable task to even determine which approach is best for a particular analysis. However, the determination of cobalt in its different oxidation states is quite another story. Few methods have been proposed and some of these are difficult to locate. Polarographic methods have been employed[1,2] along with colorimetric[3] and several potentiometric approaches[4–6]. Most methods involve an indirect determination of cobalt(III) and in most cases the cobalt(II) concentration is obtained by difference after the total cobalt concentration has been determined by a separate analysis.

The procedure described in this paper utilizes chelation and solvent extraction as a means of separating cobalt(II) and (III), and is applicable to cobalt(III) complexes in solutions of lower aliphatic carboxylic acids.

Because of the solubility properties of the cobalt acetylacetonates, a quick and easy separation by solvent extraction is possible. Once the cobalt(II) and (III) species are separated and isolated, several analytical finishes are possible. This paper deals primarily with the formation and separation of the cobalt acetylacetonates, and proposes several finishes including atomic absorption, visible spectrophotometry or a simple EDTA titration.

EXPERIMENTAL

Apparatus

Atomic absorption. Perkin Elmer Model 303 spectrophotometer equipped with a standard premix Perkin Elmer burner. A wavelength of 2410 Å, a lamp current of 20 mA, and a slit setting of 4, which is equivalent to a 1.0-mm slit opening were used.

Visible absorption. A Beckman DK-2 and a Bausch and Lomb Spectronic 20 spectrophotometer were employed.

Reagents

Acetylacetone, benzene, *n*-pentanol, and acetic acid (Eastman Organic Chemicals) were used without further purification.

Stock solution of cobalt(III) acetylacetonate. Solutions were prepared by dissolving a weighed quantity of cobalt(III) acetylacetonate (Shephard Chemical

Company) in glacial acetic acid; 2 ml of acetylacetone and a spatula tip of sodium perborate were added to insure that all of the cobalt was present in the +3 oxidation state. This stock solution was then diluted to obtain standards for calibration.

Stock solution of cobalt(II) acetylacetonate. These solutions were freshly prepared by dissolving a weighed amount of cobalt(II) acetylacetonate (Shephard Chemical Company) in glacial acetic acid.

Procedure

Pipette 2 ml of acetylacetone into a 100-ml volumetric flask and heat on a hot plate until the reagent begins to creep up the walls of the flask. Add 1 ml of sample adjusted to contain between 0 and 0.5% cobalt to the volumetric flask and allow the mixture to react with no further heating for 1–3 min. Then dilute the mixture to the mark with 20% acetic acid. Extract a 25-ml portion with 25 ml of benzene and separate the two layers into 50-ml volumetric flasks. Dilute the benzene layer containing the cobalt(III) complex to the mark with *n*-pentanol. Dilute the acetic acid layer to the mark with 20% acetic acid. Determine the cobalt concentration in both layers by atomic absorption or any other appropriate method. Standards should be prepared from the stock cobalt acetylacetonate solutions and they should be treated as described above. The concentration of the standards should be chosen so that they bracket the concentration of the samples to be analyzed.

RESULTS AND DISCUSSION

Properties of the cobalt acetylacetonates

Cobalt(II) acetylacetonate is a pink solid melting above 200° and is a 1:2 complex. It is insoluble in most organic solvents, but readily soluble in water and acetic acid. In the presence of excess of acetylacetone, the cobalt(II) acetylacetonate can be oxidized to the corresponding cobalt(III) complex by 30% hydrogen peroxide. This is a standard preparation for cobalt(III) acetylacetonate[7].

Cobalt(III) acetylacetonate is a green solid melting at 240–241° and is a 1:3 complex. It is soluble in most organic solvents, but is insoluble in water. The complex is quite stable and is reduced only under rather drastic conditions. Both the cobalt(II) and (III) acetylacetonates can be obtained commercially, and such commercially prepared complexes were used for obtaining all of the calibration data reported here.

Formation of cobalt(II) and (III) acetylacetonates

The reaction between cobalt and acetylacetone is quite slow at room temperature; therefore, it is necessary to carry out the reaction at elevated temperatures[8]. As a preliminary step in this investigation, the effect of heat on cobalt(II) and (III) acetylacetone was studied. A solution of each cobalt complex was prepared in glacial acetic acid. Each solution was then heated on a steam bath, and aliquots were withdrawn after definite time intervals for extraction and separation. The samples were then analyzed to determine their cobalt(II) and (III) content. The results obtained on heating cobalt(III) acetylacetonate solutions indicated that the concentration of cobalt(III) acetylacetonate was not affected during heating periods of up to 50 min. Thus, heating has no detrimental effect on the concentration of cobalt(III).

The results obtained on heating solutions of cobalt(II) acetylacetonate were less satisfactory. It was found that the cobalt(II) concentration decreased with a corresponding increase in the cobalt(III) concentration as the period of heating became longer. These results are shown in Fig. 1. This oxidation of cobalt(II) acetylacetonate was not surprising, and it presented the most serious problem encountered during this investigation. Since it is necessary to heat the cobalt solutions to insure complete complex formation, the heating operation must be done in such a manner that no cobalt(II) is oxidized. Figure 2 shows the effect of heat on the formation of the cobalt acetylacetonates. For this experiment solutions containing a mixture of cobalt(II) and (III) were heated on a steam bath in the presence of excess of acetylacetone for various periods of time. The total concentration of cobalt was 0.34%. This figure shows the apparent cobalt(II) and (III) levels with respect to heating time. The line, shown by small circles, indicates the build-up of cobalt(III) acetylacetonate. It should be noted that the cobalt(III) content continues to increase with increased heating time and never reaches a plateau. The upper line (dots)

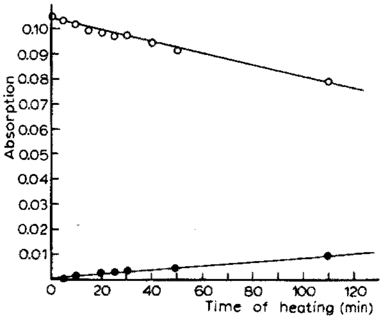

Fig. 1. Effect of heat on cobalt(II) acetylacetonate. (○) Cobalt(II), (●) cobalt(III) resulting from oxidation of cobalt(II).

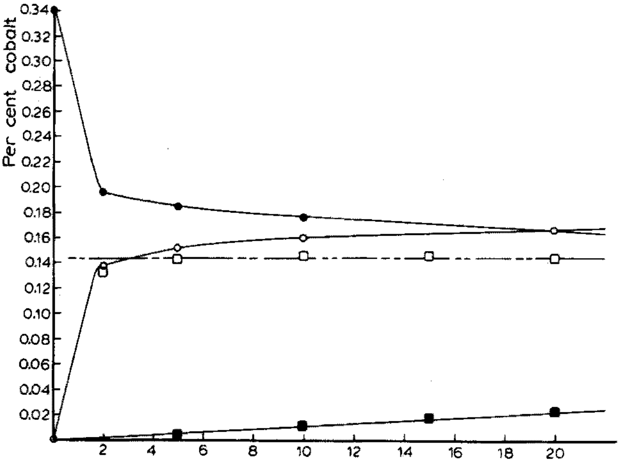

Fig. 2. Effect of heating on the formation of cobalt acetylacetonates. (●) Apparent cobalt(II) concentration, (○) apparent cobalt(III) concentration, ■ cobalt(III) resulting from oxidation of cobalt(II), □ actual cobalt(III) present.

indicates the apparent cobalt(II) concentration with time. This line actually represents cobalt in any form remaining in the 20% acetic acid solution after extraction with benzene. It can be seen that the apparent cobalt(II) concentration continues to drop with heating time. The bottom line in Fig. 2 (closed squares) indicates the rate of appearance of cobalt(III) acetylacetonate resulting from the oxidation of the cobalt(II) complex. If a correction is made for the cobalt(III) produced during the reaction period by the oxidation of cobalt(II) acetylacetonate, then the values represented by the small squares indicate the true cobalt(III) concentrations. The dashed line in Fig. 2 represents the cobalt(III) concentration found when a sample containing both cobalt(II) and (III) was added to hot (~130°) acetylacetone and allowed to stand for 3 min with no further heating. These data indicate that by adding the sample to acetylacetone previously heated to about 130°, complete reaction occurs within 3 min. Actually, the reaction has been shown to be complete after 1-min standing in the hot acetylacetone. When cobalt(II) acetylacetonate is added to hot acetylacetone and allowed to stand for 3 min, only traces of cobalt(III) can be detected.

Extraction and separation

The cobalt solutions are allowed to stand in the hot acetylacetone for 1–3 min and then they are diluted to mark with 20% acetic acid. An appropriately sized aliquot of the acetic acid solution, containing the cobalt acetylacetonates, is then extracted with an equal quantity of benzene, and the two layers are allowed to separate. The benzene layer contains the cobalt(III) acetylacetonate while the 20% acetic acid layer contains the cobalt(II) complex.

Determination of cobalt concentration

Once the cobalt(II) and (III) complexes have been separated, it is simple to determine the cobalt concentrations. Atomic absorption spectrophotometry offers the best approach to this determination as it is free of interferences resulting from the presence of other colored species in the final solutions or extracts. The benzene layer can be diluted with an equal volume of *n*-pentanol. This 50:50 mixture of benzene and *n*-pentanol burns with a steady, non-luminous flame and excellent results can be obtained. The 20% acetic acid layer can be aspirated directly into the flame with or without further dilution. Standards can be prepared by extracting solutions of known cobalt content, prepared by dissolving commercially available cobalt acetylacetonates. The calibration curves obtained in this manner are fairly linear over the range of 0–25 p.p.m. of cobalt and quite satisfactory results can be obtained by means of "bracketing".

In the absence of other colored complexes, a spectrophotometric finish can be employed for the determination of cobalt(III) acetylacetonate. Figure 3 shows the visible absorption spectra of both the cobalt(II) and (III) complexes. The cobalt(III) acetylacetonate has an absorption maximum at 592 nm and a molar absorptivity of approximately 130. The cobalt(II) complex has a maximum at 525 nm and molar absorptivity of approximately 15. Since the green color of the cobalt(III) complex could be visually observed in mixtures of cobalt(II) and (III) acetylacetonates, an evaluation of a spectrophotometric method was carried out. Beer's law plots of both the benzene-extracted cobalt(III) acetylacetonate, and 20% acetic acid solutions of the cobalt(III) complex are linear over the range of 0–50 p.p.m. of cobalt. Because of the low molar absorptivity of the cobalt(III) complex, either a 5-cm path-length cell should be used or a larger sample should be taken. When a larger sample is used, it is important to take a correspondingly larger volume of acetylacetone. This is necessary since the heat required for complexation is supplied solely by the hot acetylacetone, and the larger volume of sample cools the acetylacetone, before complexation can take place. This spectrophotometric approach is useful for, and provides information only about, the cobalt(III) content of a solution. If the total cobalt concentration is known, then the cobalt(II) concentration can be obtained by difference. Again, it should be pointed out, that other colored species (*i.e.* iron(III) which forms a colored extractable acetylacetonate complex) may cause serious interferences and therefore, the spectrophotometric approach should only be used in cases where such interferences are known to be absent.

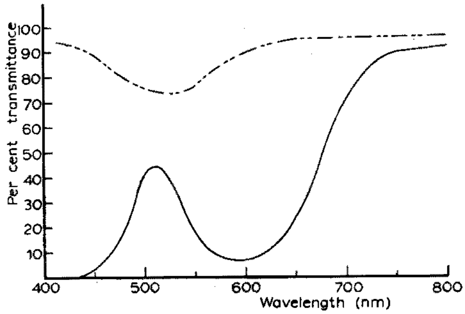

Fig. 3. Visible absorption spectra of the cobalt acetylacetonates in acetic acid. (—·-·—) Cobalt(II) acetylacetonate, (————) cobalt(III) acetylacetonate.

Table I shows the data obtained when a solution, containing a mixture of cobalt(II) and (III) acetates, was analyzed 15 times by both the atomic absorption and photometric procedures. The samples were run in groups of five over a period of 3 days. The results are expressed in percent cobalt(II) and (III) in the total sample. The standard deviation was found to be *ca.* 0.005%, with a coefficient of variation of 3%, and a repeatability of 0.015%. There is no significant difference between the atomic absorption and photometric results.

Several samples were analyzed for both cobalt(II) and (III) by the atomic absorption method. A separate and independent total cobalt determination was made on each sample. Table II shows the results obtained when the total cobalt concentration was compared to the sum of the cobalt(II) and (III) concentrations. Excellent agreement was obtained.

An EDTA titration can be employed as a third analytical finish, if other metals are known to be absent. The titration was described by FLASCHKA[9] and involves addition of an excess of EDTA and a back-titration with copper solution and 1-(2-pyridylazo)-2-naphthol (PAN) as the indicator. If the cobalt complexes are separated by extraction, then the cobalt(II) concentration can be determined by titration with EDTA. A separate titration can be conducted on the original sample for total cobalt. Hydrogen peroxide is added to an acetic acid solution of cobalt(II)

TABLE I

PRECISION DATA

Test no.	*Atomic absorption*			*Photometric*
	% Co^{2+}	*% Co^{3+}*	*Total Co*	*% Co^{3+}*
1	0.201	0.137	0.338	0.145
2	0.198	0.144	0.343	0.146
3	0.198	0.146	0.344	0.147
4	0.192	0.151	0.343	0.151
5	0.196	0.142	0.338	0.148
6	0.201	0.138	0.339	0.142
7	0.184	0.152	0.336	0.146
8	0.190	0.147	0.337	0.154
9	0.190	0.147	0.337	0.146
10	0.194	0.143	0.337	0.142
11	0.193	0.147	0.340	0.149
12	0.193	0.145	0.338	0.146
13	0.187	0.151	0.338	0.153
14	0.191	0.151	0.342	0.155
15	0.189	0.149	0.338	0.155
Standard deviation	0.004957	0.004614	—	0.004359
Coefficient of variation	2.57%	3.16%	—	2.94%
Repeatability	0.015%	0.014%	—	0.013%

TABLE II

COMPARISON OF TOTAL COBALT DETERMINATION TO COBALT(II) AND (III) DETERMINATION

% Co^{2+}	*% Co^{3+}*	*% Co^{2+} + % Co^{3+}*	*Total % Co*
0.157	0.128	0.285	0.281
0.135	0.139	0.274	0.274
0.159	0.130	0.289	0.281
0.160	0.124	0.284	0.294
0.162	0.124	0.286	0.284
0.176	0.117	0.293	0.284
0.172	0.113	0.285	0.287
0.144	0.134	0.278	0.282
0.185	0.112	0.297	0.297

and (III) to reduce all cobalt to the +2 oxidation state before the total cobalt is titrated.

The atomic absorption method used after the acetylacetone extraction, provides the means for the determination of both cobalt(II) and (III) by a direct measurement. A combination of the photometric method and the EDTA titration can be used to obtain the cobalt(II) and (III) concentrations, if atomic absorption is not available. Either of these methods, plus a total cobalt determination can provide the same information, but one of the species must be determined by difference. The atomic absorption method also offers the advantage of being free from interferences of other metals that may be present.

A comparison was made between the determination of cobalt(III) by the acetylacetone extraction method and a polarographic cobalt(III) determination. The polarographic method is based on the following principle. If samples containing cobalt(III) are added to solutions of iron(II), then the cobalt will be reduced and the iron oxidized. The iron(III), which is formed in an amount equivalent to the cobalt(III) concentration, is then determined polarographically. The polarographic method was calibrated, completely independent of the acetylacetone method, and was conducted by a different laboratory. Table III shows the results obtained by the two different methods conducted in two different laboratories. The samples were prepared by oxidizing cobalt(II) acetate in glacial acetic acid with sodium perborate. The results are in good agreement, and even at the low concentration level, results are not significantly different.

TABLE III

COMPARISON OF ACETYLACETONE METHOD WITH POLAROGRAPHIC METHOD

Atomic absorption		*Photometric* % Co^{3+}	*Polarographic* % Co^{3+}
% Co^{2+}	% Co^{3+}		
0.362	0.015	0.014	0.000
0.340	0.028	0.023	0.003
0.337	0.024	0.024	0.004
0.316	0.042	0.042	0.015
0.095	0.257	0.258	0.256
0.069	0.272	0.260	0.295
0.069	0.256	0.252	0.288
0.181	0.151	0.152	0.156
0.181	0.156	0.154	0.162
0.181	0.156	0.155	0.162

The author gratefully acknowledges the assistance of Mr. JAMES SALYER and Mrs. RUTH S. JESSEE who conducted most of the experimental work reported here. Also, he wishes to thank Dr. GERALD P. MORIE for his assistance and cooperation in performing the polarographic measurements.

SUMMARY

A method for the separation and determination of cobalt(II) and (III) has been developed. The acetylacetonate complexes of cobalt are utilized for the separation, and analytical measurements are made by atomic absorption or visible absorption spectrophotometry. The sample is reacted with hot acetylacetone and diluted with 20% acetic acid. The cobalt(III) complex is separated by extraction with benzene. The benzene layer is then diluted with *n*-pentanol and the cobalt(III) concentration is determined by atomic absorption spectrophotometry. The cobalt(II) concentration can be determined in the 20% acetic acid layer by atomic absorption. In the absence of other metals which form colored acetylacetonate complexes, the cobalt(III) concentration can be determined by visible absorption spectrophotometry directly on the 20% acetic acid solution. The total cobalt concentration can be determined by any acceptable method for cobalt and the cobalt(II) concentration then obtained by difference.

RÉSUMÉ

On a développé une méthode pour la séparation et la détermination du cobalt(II) et (III). Les complexes de l'acétylacétonate de cobalt sont utilisés pour la séparation et les mesures analytiques sont effectuées par spectrophotométrie d'absorption atomique ou d'absorption dans le visible. On fait réagir l'échantillon avec de l'acétylacétone chaude et on dilue avec de l'acide acétique à 20%. Le complexe de cobalt(III) est séparé par extraction dans le benzène. La couche de benzène est alors diluée avec du n-pentanol et la concentration du cobalt(III) est déterminée par spectrophotométrie d'absorption atomique. La concentration du cobalt(II) peut être déterminée dans la couche de l'acide acétique à 20% par spectrophotométrie d'absorption atomique. En l'absence d'autres métaux qui forment des complexes colorés sous forme d'acétylacétonates, la concentration du cobalt(III) peut être déterminée directement par spectrophotométrie d'absorption dans le visible dans la solution à 20% d'acide acétique. La concentration totale du cobalt peut être déterminée par une méthode valable quelconque pour le cobalt et la concentration du cobalt(II) peut alors être obtenue par différence.

ZUSAMMENFASSUNG

Es wurde eine Methode zur Trennung und Bestimmung von Kobalt(II) und -(III) entwickelt. Die Acetylacetonat-Komplexe des Kobalts werden für die Trennung verwendet und analytische Messungen mit Hilfe der Atomabsorption oder der sichtbaren Spektralphotometrie durchgeführt. Die Probe lässt man mit heissem Acetylaceton reagieren und verdünnt mit 20%-iger Essigsäure. Der Kobalt(III)-Komplex wird mit Benzol extrahiert. Die Benzolphase wird dann mit *n*-Pentanol verdünnt und die Kobalt(III)-Konzentration mit der Atomabsorption bestimmt. Die Kobalt(II)-Konzentration kann auf die gleiche Weise in der 20%-igen Essigsäure bestimmt werden. In Abwesenheit anderer Metalle, welche gefärbte Acetylacetonate bilden, kann die Kobalt(III)-Konzentration auch spektralphotometrisch direkt in der 20%-igen Essigsäure bestimmt werden. Bestimmt man die Gesamtkonzentration an Kobalt mit einer geeigneten Methode, so ergibt sich die Kobalt(II)-Konzentration aus der Differenz.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF STABILITY CONSTANTS OF POLYNUCLEAR TTHA COMPLEXES BY MEANS OF A DIGITAL COMPUTER

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(Received October 13th, 1968)

Many polyaminopolycarboxylic acids form binuclear and protonated mononuclear metal complexes, which exist simultaneously over a wide pH range. The determination of the respective stability constants is therefore somewhat complicated. Potentiometric pH titration is often a convenient method for studying complex formation and determining the stability constants. However, the oldfashioned algebraic way of calculating the constants from the titration curves is very time-consuming, and the approximations introduced are often not justified. By means of a high-speed digital computer the stability constants can, however, easily be calculated without introducing questionable approximations.

Most of the authors who have applied computer techniques for the calculation of stability constants, have studied equilibria involving mononuclear complexes only[1-4]. INGRI AND SILLÉN have, however, introduced a computer program which can be used for studying polynuclear complex formation. The last version of it is written in ALGOL[5]. The program is a complicated one, and it takes, as they say, "a considerable effort to master all details in a program of this size". Such generalized programs should, if possible, be avoided, as the size and computation time of the program, and the risk of making errors and difficulties of finding them, increase rapidly as the generalization is increased. If all the data obtained from the experimental curves are utilized, the computations can, in many cases, be simplified appreciably.

The present paper describes a simpler program which has been used for the calculation of the stability constants of the bi- and mononuclear complexes of triethylenetetraminehexaacetic acid with lead, zinc and cadmium, respectively. The programs were written in FORTRAN IV. All computations were carried out on a CDC 3300 computer.

EXPERIMENTAL

Materials

Triethylenetetraminehexaacetic acid (TTHA; Geigy Chemical Co., Basel, Switzerland) was recrystallized once from a minimum amount of hot water and dried in a vacuum desiccator. The purity was checked by potentiometric titration and found satisfactory. The purified product had previously[6] been analyzed and was found sufficiently pure. Solutions of lead(II), zinc(II), and cadmium(II) were prepared from the respective nitrate salts. The solutions were standardized by titration with EDTA and with suitable indicator-buffer tablets (E. Merck AG) as indicator. Standard sodium hydroxide was prepared by dissolving reagent-grade sodium hydroxide in carbon dioxide-free water and standardized by potentiometric titration against potassium hydrogen biiodate.

Apparatus

The potentiometric pH titrations were performed in a double-walled glass cell, the temperature of the solution being kept at 25.0°. The pH was measured with a Beckman Research pH meter and glass and calomel electrodes. The meter was standardized with 0.05 *M* potassium hydrogen phthalate and 0.01 *M* borax buffers, with pH values referring to the conventional activity pH scale given by National Bureau of Standards. The pH values were converted to hydrogen ion concentrations by assuming the activity coefficient f_H of the hydrogen ion to be 0.80[7,8]. The hydroxyl ion concentration was calculated by means of the equation

$$[H^+]\ [OH^-] = K_w \cdot (f_H f_{OH}/a_{H_2O})^{-1}$$

The activity constant of water (K_w) at 25° and the value of the expression $f_H \cdot f_{OH}/a_{H_2O}$ in 0.1 *M* potassium chloride at 25° are reported in the literature[9]. $[H^+] \cdot [OH^-]$ was calculated to be $1.61 \cdot 10^{-14}$ in 0.1 *M* potassium chloride at 25°. The ionic strength of all the solutions to be titrated was 0.1 *M* in potassium nitrate. The concentration of TTHA was approximately $5 \cdot 10^{-4}$ *M*.

CALCULATIONS

The experimental data were obtained by potentiometric pH titrations. The species which had to be considered in the calculations were found from a study of the titration curves. The general approach for the calculations was the usual method of least squares. To apply the method to the non-linear equations studied, one had to expand the function in a Taylor series. Derivatives of second and higher orders were discarded, and it was assumed that one could find approximate values for the unknown parameters (stability constants)[10]. The correction terms that were introduced by this procedure were minimized by repeated computations. It was found that the correlation between the different stability constants was considerable and that a simultaneous convergence was difficult to obtain. Hence, the constants were treated one at a time as unknown parameters and the whole sequence repeated several times. This procedure was found to be satisfactory, provided that a certain concentration of the complex in question was present in the pH region studied. Because of the above-mentioned procedure, the normal equations were reduced to one single equation, and a subroutine solving a set of linear equations was therefore not necessary. However, such a subroutine, solving the equations by elimination using largest pivotal divisor, was tried during the preliminary calculations. One complication with the least squares method was that an explicit relationship between the measured quantities *a* and *H* could not be given. Consequently, the derivatives could not be found by ordinary algebraic calculations. However, by treating the equations numerically, the problems were overcome. The equations which define the relationship between *a* and *H* can be simplified to the following system:

$$f_1(M, H, K_1, K_2, K_3, K_4) = 0 \tag{1}$$

$$a = f_2(M, H, K_1, K_2, K_3, K_4) \tag{2}$$

H is measured as a function of a, and K_{1-4} are the stability constants. The metal concentration M is unknown and must be eliminated. Equation (1) is of the third degree in M. When approximate values are used for the K's, eqn. (1) can be solved numerically with respect to M for each value of H by finding the value of M that makes $f_1(M) \approx 0$ within a given limit (eqn. (1) showed only one solution in M). This value of M can then be inserted in eqn. (2), and a calculated. The derivatives were calculated numerically by means of equations such as

$$\frac{\partial a}{\partial K_1} = \frac{a(K_1 + \Delta K_1) - a(K_1)}{\Delta K_1} \tag{3}$$

and similarly for the other derivatives. The ΔK_n was given by $\Delta K_n = R \cdot K_n$, and R was reduced stepwise till no changes in the results were observed. The correction terms could then be calculated, and new values of the constants were found. The calculations were repeated till no changes in the constants were observed.

When a set of constants had been determined, the experimental and calculated titration curves were printed out, together with the concentration of the different complexes at each point on the titration curve. These data constituted the necessary check for the results of the calculations.

The method described above was applied to a system of bi- and mononuclear complexes. The method can equally well be applied to systems of polynuclear complexes with more than two metal atoms per ligand molecule.

TTHA complexes

In Fig. 1 the titration curves for mixtures of lead and TTHA are represented. The pH of the solution is drawn as a function of a, the number of mole of alkali added per mole of the acid. The titration curves for mixtures of TTHA and zinc and cadmium, respectively, were not much different. The titration curves indicate that the species M_2A, MH_2A, MHA and MA must be considered in mixtures of the metal M and the acid H_6A, the charge signs being omitted. The stability constants were defined by the following equilibria:

$$K_1:\ 2M + A = M_2A \tag{4}$$

$$K_2:\ M + H_2A = MH_2A \tag{5}$$

$$K_3:\ M + HA = MHA \tag{6}$$

$$K_4:\ M + A = MA \tag{7}$$

The functional relationship between a and pH is defined implicitly through the equations:

$$C_M = [M] + [MA] + [MHA] + [MH_2A] + 2[M_2A] \tag{8}$$

$$C_A = Q[A] + [MA] + [MHA] + [MH_2A] + [M_2A] \tag{9}$$

$$6C_A - a \cdot C_A + [OH^-] = [H^+] + P \cdot [A] + [MHA] + 2[MH_2A] \tag{10}$$

where C_M and C_A are the total concentration of metal and acid, respectively, and the constants Q and P are defined by the equations:

$$Q = 1 + \frac{[H]}{k_6} + \frac{[H]^2}{k_5k_6} + \ldots. + \frac{[H]^6}{k_1k_2k_3k_4k_5k_6} \tag{11}$$

$$P = \frac{[H]}{k_6} + 2\frac{[H]^2}{k_5k_6} + \ldots + 6\frac{[H]^6}{k_1k_2k_3k_4k_5k_6} \tag{12}$$

The k's represent the respective dissociation constants of the acid H_6A. The constants given by BOHIGIAN AND MARTELL[11] were used for the calculations. Equation (10) is found by accounting for the six equivalents of hydrogen ions of the TTHA. The electroneutrality relationship could be used instead of eqn. (10), but the author preferred eqn. (10) because of its simplicity, *i.e.* the concentration of the anion of the metal salt and the cation of the alkali hydroxide added can be omitted. If the four stability constants are introduced, eqns. (8), (9) and (10) can be rewritten:

$$C_M = [M] + [K_4 + K_3P_1 + K_2P_2]\,[A]\,[M] + 2 \cdot K_1 \cdot [A]\,[M]^2 \tag{13}$$

$$C_A = Q[A] + [K_4 + K_3P_1 + K_2P_2]\,[A]\,[M] + K_1\,[A]\,[M]^2 \tag{14}$$

$$6C_A - a \cdot C_A + [OH^-] = [H^+] + P \cdot [A] + [K_3P_1 + 2K_2P_2]\,[A]\,[M] \tag{15}$$

where P_1 and P_2 are defined by the equations

$$P_1 = \frac{[H]}{k_6} \quad \text{and} \quad P_2 = \frac{[H]^2}{k_5k_6} \tag{16}$$

[A] in eqn. (14) can now be expressed as a function of [M], and inserted in eqns. (13) and (15). Two equations of the type represented in eqns. (1) and (2) are obtained, which then can be treated as described above. The program for the calculations, written in FORTRAN IV, is given at the end of this paper.

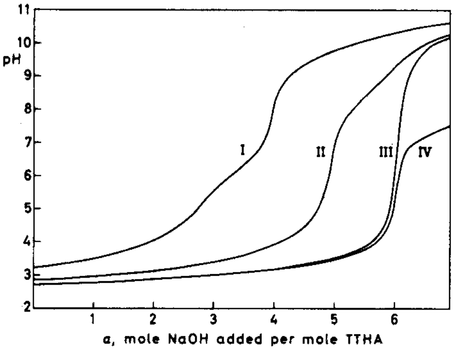


Fig. 1. Titration curves of $5 \cdot 10^{-4}$ M TTHA (I) and 1:1 (II), 2:1 (III) and 3:1 (IV) mixtures of lead(II) and TTHA.

RESULTS AND DISCUSSION

The titration curves of TTHA and of mixtures of lead and TTHA are plotted in Fig. 1. The corresponding curves for zinc and cadmium were similar. The titration curve of the acid exhibits a slight inflexion at an *a* value of 3 and a well-defined inflexion at $a=4$, which is in accordance with earlier data[11]. The titration curves in the presence of metal are similar to those found for the copper–TTHA complexes[6]. A 1:1 mixture of metal and acid exhibits inflexions at $a=5$ and $a=6$, whereas a 2:1 mixture shows one steep inflexion at $a=6$. The inflexion at $a=5$ for the 1:1 mixtures was most pronounced for cadmium, and least pronounced for zinc. For cadmium the inflexion did not, however, occur exactly at $a=5$, but at $a=4.8$. An explanation for this was not found. All three 1:1 curves showed only a slight inflexion at $a=6$. The titration curves of 3:1 mixtures of metal and TTHA were similar to the 2:1 curves up to $a=6$. Further addition of alkali resulted in the formation of metal hydroxide. The position of the buffer region for $a>6$ was consistent with the pH region where the respective metal hydroxides are precipitated. This was checked by separate titrations of the corresponding metal solutions in absence of TTHA. This showed that maximum two metal atoms could be coordinated to one TTHA molecule. The shape of the 3:1 curve below $a=6$ was slightly different for the three metals. The 3:1 curve with zinc coincided completely with the 2:1 curve of this metal, whereas with lead, and still more distinctly with cadmium, the 3:1 curves were situated below the respective 2:1 curves in the region $a=4$–6.

These experiments indicate the existence of the complexes MHA, MA and M_2A. In 1:1 mixtures a mononuclear hydrogen complex is formed which is neutralized when the pH is increased above 7:

$$M^{2+}+H_6A = MHA^{3-}+5H^+$$

$$MHA^{3-} = MA^{4-}+H^+$$

From the shape of the titration curves at $a=4$ it is evident that a MH_2A complex is not formed to any great extent. The existence of such a complex could, however, not be entirely excluded, and it was therefore included in the equations. In the 2:1 mixtures a binuclear complex is obviously dominant:

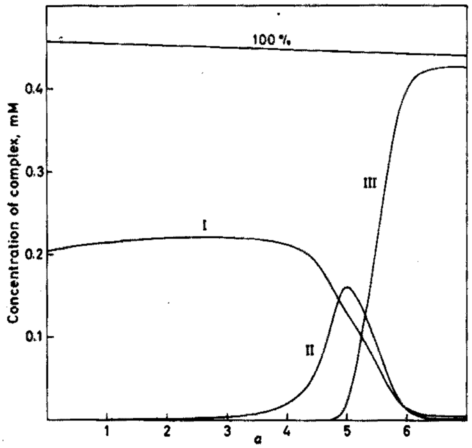
$$2M^{2+}+H_6A = M_2A^{2-}+6H^+$$

The stability constants of the complexes were calculated as described above. The results are given in Table I. As initial values of the constants the values[6] of the copper complexes of TTHA were used. The initial values were, however, of little importance, as the method would almost always converge. The computations were started by calculating K_1 from the region below $a=6$ of the 2:1 curve; K_3 was then calculated from the region below $a=5$ of the 1:1 curve, and K_4 from the region between $a=5$ and $a=6$ of the same curve.

TABLE I

STABILITY CONSTANTS OF TTHA COMPLEXES

Complex	$\log K_1$ M_2A^{2-}	$\log K_3$ MHA^{3-}	$\log K_4$ MA^{4-}
Pb^{2+}	28.1	14.9	16.8
Zn^{2+}	27.9	13.7	16.2
Cd^{2+}	25.3	15.8	17.6



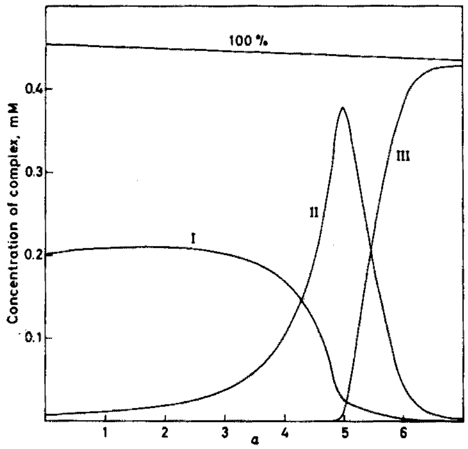


Fig. 2. The concentration of Zn_2A^{2-} (I), $ZnHA^{3-}$ (II) and ZnA^{4-} (III) drawn as a function of *a* for a 1:1 mixture of zinc(II) and TTHA.

Fig. 3. The concentration of Pb_2A^{2-} (I), $PbHA^{3-}$ (II) and PbA^{4-} (III) drawn as a function of *a* for a 1:1mixture of lead(II) and TTHA.

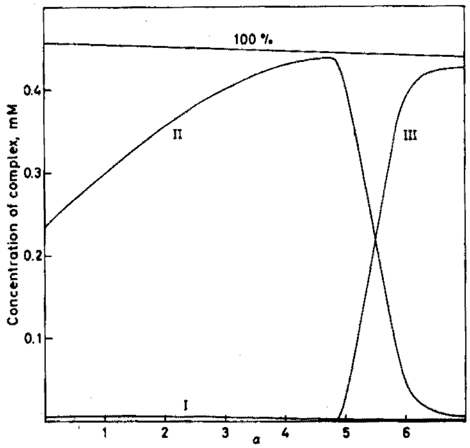


Fig. 4. The concentration of Cd_2A^{2-} (I), $CdHA^{3-}$ (II) and CdA^{4-} (III) drawn as a function of *a* for a 1:1 mixture of cadmium(II) and TTHA.

The calculations gave no evidence of any MH_2A complexes. In Figs. 2, 3 and 4 the concentrations of M_2A, MHA and MA in the 1:1 mixtures of zinc, lead and cadmium respectively, are plotted as a function of *a*. These Figs. clearly demonstrate the difference in the stability of the respective complexes. For zinc, the M_2A complex predominates for *a* values below $a=4.9$, and MHA is only present in major amounts between $a=4.9$ and $a=5.3$, whereas for cadmium the MHA complex predominates in the whole range below $a=5.5$. Lead takes an intermediate position between zinc and cadmium. For all metals the MA complex predominates for *a* values above 5.5.

For the 2:1 mixtures it was similarly found that M_2A predominated in the whole range of the zinc–TTHA and lead–TTHA titration curves, whereas for cadmium the MHA complex was present in major concentration for *a* values below 5.5, M_2A predominating only for higher *a* values.

The stability constants of the MA complexes of zinc, lead and cadmium have recently been reported by Souček *et al.*[12]. They found the values 20.1, 19.5 and 19.8, respectively, for log K of the three complexes. They did not, however, give any values for the stability constants of the MHA and M_2A complexes, although the presence of these complexes will definitely influence the values calculated for the MA complexes. Anyway, with reference to the present titration curves the constants reported by Souček *et al.* seem highly improbable.

The constant of the ZnA^{4-} complex has also been reported by Dyatlova *et al.*[13], who found log $K=17.4$, by means of high-frequency titrations. This value is not too far from the present value. The other constants given in Table I have not previously been reported.

Conradi *et al.*[14] have published the stability constants of the CdH_2A^{2-} and Cd_2HA^- complexes. In the present investigation no evidence was found for any of these species.

The author thanks the Geigy Chemical Company, Basel, for a gift of the TTHA sample. I also wish to thank my wife Tone Lund for performing the titrations.

APPENDIX

```
      PROGRAM KAWL 01
C     CALCULATION OF THE STABILITY CONSTANTS OF TTHA COMPLEXES
C     TITRATION CURVES OF 1/1 AND 2/1 MIXTURES ARE STUDIED IN THIS PROGRAM
C
C     R = SEE TEXT
C     IS = DETERMINE WHICH OF THE STABILITY CONSTANTS TO BE CALCULATED
C     LIF = THE NUMBER OF CYCLES FOR EACH CONSTANT
C     NMAX = THE TOTAL NUMBER OF EXPERIMENTAL POINTS
C     N6 = THE NUMBER OF EXPERIMENTAL POINTS OF THE FIRST TITRATION CURVE
C     CLUT = THE CONCENTRATION OF STANDARD SODIUM HYDROXIDE SOLUTION
C     CAA = THE CONCENTRATION OF STANDARD TTHA SOLUTION
C     CMA = THE CONCENTRATION OF STANDARD METAL SOLUTION
C     CM1,CM2 = NUMBER OF ML OF STANDARD METAL SOLUTION ADDED TO 50 ML TTHA
C     VML1,VML2 = THE TOTAL INITIAL VOLUME OF THE 1/1 AND 2/1 MIXTURES
C     SK = THE DISSOCIATION CONSTANTS OF THE TTHA
C     NSK = THE NUMBER OF DISSOCIATION CONSTANTS OF TTHA
C     PSK = - LOG SK
C     AK,AKA = THE STABILITY CONSTANTS OF THE METAL-TTHA COMPLEXES
C     VML = THE NUMBER OF ML ALKALI ADDED
C     PH = THE PH OF THE SOLUTION
C     H = THE CONCENTRATION OF HYDROGEN IONS
C     AEXP = THE NUMBER OF MOLE ALKALI ADDED PER MOLE OF THE TTHA
C     ABER = CALCULATED VALUES CORRESPONDING TO THE AEXP VALUES
C     N1,N2 = FIRST AND LAST POINT OF THE REGION OF THE CURVE STUDIED
C     MM = THE NUMBER OF PARAMETERS WHICH ARE TREATED SIMULTANEOUSLY
C
      DIMENSION VML (200), PH (200), AEXP (200), H (200), DERIV (5,200),
     1APROD (2,2), BPROD (2), SOLN (6), SK (6), ABER (5,200), AK (6),
     2AKA (4,5), DELK (6), PSK (6), P (6), XMA (10), Y (10), VMLB (200),
     3XM2A (200), XMH2A (200), XMHA (200), XM1A (200), XMX (200), CMX (200)
      R = 0.1 § IS = —1 § LIF = 5 § KK2 = 7
      NMAX = 88 § N6=40
      CLUT=6.930E-02 § CAA=1.000E-03 § CMA=1.000E-02
      CM1=5.0 § CM2=10.0
      VML1=110.0 § VML2=115.0
      NSK=6
      READ 104, (AK (I), I=1,4)
```

```
      READ 102, (PSK (1), I=1,NSK)
      READ 102, (VML (I), I=1,NMAX)
      READ 102, (PH(I),I=1,NMAX)
      PRINT 204,AK(1),AK(2),AK(3),AK(4)
  102 FORMAT (13F6.0)
  104 FORMAT (8E10.3)
  204 FORMAT (/2X,6HAK= ,4E12.3,//)
C
      DO 9 I=1,NSK
    9 SK(I)=10.0**(-PSK(I))
      DO 8 I=1,NMAX
    8 H(I)=1.0/(0.80*10.0**PH(I))
      DO 6 I=1,NMAX
    6 AEXP(I)=CLUT*VML(I)/(CAA*50.0)
C
      DO 37 KK=1,KK2
C
      IF(KK-KK2)46,45,45
   45 MM=1
      DO 47 J=1,4
   47 AKA(J,1)=AK(J)
      N3=1 § N4=NMAX
      GO TO 48
   46 CONTINUE
C
      M=1
      MM=M+1
      L=1
      IS=IS+2
      IF(IS-5)1,4,2
    4 IS=4
      GO TO 1
    2 IS=1
    1 GO TO (16,18,26,28)IS
   16 N1=51 § N2=59
      GO TO 22
   18 CONTINUE
      GO TO 22
   26 N1=9 § N2=23
      GO TO 22
   28 N1=27 § N2=34
   22 CONTINUE
      PRINT 206,KK,IS
  206 FORMAT(/2X,5HKK= ,I3,2X,5HIS= ,I3,/)
C
C     HERE EACH CYCLE STARTS. IT ENDS WITH STATEMENT NR. 100
C
   38 CONTINUE
      DO 20 J=1,4
      DO 20 K=1,MM
   20 AKA(J,K)=AK(J)
      DELK(1)=R*AKA(IS,1)
      AKA(IS,1)=AKA(IS,1)+DELK(1)
      N3=N1 § N4=N2
   48 CONTINUE
C
C     CALCULATION OF XM (M), XA (A) AND ABER FOR EACH VALUE OF H
C     SEE THE EQUATIONS 13, 14 AND 15 IN THE TEXT
C
      DO 60 K=1,MM
      DO 19 I=N3,N4
      II=1
      IF(I-N6)23,23,27
   23 CM=CMA*CM1/(VML1+VML(I))
```

```
      CA=CAA*50.0/(VML1+VML(I))
      GO TO 25
   27 CM=CMA*CM2/(VML2+VML(I))
      CA=CAA*50.0/(VML2+VML(I))
   25 CONTINUE
      P(1)=H(I)/SK(6)
      DO 40 JJ=2,6
      JP2=7–JJ
   40 P(JJ)=P(JJ–1)*(H(I)/SK(JP2))
      PP=P(1)+2.0*P(2)+3.0*P(3)+4.0*P(4)+5.0*P(5)+6.0*P(6)
      Q=1.0+P(1)+P(2)+P(3)+P(4)+P(5)+P(6)
      S1=AKA(4,K)+AKA(3,K)*P(1)+AKA(2,K)*AKA(3,K)*P(1)*H(I)
      S2=AKA(1,K)
      S3=AKA(3,K)*P(1)+2.0*AKA(2,K)*AKA(3,K)*P(1)*H(I)
      XMA(1)=1.OE–50
      DELXM=1.OE–04
   17 XMA(2)=XMA(1)+DELXM
      II=II+I
      IF(II–200)63,64,64
   64 PRINT 231,M,K,I,II,XMA(1),XMA(2),Y(1),Y(2),DELXM
  231 FORMAT (2X,21HM,K,I,II,XMA,Y,DELXM,2X,4I4,5E12.3)
      GO TO 62
   63 CONTINUE
      DO 3 J=1,2
      XA=CA/(Q+S1*XMA(J)+S2*XMA(J)*XMA(J))
      Y(J)=–CM+XMA(J)+S1*XA*XMA(J)+2.0*S2*XA*XMA(J)*XMA(J)
    3 CONTINUE
      IF(Y(1)*Y(2))76,72,73
   72 IF(Y(2))14,77,14
   77 XMA(1)=XMA(2)
      GO TO 14
   76 IF(DELXM–((1.0E–08)*XMA(1)))14,15,15
   15 DELXM=0.1*DELXM
      GO TO 17
   73 XMA(1)=XMA(2)
      GO TO 17
   14 XM=XMA(1)
      XA=CA/(Q +S1*XM+S2*XM*XM)
      ABER (K,I)=–(–6.0*CA–(1.61E–14)/H(I)+H(I)+PP*XA+S3*XA*XM)/CA
      XM2A(I)=AKA(1,MM)*XA*XM*XM
      XMH2A(I)=AKA(2,MM)*P(2)*XA*XM
      XMHA(I)=AKA(3,MM)*P(1)*XA*XM
      XM1A(I)=AKA(4,MM)*XA*XM
      XMX(I)=XM
      CMX(I)=2.0*XM2A(I)+XMH2A(I)+XMHA(I)+XM1A(I)+XMX(I)
      VMLB(I)=ABER(MM,I)*CAA*50.0/CLUT
   19 CONTINUE
   60 CONTINUE
C
C     OUTPUT WHEN KK=KK2
C
      IF(KK–KK2)42,41,41
   41 PRINT 211
  211 FORMAT(//)
      DO 201 I=1,NMAX
  201 PRINT 202,I,H(I),XM2A(I),XMH2A(I),XMHA(I),XM1A(I),
     1XMX(I),CMX(I),PH(I),AEXP(I),ABER(MM,I),VMLB(I),VML(I),I
  202 FORMAT (2X,I3,7E12.3,5F8.3,I5)
      GO TO 62
C
C     CALCULATION OF THE DERIVATIVES OF ABER
C
   42 CONTINUE
      DO 29 I=N1,N2
```

```
      DO 30 J=1,M
   30 DERIV(J,I)=(ABER(J,I)-ABER(MM,I))/DELK(J)
   29 DERIV(MM,I)=AEXP(I)-ABER(MM,I)
C
C     CALCULATION OF THE COEFFICIENTS OF THE NORMAL EQUATIONS
C
      DO 31 J=1,M
      DO 32 K=1,M
   32 APROD(J,K)=0.0
   31 BPROD(J)=0.0
      DO 33 K=1,M
      DO 33 J=1,M
      DO 33 I=N1,N2
   33 APROD(J,K)=APROD(J,K)+DERIV(K,I)*DERIV(J,I)
      DO 34 J=1,M
      DO 34 I=N1,N2
   34 BPROD(J)=BPROD(J)+DERIV(J,I)*DERIV(MM,I)
C
C     CALCULATION OF THE CORRECTION TERM (SOLN) WHEN M=1
C
      IF(M-1)87,87,88
   87 SOLN(IS)=BPROD(1)/APROD(1,1)
      M1=IS § M2=IS § M3=1
      GO TO 89
   88 CONTINUE
   89 CONTINUE
C
C     CALCULATION OF THE NEW AK, AVOIDING NEGATIVE VALUES
C
      DO 86 I=M1,M2,M3
      IF(AK(I)+1.0*SOLN(I))80,80,81
   80 IF(AK(I)+0.1*SOLN(I))82,82,83
   82 AK(I)=0.01*AK(I)
      GO TO 86
   83 AK(I)=0.1*AK(I)
      GO TO 86
   81 AK(I)=AK(I)+SOLN(I)
   86 CONTINUE
C
      PRINT 225,SOLN(1),SOLN(2),SOLN(3),SOLN(4)
      PRINT 205,AK(1),AK(2),AK(3),AK(4)
  225 FORMAT( 2X,6HSOLN= ,4E12.3)
  205 FORMAT(2X,6HAK= ,4E12.3,/)
C
C     TEST FOR THE NUMBER OF CYCLES
C
      IF(L-LIF)36,7,7
   36 L=L+1
  100 GO TO 38
C
    7 CONTINUE
      DO 10 I=N1,N2
   10 PRINT 202,I,H(I),XM2A(I),XMH2A(I),XMHA(I),XM1A(I),
     1XMX(I),CMX(I),PH(I),AEXP(I),ABER(MM,I),VMLB(I),VML(I),I
   37 CONTINUE
   62 CONTINUE
      END
```

SUMMARY

The complex formation between triethylenetetraminehexaacetic acid (TTHA) and lead(II), zinc(II) and cadmium(II) has been studied by means of potentiometric pH titrations. The stability constants of $PbHA^{3-}$, PbA^{4-}, Pb_2A^{2-}, $ZnHA^{3-}$, ZnA^{4-},

Zn_2A^{2-}, $CdHA^{3-}$, CdA^{4-} and Cd_2A^{2-} complexes have been calculated by means of a high-speed digital computer. The numerical procedure used is applicable to all problems of this type. A program for the calculations, written in FORTRAN, is given.

RÉSUMÉ

La formation de complexes entre l'acide triéthylènetétraminehexaacétique (TTHA) et le plomb(II), le zinc(II) et le cadmium(II) a été étudiée par titrations potentiométriques du pH. Les constantes de stabilité des complexes $PbHA^{3-}$, PbA^{4-}, Pb_2A^{2-}, $ZnHA^{3-}$, ZnA^{4-}, Zn_2A^{2-}, $CdHA^{3-}$, CdA^{4-} et Cd_2A^{2-} ont été calculées au moyen d'une machine à calculer digitale de haute vitesse. Le procédé numérique utilisé est applicable à tous les problèmes de ce type. On donne un programme pour les calculs, écrit en FORTRAN.

ZUSAMMENFASSUNG

Die Komplexbildung zwischen Triäthylentetraaminhexaessigsäure (TTHA) und Blei(II), Zink(II) und Cadmium(II) wurde mittels potentiometrischer pH-Titration untersucht. Die Stabilitätskonstanten von $PbHA^{3-}$-, PbA^{4-}-, Pb_2A^{2-}-, $ZnHA^{3-}$-, ZnA^{4-}-, Zn_2A^{2-}-, $CdHA^{3-}$-, CdA^{4-}- und Cd_2A^{2-}-Komplexen wurden mit einem Rechner ermittelt. Das numerische Verfahren ist für alle Probleme dieser Art anwendbar. Ein Programm für die Berechnungen in FORTRAN wird angegeben.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

POTENTIOMETRIC TITRATIONS WITH ION-EXCHANGE MEMBRANE ELECTRODES

PART IV. A FURTHER STUDY OF EXPERIMENTAL VARIABLES

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(Received October 2nd, 1968)

In two recent papers[1,2] the theoretical aspects of the use of ion-exchanging membrane electrodes in potentiometric titrations were discussed. Some experimental results obtained with these systems have also been described[3]. In this paper, the influence of several experimental variables is considered. The following subjects are discussed: (*a*) the influence of the concentration and the kind of the reference solution on the shape as well as on the position of the titration curves; (*b*) the pre-treatment of the membrane; (*c*) the effect of variables such as titration speed, and the surface area and rotational speed of the membrane; (*d*) the capacity of the membrane; (*e*) the influence of the counter ion; (*f*) the concentration of the titrated solution and of the reagent; and (*g*) the influence of inert salts. The analytical aspects of the method are also discussed.

In the previous paper[3], it was shown that in titrations where the counter ion initially present in the solution to be titrated was precipitated, difficulties were encountered because of diffusion of the counter ion into and through the membrane. Accordingly most of the experiments described below, were made with titrations in which the counter ion initially present was precipitated.

EXPERIMENTAL

The apparatus used in the experiments as well as the titration conditions were similar to those described previously[3].

RESULTS

The influence of the concentration and the kind of the reference solution on the shape and position of the titration curves

The importance of the choice of the reference solution has already been demonstrated[3]. It was shown that the reference solution preferably would contain ions that do not form precipitates or complexes with the ions present in the solution to be titrated and in the reagent. In some experiments it was shown that membranes of different make can behave quite differently when the reference solution is not chosen according to this rule.

The influence of the concentration and the diffusion coefficient of the counter ions in the inert reference solution is described below. In this respect, two types of effect must be considered: (*a*) on the position of the titration curves as a whole; and (*b*) on the exact shape of the titration curves. To study the first of these points, two series of titrations were performed with cation-exchanging membranes (sulphonated polyethylene). In the first series, solutions of 0.01 *M* potassium chloride were titrated with 0.1 *M* silver nitrate, with several different concentrations (0.003 to 0.1 *M*) of potassium nitrate as the reference solution. In the second series the same titrations were done, but 0.01 *M* solutions of lithium, sodium, or potassium nitrate, or nitric acid were used as reference (Fig. 1a). In both cases, the theoretically expected effect (see Fig. 7, Part I[1]) was qualitatively obtained.

In studies of the effect on the shape of the titration curves, several experiments were made with the membrane in the same ionic form as the counter ion initially present in the solution to be titrated. However, the nature of the counter ion present in the reference solution (and so the diffusion coefficient) was varied. With precipitation titrations in which silver chloride was precipitated, the influence of the counter ion of the reference solution was very small (Fig. 1b). The influence of the diffusion coefficient of the counter ion of the reference solution was much greater in the case of acidimetric titrations (Fig. 1c; compare curves a and b with c and d). Moreover, the determination of the equivalence point was not very reliable in these cases. The reason for the deviation between the experimental results obtained for precipitation and acidimetric titrations is not known as yet. It should be noted that in other cases, small experimental differences between these two titration types were found.

The influence of varying the concentration of the reference solution on the shape of the titration curves was investigated. With precipitation titrations in which silver chloride was precipitated no influence was found; with acidimetric titrations, there was no effect on the shape of the curves up to the equivalence point and only a very slight effect thereafter, when the potassium chloride reference solution was held at 0.1, 0.03 and 0.01 *M*. The explanation of these data must be sought in the exchange with and the diffusion through the membrane of the counter ions. This effect is enlarged, when the concentrations of the solutions surrounding the membrane are increased, because in that case the Donnan potentials are lowered and thus the permselectivity of the membrane is decreased.

The pre-treatment of the membrane

In order to examine the effect of the ionic form in which the membrane is present before the titrations, a series of titrations of 0.01 *M* sodium chloride with 0.1 *M* silver nitrate was carried out. The membranes used were pre-treated with solutions of 0.01 *M* potassium, sodium or lithium nitrate; in each case 0.01 *M* sodium nitrate was used as the reference solution. There were only very small differences between the results; with the membrane in the K^+-form, the decrease in the membrane potential after the equivalence point was slightly smaller than with membranes in the Li^+-form. With acidimetric titrations, similar results were obtained. However, much greater differences were found in this case when the membranes were used, in different initial ionic forms (Fig. 1c; compare curves a and c with b and d).

On theoretical grounds it can be said that the initial ionic form of the membrane can exert a certain influence on the shape of the titration curves. The influence

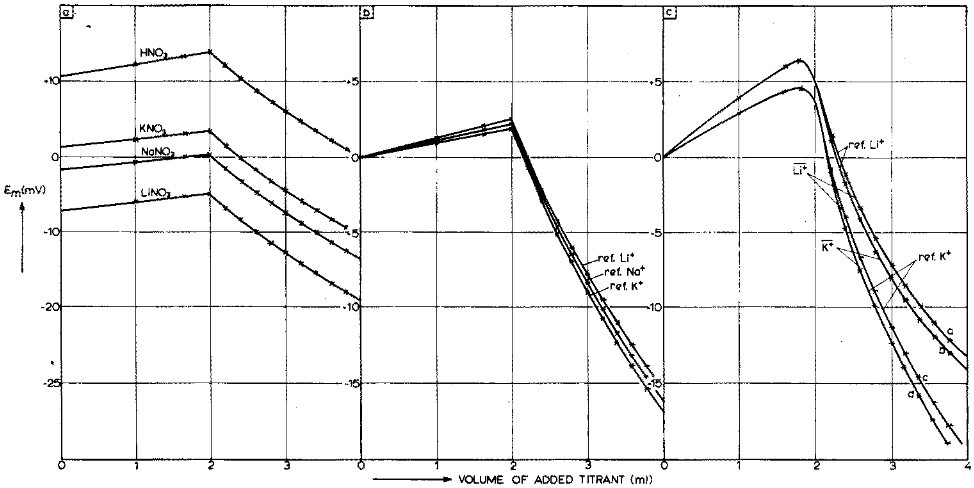

Fig. 1. Effect of altering the counter ion in the reference solution. (a) Titration of 20 ml of 0.01 *M* potassium chloride with 0.1 *M* silver nitrate, with sulphonated polyethylene membranes. Initial ionic form of the membranes: K^+; reference solution: 0.01 *M* $LiNO_3$, $NaNO_3$, KNO_3 and HNO_3 as indicated. (b) Titration of 20 ml 0.01 *M* sodium chloride solution with 0.1 *M* silver nitrate, with Permaplex C 20 membranes, that were previously converted to the Na^+-form. Reference solution: 0.01 *M* $LiNO_3$, $NaNO_3$ or KNO_3 as indicated. (c) Titration of 0.01 *M* sodium hydroxide with 0.1 *N* hydrochloric acid, with cation-exchanging Permaplex C 20 membranes. Ionic form of the membranes: Li^+ (titrations a and c); K^+ (titrations b and d). Reference solution: 0.01 *M* LiCl (titrations a and b); 0.01 *M* KCl (titrations c and d)

stems from the exchange of counter ions inside the membrane with counter ions present in the reference solution and the solution to be titrated. As a result of this exchange, the membrane potential can be altered, for this potential is governed primarily by the concentrations and the diffusion coefficients of the ionic species present in the solutions surrounding the membrane. The actual influence on the membrane potential is of course dependent on the velocities of the exchange reactions at both sides of the membrane.

Titration conditions

The titration speed could be varied by means of different waiting periods between the addition of the reagent and the registration of the membrane potential. Titrations of 0.01 *M* solutions of potassium chloride with 0.1 *M* silver nitrate were performed, in which waiting periods of 0.25, 0.5, 1 and 2 min were applied. For this titration, the shape of the titration curves was not affected by the titration rate. Such an influence would be expected only when the membrane potential varies considerably after the addition of the reagent. With the same titrations as mentioned above, the possible influence of the rotation speed of the membrane was also investigated. Rotation speeds of 600, 900 and 1200 r.p.m. had no effect on the titration curves. This is in accordance with the postulation that the membrane potential is determined by internal membrane conditions (complete membrane diffusion control).

The influence of the membrane surface area was investigated for titrations of 0.025 *M* solutions of potassium sulphate with 0.25 *M* barium chloride and of 0.01 *M* solutions of potassium chloride with 0.1 *M* silver nitrate (Fig. 2). In both cases a small effect was found. Theoretically, the surface area should not have any effect[4], but certain side effects are to be expected. The most important one appears to be the ratio of the membrane surface that is in direct contact with the solutions and the membrane surface area that is shielded by the membrane holder.

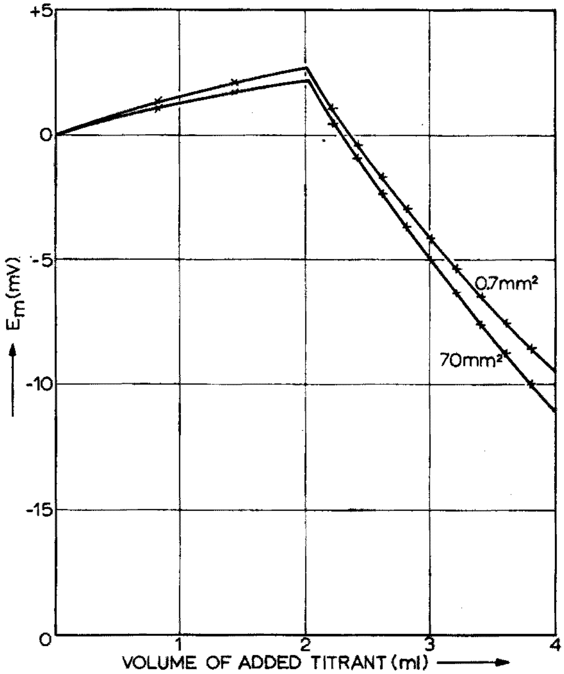

Fig. 2. Titration of 20 ml of 0.01 M potassium chloride with 0.1 M silver nitrate, with Permaplex C 20 membranes in the K^+-form and 0.01 M KNO_3 as the reference solution. Total surface of the membranes 150 mm²; surface area available for diffusion 0.7 or 70 mm².

Capacity of the membrane

Membranes made of sulphonated polyethylene with greatly varying capacity were used as electrodes for titrations of 0.01 M solutions of silver nitrate with 0.1 M alkali metal halides and hydrochloric acid as well as the reverse titrations. The variations in the capacities of the membranes were obtained by applying different sulphonating conditions (time and temperature). The capacities were determined coulometrically, by means of the exchange reaction:

$$\overline{H}^+ + K^+ \rightarrow H^+ + \overline{K}^+$$

The coulometric titrations (constant generating current) were done with membranes that had previously been converted to H^+-form with a dilute solution of nitric acid; the membranes were washed with twice distilled water to free them from sorbed nitric acid and the exchange reaction was carried out in a coulometric cell, with 0.1 M potassium nitrate as the base solution and a glass electrode for the detection of the end-point of the titration.

Owing to the low mechanical strength of these sulphonated polyethylene

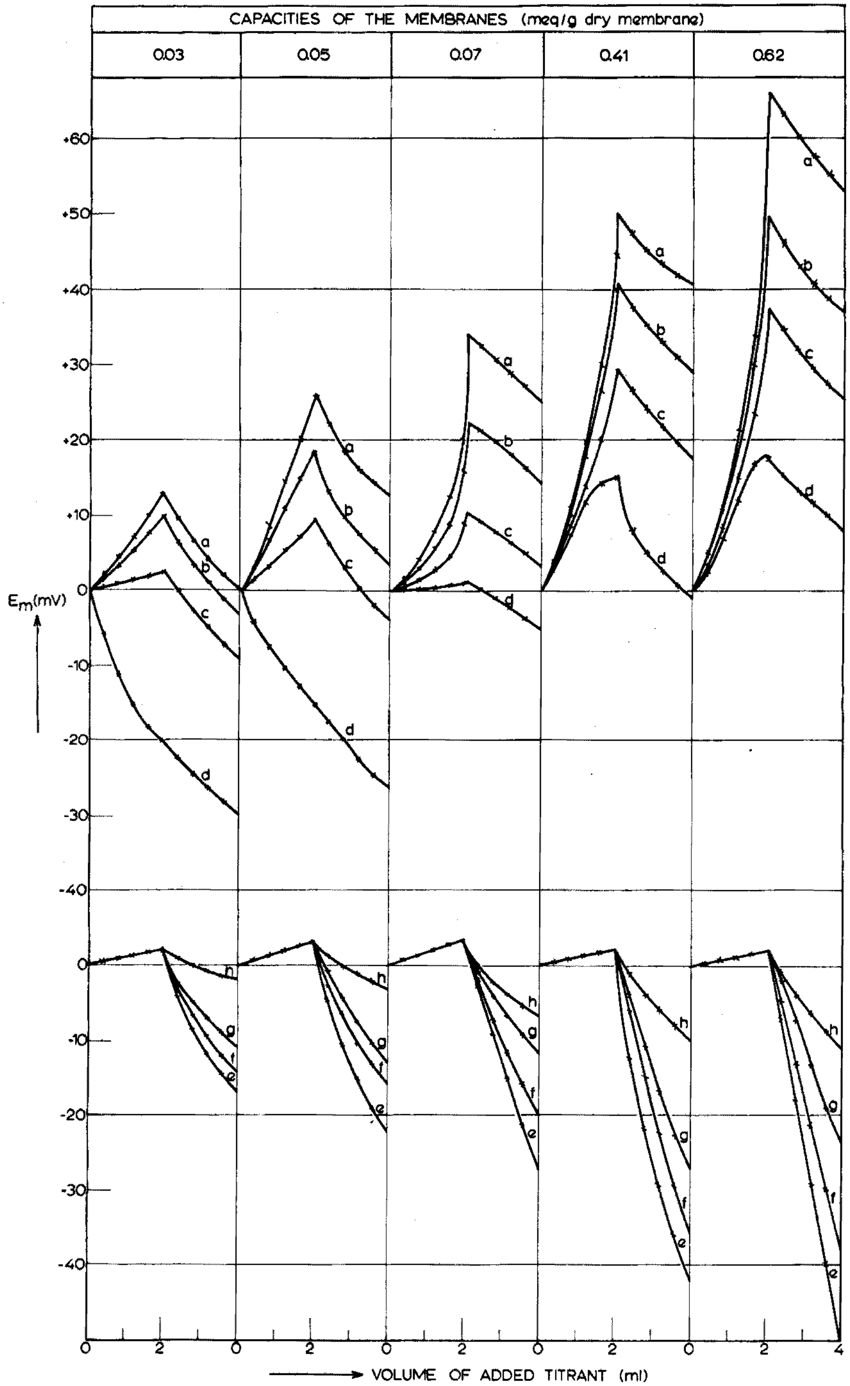

Fig. 3. Influence of the capacity of the membranes on the shape of the titration curves. Sulphonated polyethylene membranes in the K$^+$-form were used with 0.1 *M* KNO_3 as reference solution. Titrations of 20 ml of 0.01 *M* silver nitrate with 0.1 *M* solutions of (a) LiCl, (b) NaCl, (c) KCl and (d) HCl, or 20 ml of 0.01 *M* solutions of (e) LiCl, (f) NaCl, (g) KCl and (h) HCl with 0.1 *M* silver nitrate. The capacities of the membranes are indicated as meq/g of dry membrane.

membranes, no further experiments could be undertaken. The influence of the capacity on the titrations can be seen in Fig. 3. On the whole the results are in accordance with the theoretically expected effect (Fig. 5 of Part I[1]), for with increasing capacity, the membrane potentials during the titration also show increasing variations.

The influence of the counter ion

From the calculated titration curves (see Fig. 5 of Part I[1]), it was concluded that the counter ions present in the solution to be titrated, the reference solution and the reagent should not have any effect, provided that the capacity of the membrane is greater than the concentrations of the surrounding solutions. In order to investigate this matter, 0.01 *M* solutions of potassium chloride, bromide, iodide and thiocyanate were titrated with 0.1 *M* silver nitrate, with a cation-exchanger Permaplex C 20 membrane and 0.01 *M* potassium nitrate as the reference solution. In practice also, no influence of the counter ion was found. With anion-exchanger membranes, however, the counter ion did have a definite effect (Fig. 4). This was found for titrations of different chlorides with silver nitrate solution (Asahi CA 2 membranes) and for titrations of different sulphates with barium chloride solution (Permaplex A 20 membranes). The reason for the different behaviour of cation- and anion-exchange membranes in this respect has not yet been established. In general, the results obtained with cation-exchange membranes are more in agreement with theory than those obtained with anion-exchange material.

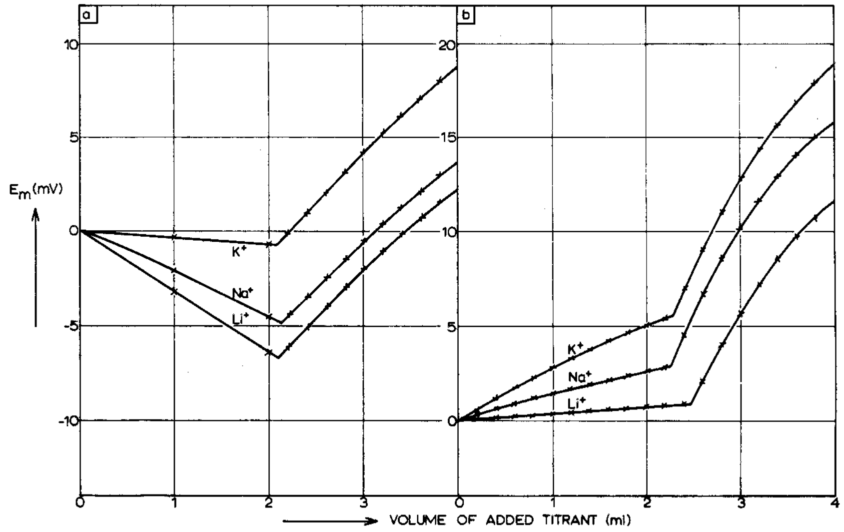

Fig. 4. Effect of counter ion with anion-exchanger membrane. (a) Titration of 20 ml of 0.01 *M* potassium, sodium or lithium chloride with 0.1 *M* silver nitrate, with anion-exchange Asahi CA 2 membranes in the Cl^--form; 0.01 *M* KNO_3 was used as reference solution. (b) Titration of 20 ml of 0.025 *M* potassium, sodium or lithium sulphate with 0.25 *M* barium chloride, with anion-exchange Permaplex A 20 membranes in the Cl^--form; 0.025 *M* KCl was used as the reference solution.

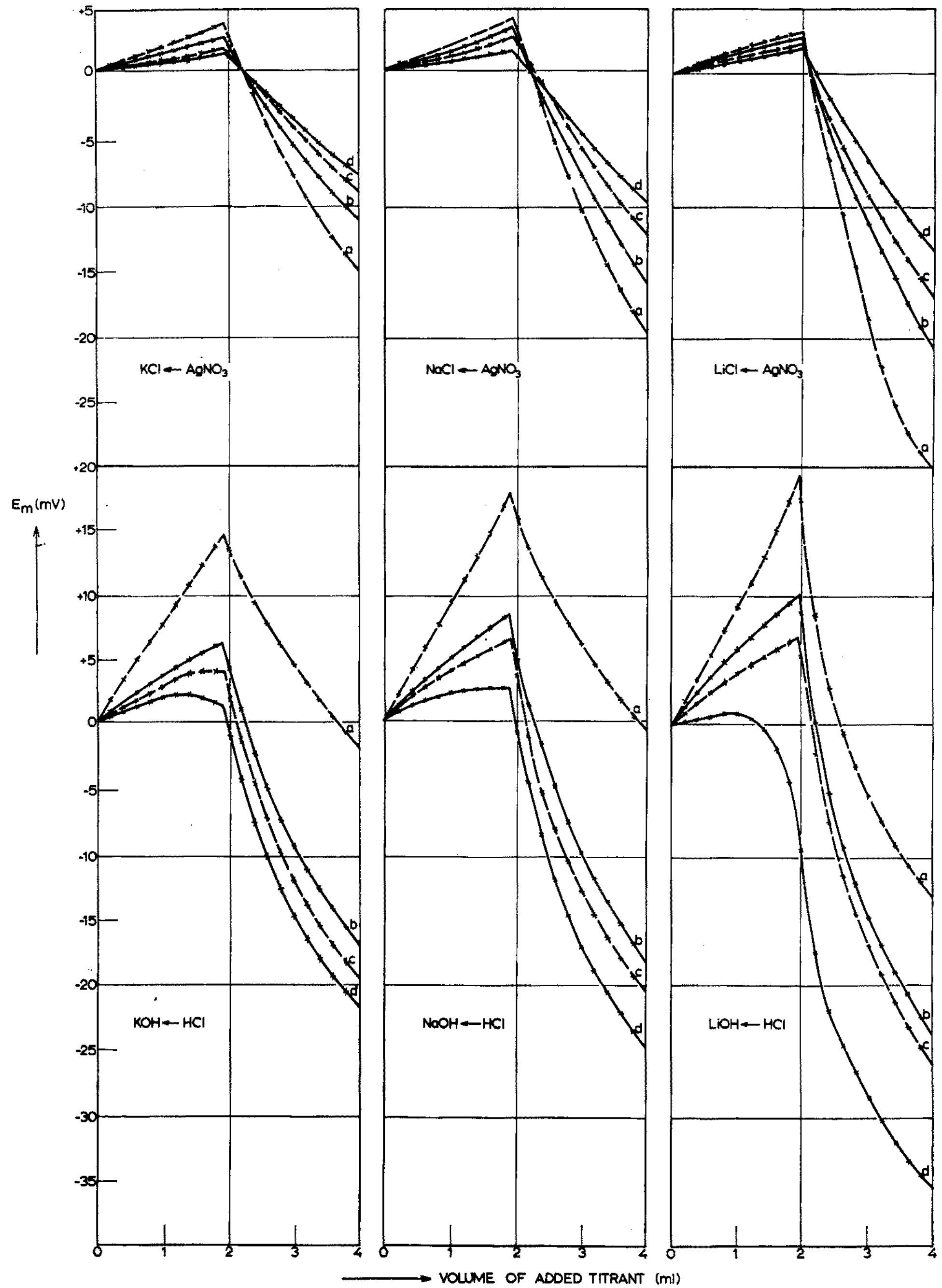

Fig. 5. Effect of the concentrations of titrand and titrant. The following concentrations were used:

curves a: 0.1 *M* solution titrated with 1.0 *M* reagent solution;
curves b: 0.01 *M* solution titrated with 0.1 *M* reagent solution;
curves c: 0.005 *M* solution titrated with 0.05 *M* reagent solution;
curves d: 0.002 *M* solution titrated with 0.02 *M* reagent solution.

Concentration of the titrated solution and the reagent

Figure 5 shows the titration curves obtained for precipitation and acidimetric titrations, when the concentrations of the titrated solutions were varied between 0.003 M and 0.1 M, the concentration ratio between the titrand and titrant being kept constant at a value of ten. In these tests, cation-exchange Permaplex C 20 membranes were used for titrations of potassium, sodium or lithium chloride with silver nitrate, and titrations of potassium, sodium or lithium hydroxide with hydrochloric acid. The membranes had previously been converted to the same ionic form as the counter ions present in the solution to be titrated. In the case of the precipitation titrations, the reference solution contained the alkali metal nitrates corresponding to the alkali metal ion present in the titrand. For acidimetric titrations, the corresponding alkali metal chlorides were taken. The concentration of the reference solution was equal to the concentration of the solution to be titrated. For both types of titration, the curves were definitely affected by concentration. In the case of acidimetric titrations, however, the deviations were greater and occurred in the direction opposite to the precipitation case.

In further experiments, varying quantities of cesium chloride were titrated with 0.1 M silver nitrate (Fig. 6a), and different amounts of potassium hydroxide solution were titrated with 0.1 M hydrochloric acid (Fig. 6b). As can be seen, the steepness of the titration curves after the equivalence point becomes greater when the initial concentration of the solution to be titrated is smaller. This effect is theoretically justified, for with smaller concentrations, the relative change in the Donnan potentials becomes larger, which results in a steeper titration curve after the equivalence point.

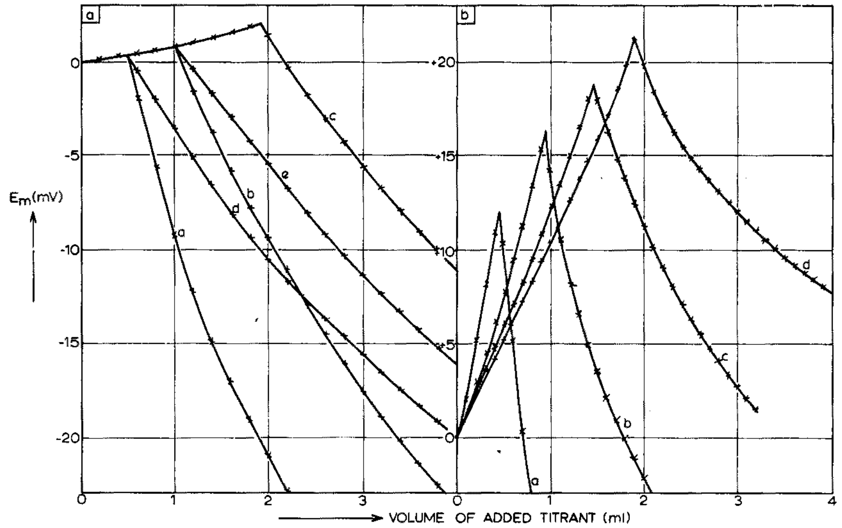

Fig. 6. Effect of the concentration of titrand. (Permaplex C 20 membranes in the K^+-form and 0.01 M potassium nitrate as reference solution.) (a) Titration of cesium chloride with 0.1 M silver nitrate. (a.) 20 ml of 0.0025 M CsCl; (b.) 20 ml of 0.005 M CsCl; (c.) 20 ml of 0.01 M CsCl; (d.) 20 ml of solution, containing 0.0025 M CsCl and 0.0075 M KNO_3; (e.) 20 ml of solution, containing 0.005 M CsCl and 0.005 M KNO_3. (b) Titration of different amounts of potassium hydroxide with 0.1 M hydrochloric acid. (a.) 0.5, (b.) 1.0. (c.) 1.5 and (d.) 2.0 ml of 0.1 M hydroxide solution was used; the total volume of the solution to be titrated was kept at 20 ml.

This matter was investigated further by adding an indifferent salt to the solutions to be titrated, keeping the total concentration of this solution constant. As can be seen from Fig. 6a the steepness of the titration curves after the equivalence point were then independent of the initial concentration of the solution to be titrated.

The presence of inert salts

As indicated above, the presence of inert salts in the solution had a definite effect. To investigate this matter further, increasing amounts of inert salt were added to the solution to be titrated (Fig. 7). As was to be expected, the change of the membrane potential became progressively smaller during the titration in these cases, thus the practical application of the method is severely restricted. For example, many redox and compleximetric titrations are carried out in strongly buffered or acid solutions and in these cases, satisfactory results can not be expected.

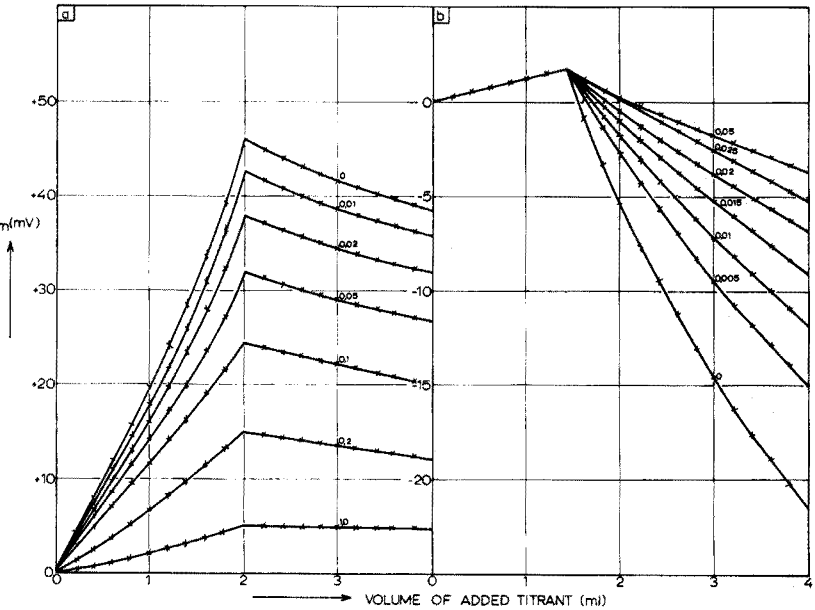

Fig. 7. Effect of inert electrolytes. Inert salt (KNO_3) was added to the solution; the added concentrations (moles/litre) are indicated on each curve. (a) Titration of 20 ml of 0.01 *M* lead nitrate with 0.1 *M* potassium sulphate with Asahi CK 1 cation-exchanging membrane in the K^+-form and 0.02 *M* KCl as reference solution. (b) Titration of 20 ml of 0.007 *M* potassium chloride with 0.1 *M* silver nitrate, with Permaplex C 20 membranes in the K^+-form and 0.01 *M* KNO_3 as reference solution.

ANALYTICAL ASPECTS

In the foregoing experiments, the emphasis was laid on the shape of the titration curves in order to verify the theoretically calculated curves. For analytical applications the exact location and the error in the determination of the equivalence point are very important. Accordingly cesium chloride solutions were titrated with silver nitrate, the concentrations of the solutions used having been accurately determined by potentiometric titration with silver electrodes; Permaplex C 20 membranes were used throughout these investigations. With the membrane electrodes, the equivalence point was found at 1.95 ml, which was exactly the value found by the potentiometric titrations with the silver electrode. The relative standard deviation of the determination of the equivalence point was 0.35%. A series of titration results with the membrane electrodes are shown in Table I. It can be seen that excellent agreement was found between the added amount of cesium chloride solution and the volume of reagent solution needed for the titration.

With acidimetric titrations in which anion-exchange membranes (Permaplex A 20) were used, identical results were obtained.

When the application of the membrane electrodes is not hampered by the

TABLE I

RESULTS OBTAINED IN TITRATIONS OF CESIUM CHLORIDE WITH 0.01 *M* SILVER NITRATE WITH CATION-EXCHANGE MEMBRANES (PERMAPLEX C 20)[a]

CsCl solution added (ml)	*$AgNO_3$ consumed*[b] *(ml)*					
1	0.95	0.93	0.94	0.94		
2	1.85	1.87	1.87	1.87	1.87	1.86
3	2.81	2.83	2.83	2.82		
4	3.74	3.74	3.72	3.73		

[a] With a silver electrode 1.87 ml of $AgNO_3$ (mean of four determinations) was used for titrating 2 ml of CsCl solution. The total volume of solution to be titrated was 20 ml in all cases. 0.01 *M* KNO_3 was used as the reference solution.

[b] End-points were determined graphically.

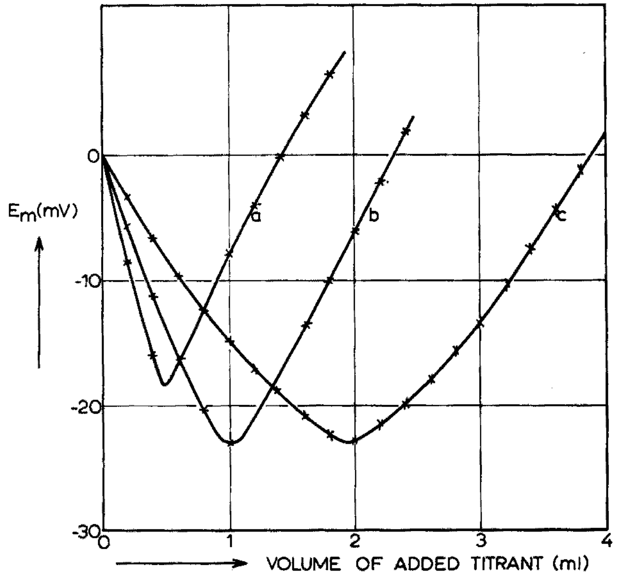

Fig. 8. Titration of slightly acidified solutions of 0.1 *M* iron(III) chloride with 0.1 *M* EDTA, with cation-exchange membranes of the sulphonated polyethylene type. The membranes were used in the K^+-form and 0.1 *M* KCl was used as reference solution. (a) 0.5, (b) 1.0 and (c) 2.0 ml of 0.1 *M* iron(III) chloride was used for the titration; the total volume of the solution to be titrated was kept at 20 ml.

presence of inert salts, redox and compleximetric titrations can also be performed. An example is given in Fig. 8, where solutions containing different amounts of iron(III) were titrated with solutions of EDTA.

CONCLUSIONS

The following conclusions can be drawn from the work described above.

In some cases, small deviations are found between the experimental and the theoretically calculated titration curves; in this respect, the results obtained with cation-exchange membranes are more in accordance with theoretical expectations than is the case for anion-exchange material. The same holds for precipitation titrations as compared with acidimetric titrations. These deviations are probably due to the lack of complete permselectivity of the membranes, and to the exchange of counter ions between the membrane and the surrounding solutions. However, the effects illustrated in Fig. 4 cannot be explained in this manner.

The deviations mentioned above do not impede the analytical application of the method. However, it is necessary to choose a membrane for the titration in such a way that the ion to be precipitated from the solution is a counter ion to the ion in the membrane. A further limitation is found in the interfering effect of the presence of foreign inert salts.

Apart from these limitations, excellent results can be obtained; the accuracy and the precision of the method appear to be good.

SUMMARY

The effects of various experimental parameters on the shapes of potentiometric titration curves obtained with ion-exchange membrane electrodes are described. Particular attention is given to the nature of the reference solution, the pretreatment and capacity of the membrane, the effect of counter ions, and the effects of varying concentrations of titrant and titrand, as well as of inert electrolytes. The analytical aspects of the methods are discussed.

RÉSUMÉ

On examine l'influence de divers paramètres expérimentaux sur les courbes de titrage potentiométrique obtenues au moyen d'électrodes à membrane échangeuse d'ions. Une attention toute particulière est portée sur la nature de la solution de référence, le prétraitement et la capacité de la membrane, l'influence des concentrations de la solution à titrer et du réactif, ainsi que des concentrations des électrolytes inertes. Les aspects analytiques des méthodes sont discutés.

ZUSAMMENFASSUNG

Es werden die Einflüsse zahlreicher experimenteller Parameter auf die Gestalt potentiometrischer Titrationskurven bei der Verwendung von Ionenaustauscher-Membranelektroden beschrieben. Besonder Aufmerksamkeit wurde gerichtet auf die Natur der Vergleichslösung, die Vorbehandlung und die Kapazität der Membrane, den Einfluss des Zählions und die Einflüsse der variierenden Konzentrationen des Titers, der Lösung ebenso wie des inerten Elektrolyten. Die analytischen Aspekte der Methode werden diskutiert.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SEPARATION OF URANIUM FROM PHOSPHORIC ACID BY REVERSED-PHASE COLUMN CHROMATOGRAPHY

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(Received October 25th, 1968)

Several methods have been proposed for the analysis of uranium in various media, but very little information is available concerning concentrated phosphoric acid solutions. The complexing abilities of phosphate and pyrophosphate pose an interference to the usual methods, and a means of separation is necessary. The procedure of FRANÇOIS[1], involving the extraction of uranyl ion with tri-*n*-butyl phosphate followed by color-development in dibenzoylmethane, while not quantitative in a single extraction, will after multiple extractions yield a quantitative result. Repetitive manual extractions have been considered inconvenient and time-consuming, while, on the other hand, column chromatography is often used to provide multiple extractions efficiently. In the present work, reversed-phase column chromatography has been examined, and a valuable separation has resulted that eliminates the handling that would otherwise be necessary. Columns packed with tri-*n*-butyl phosphate supported on silica gel have been used and are discussed. A similar system has been employed by HAMLIN *et al.*[2] for aqueous solution and the present investigation is a useful extension to that work.

EXPERIMENTAL

Column preparation

Prepare a column of 35–40% tri-*n*-butyl phosphate on silica gel by depositing tri-*n*-butyl phosphate from an *n*-pentane solution. Evaporate the *n*-pentane under an infrared lamp facilitated by occasional stirring. Slurry the coated support with water, pour into a glass column, and wash first with water to remove excess of liquid phase and then with saturated aluminum nitrate solution to condition the column for sample introduction. Phosphoric acid solutions are introduced in saturated aluminum nitrate.

The aluminum nitrate solution (900 g $Al(NO_3)_3 \cdot 9H_2O$/l) and the water eluents were both saturated with tri-*n*-butyl phosphate. The flow rates of the eluents could be controlled with air pressure to 1–2 ml/min.

Uranium analysis

Uranyl ion is extracted from the acidic, concentrated aluminum nitrate solution with tri-*n*-butyl phosphate. An aliquot of the extractant containing the uranyl ion is reacted with dibenzoylmethane and the characteristic yellow-green color of the uranyl complex read spectrophotometrically.

Phosphate analysis

The colorimetric molybdovanadate procedure[3] is used for the phosphate analysis. Because of the many analyses required, a Technicon AutoAnalyzer was employed.

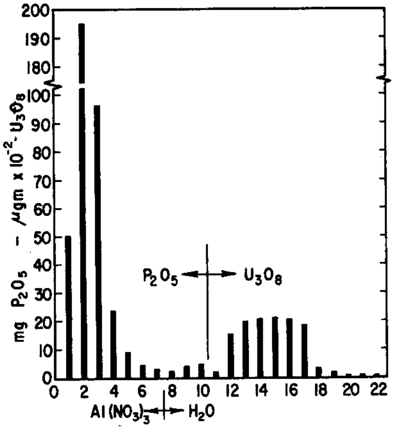
PROCEDURE

Pack 12 g of coated material, prepared as described above, into a 1.2-cm glass column and wash with 25 ml of water followed by 15 ml of saturated aluminum nitrate solution. Mix a sample aliquot containing greater than 100 μg of U_3O_8 with approximately an equal volume of saturated aluminum nitrate solution and introduce it onto the column. A small plug of glass wool at the top of the column will prevent agitation of the packing material. Elute the phosphoric acid with 25 ml of aluminum nitrate solution and change the solvent to water. In order to prevent uranium, which may be held at the top of the column, from back-diffusing into the solvent reservoir, add small aliquots of water (*ca.* 1 ml) initially and allow each to percolate into the column. Once the uranium has been displaced down the column, complete elution can be made with larger volumes of water directly into a 25-ml volumetric flask. Take a 10-ml aliquot for the uranium analysis. The column should be washed with 25 ml of water and conditioned with aluminum nitrate between separations.

RESULTS AND DISCUSSION

Columns containing 75–80 ml of packing were used to investigate the separation. While the analysis time is longer, larger quantities of material can be handled, so that the many partial analyses are more convenient and accurate.

Figure 1 shows the separation of a solution containing 396 mg (24.9%) phosphoric acid and 34 mg of U_3O_8. Separation is complete and recovery yields 410 mg of phosphoric acid and 33 mg of U_3O_8. No uranium is detected in the phosphoric



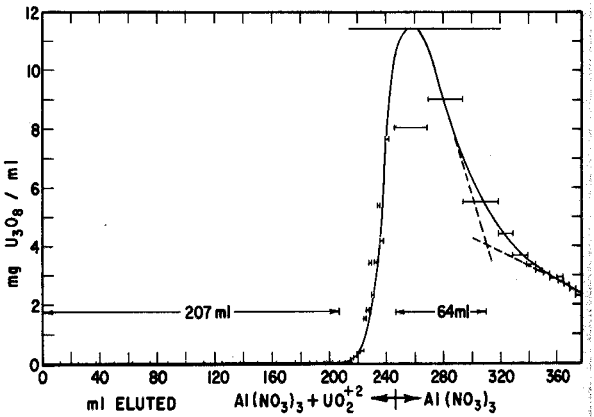


Fig. 1. Separation of uranium from phosphoric acid.

Fig. 2. Evaluation of column capacity.

acid fractions, which indicates complete retention of uranyl ion in the tri-*n*-butyl phosphate liquid phase during the elution with aluminum nitrate.

To evaluate the capacity of the column, a solution containing 11.4 mg of U_3O_8/ml of aluminum nitrate solution was passed through the column until uranium was detected. The uranium concentration was followed until it reached a constant value of 11.4 mg/ml. At this point, aluminum nitrate solution containing no uranium was introduced and the mobile phase volume of the column evaluated. The curves are shown in Fig. 2. Subtracting the mobile phase volume from the volume to initial uranium detection yields $207-64=143$ ml of standard solution. Thus, 143 $(11.4)=1630$ mg or over 1.5 g of uranium as U_3O_8 can feasibly be retained on the column.

Evidence of an equilibrium partitioning process is shown by the sharp front. Elution can probably be made with aluminum nitrate after long times, while water hastens the elution by pushing the equilibrium in favor of the mobile phase.

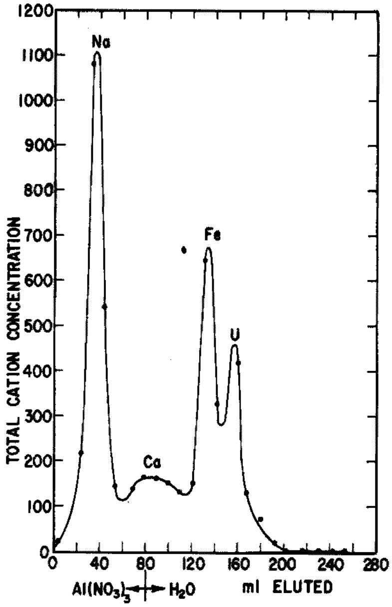


Fig. 3. Separation of components in a sandstone ore.

An interesting separation was obtained with a sandstone ore (0.92% U_3O_8). The ore was leached by acid digestion and the clear solution introduced onto the column. The resulting separation is shown in Fig. 3. The major components of the ore as determined by an emission spectrographic analysis were determined in each of the several collected fractions by atomic absorption spectroscopy. While the analysis scheme described by FRANÇOIS is entirely adequate for such ores, it is interesting that the separation does occur; U_3O_8 recovery was 0.95%.

With the separation defined, smaller columns were prepared to obtain a faster analysis. Columns containing *ca.* 13 ml of packing were used for analytical separations.

Table I shows the accuracy obtainable from the method at two concentration levels. Degeneration of the column is seen at the higher concentration with rapidly increasing error after 4 separations. As much as 1.2 g of phosphoric acid solution could be separated without adverse effect to the column at the lower concentration.

TABLE I

PRECISION AND ACCURACY AT TWO CONCENTRATION LEVELS

184 p.p.m. U_3O_8	*1.15%* U_3O_8
181	1.16
199	1.14
163	1.13
176	1.10
214	1.01
190	0.95
187 ± 17.9	1.08 ± 0.077
	(1st four) 1.13 ± 0.026

Since a "band" distribution is not necessary, the sample volume is not important as long as all of the uranium is retained on the column during the phosphoric acid elution. The proposed analytical separation of concentrated phosphoric acid from uranium is simple, fast and accurate and may be applicable to other media.

SUMMARY

Uranium and phosphate can be quantitatively separated on a column containing tri-*n*-butyl phosphate on silica gel. Phosphate can be eluted with saturated aluminum nitrate solution before the elution of uranium with water. The procedure is simple, rapid and versatile.

RÉSUMÉ

L'uranium et le phosphate peuvent être séparés quantitativement dans une colonne contenant du tri-*n*-butyl-phosphate sur du silica gel. Le phosphate peut être élué avec une solution saturée de nitrate d'aluminium avant l'élution de l'uranium avec l'eau. Le procédé est simple, rapide et présente de multiples possibilités.

ZUSAMMENFASSUNG

Uran und Phosphat können quantitativ voneinander getrennt werden mit einer Kolonne, die Tri-*n*-butylphosphat auf Silicagel enthält. Zuerst wird das Phosphat mit gesättigter Aluminiumnitratlösung eluiert und danach das Uran mit Wasser. Das Verfahren ist einfach, schnell und wandelbar.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF TRACES OF HYDROGEN, NITROGEN AND OXYGEN IN AQUEOUS SOLUTIONS BY GAS CHROMATOGRAPHY

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(Received October 28th, 1968)

For the determination of small amounts of dissolved hydrogen, nitrogen and oxygen in aqueous samples, gas chromatography is an attractive technique. The dissolved gases must be isolated from the liquid before their chromatographic separation and determination can be performed. For this isolation process four general methods can be used[1]: (*a*) direct injection of the sample (to the column or a pre-column unit); (*b*) boiling methods; (*c*) vacuum extraction; or (*d*) stripping methods.

Direct injection of the sample. In this method the water sample is injected directly on to the chromatographic column; the gases are liberated from the absorbed liquid and eluted through the column in the usual way. For the absorption of water, a heated pre-column filled with granular calcium sulphate can be used. This method has been applied by KILNER AND RATCLIFF[2] for the determination of hydrogen in quantities of 1–100 μl in water samples of 0.2–0.3 ml. The limited sample volume and the risk of atmospheric contamination during sampling make this method of direct injection less attractive if micro amounts of hydrogen, nitrogen or oxygen have to be determined.

Boiling methods. In these methods the gaseous constituents are removed by boiling the liquid phase. The evolved gases can be taken up during[3] or after[4] the boiling process by the carrier gas stream of the chromatograph. They can also be removed after boling with the aid of a syringe and injected into a conventional gas chromatograph[5]. However, the complete removal of micro amounts of gases from liquids is very difficult when this method is used, hence the methods are unsuitable for trace analysis.

Vacuum extraction. In this method a relatively small amount of sample is introduced into a large evacuated vessel[6–8]. The dissolved gases are extracted from the stirred liquid into the evacuated chamber. After the extraction process, the gases are compressed to a small volume with the aid of mercury and finally transferred by the carrier gas stream to the chromatographic column. Preliminary tests showed that ice formation during extraction is a serious drawback of this method.

Stripping technique. Here the dissolved gases are stripped from the liquid sample by a gas stream. In the method of SWINNERTON *et al.*[9], a finely dispersed helium stream is passed through the water sample. The stripped gases are carried directly by the helium stream into the chromatograph for analysis.

For samples with a volume of 1–3 ml, the stripping of dissolved gases is very effective, so that their longitudinal dispersion in the stripping gas is small and sharp peaks in the chromatogram can be obtained. For sample sizes exceeding 3 ml, the stripping is less effective and the longitudinal dispersion of the stripped gases in the helium is increased.

The study described in this paper was concerned with the determination of micro amounts of hydrogen, nitrogen and oxygen in water from reactor loops, hence the stripping technique was preferred. On account of the limited sensitivity of the chromatographic detector available, the sample volume needed was, however, often rather large, being 10 ml or even more. When the method of SWINNERTON *et al.*[9] was used, the longitudinal dispersion of the stripped gases in the helium stream was therefore excessive, so that the stripped gases had to be concentrated. This concentration was accomplished by modifying the method of LEWIS AND MELNICK[10] for the determination of gases in metals by vacuum fusion. In the modified method, the helium stream with the stripped gases was passed through a gas trap filled with granular molecular sieve 5A at liquid nitrogen temperature and thence to the chromatographic column. In the gas trap (the absorption tube in Fig. 2), hydrogen, nitrogen and oxygen are absorbed completely from the helium stream*. When this stripping is completed, the vacuum flask with liquid nitrogen is removed and the trap is warmed up gradually in air to room temperature so that hydrogen, nitrogen and oxygen are desorbed from the molecular sieve. The desorbed gases are taken up by the helium gas stream and carried to the chromatograph for analysis. In the gas trap, some preliminary separation of the gases occurs, so that the chromatographic column has an additional function only. When this concentration method is used, the design of the stripping chamber in the sampling tube can be simplified. The

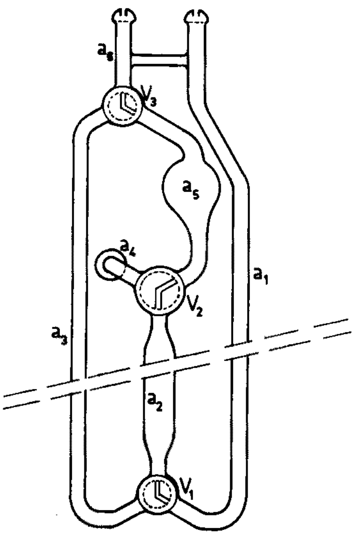

Fig. 1. Sampling tube with stripping chamber (a_2).

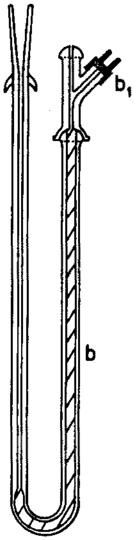

Fig. 2. Absorption tube (b), the right leg is filled with molecular sieve. Serum cap (b_1) is used for gas injection for calibration.

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* For the complete absorption of hydrogen, pretreatment of the molecular sieve by heating at 300° in a helium stream is essential.

fritted glass disk used by SWINNERTON for the fine dispersion of the stripping gas can be omitted and the sampling tube can be designed in such a way that it can be connected directly to the vessel with the bulk liquid to be analysed.

With the method described, above 1 µl of dissolved hydrogen, nitrogen and oxygen can easily be detected in water samples of 30 ml or more.

EXPERIMENTAL

Chemicals

Helium. The cylinder gas used contained the following maximum concentrations of impurities: 0.5 p.p.m. H_2, 8 p.p.m. N_2, 1 p.p.m. O_2, 14 p.p.m. Ar by weight.

Linde Molecular Sieve 5A. This was used as 1/16-in pellets, and as 30–60 mesh powder obtained from pellets by grinding and sieving. Both forms were heated at 300° in a helium stream for 4 h before use.

Apparatus

Glass equipment was used with ball joints and spring-loaded stopcocks. The important parts are the sampling tube and the absorption tube.

Sampling tube a (Fig. 1). This was constructed with three-way stopcocks V_1 and V_3 of 2-mm bores and three-way stopcock V_2 of 4-mm bore. The volume of the stripping chamber a_2 in the standard sampling vessel was about 30 ml and its internal diameter 13 mm. The volume of the stripping chamber can be varied between wide limits; its diameter must be sufficiently small that the flattened gas bubbles of helium, developed at the bottom of the tube during stripping "scrub" along the walls of the vessel.

Absorption tube b (Fig. 2). This tube was U-shaped, with a length of 20 cm. The internal diameter of the leg filled with molecular sieve pellets was 5 mm, and the diameter of the capillary tube was 2 mm. The rubber cap b_1 on the top of the tube was used for the injection of gases for calibration purposes. The capillary part of the tube was connected to the chromatographic column via a metal capillary tube of 0.5-mm internal diameter.

Flow control valve. Brooks Flow Controller ELF model 8743.

Chromatograph. A Pye Argon Chromatograph type 12001 equipped with an ionisation detector with a 20 mC strontium-90 source was used. The chromatographic column was a glass tube with a length of 120 cm and an internal diameter of 4 mm, filled with molecular sieve powder 30–60 mesh and held at 125°. The helium carrier stream through the column had a speed of 60 ml/min (at atmospheric pressure) during the measurements.

Sampling

The dry sampling tube was flushed and filled with helium. Then the top of tube a_1 (Fig. 1) was connected to the outlet tube of the vessel containing the bulk liquid and water from the vessel was passed through tubes a_1, a_3 and a_6. After a considerable overflow, valves V_1 and V_2 were turned and the liquid was forced into the stripping chamber a_2; the excess of liquid was led away via tube a_4. After a further considerable overflow, tubes a_1 and a_3 were connected again by turning valve V_1; valve V_2 was turned so that the helium gas in tube a_5 was in direct contact with the liquid in the stripping chamber. (In this way considerable pressure variations in the stripping chamber on heating or cooling of the sample were avoided.) Tubes a_1, a_3 and a_6 were then emptied and dried, and the sampling tube was connected with tubes e and f of the glass equipment (Fig. 3).

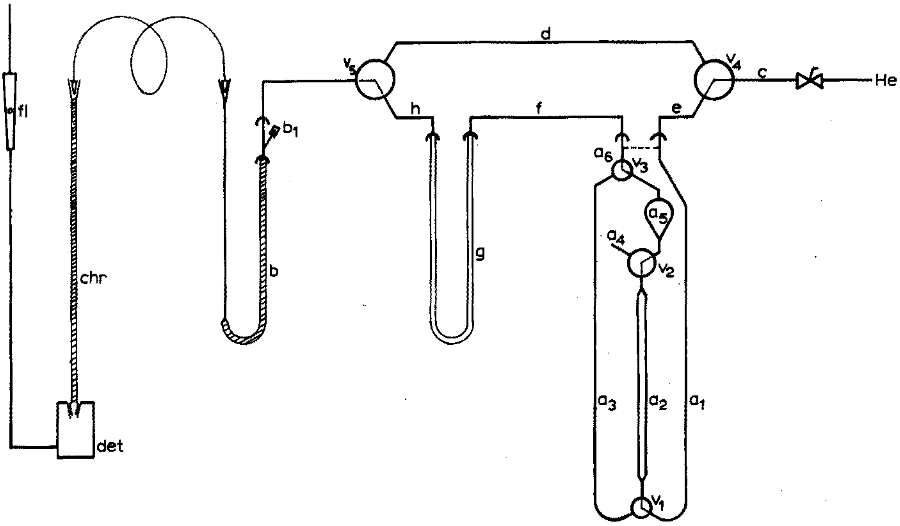

Fig. 3. Analytical equipment. (a) Sampling tube; (b) absorption tube; (g) water trap; (chr) chromatographic column; (det) detector; (fl) gasflow meter.

Analytical procedure

Helium was passed first through a reduction valve and then through a tube filled with molecular sieve pellets held at liquid nitrogen temperature, in order to reduce the concentrations of the impurities to a level where they do not cause a measurable blank. The helium was then passed through the flow controlling valve and finally introduced into the glass apparatus (Fig. 3) at tube c. By means of the three-way valves V_4 and V_5 (4-mm bores), the helium was led through tube d and absorption tube b held at room temperature, and then to the chromatographic column.

When the analytical procedure was started, valves V_4 and V_5 were turned and the helium stream was passed through tubes e, a_1, a_3, a_6, f, g and h to absorption tube b. After the chromatographic recorder had returned to its original position (all air from tubes e, a_1, a_3 and a_6 having been driven out), the absorption tube b and the empty water collecting tube g were immersed in liquid nitrogen, and after a few minutes the stripping process was started. This stripping was achieved by turning valve V_3 and, carefully, valve V_1, in such a way that helium from a_1 passed through stripping chamber a_2 and tubes a_5 and a_6. At the beginning of the stripping, the helium bubbles formed in chamber a_2 forced some water into tube a_5.

After 20 min, stripping was complete; valves V_4 and V_5 were then turned so that helium from tube c passed again via tube d to the absorption tube b. After the chromatographic recorder had returned to its original position the Dewar filled with liquid nitrogen was removed from the absorption tube and the tube was allowed to warm up in air to room temperature. During the warming up hydrogen, oxygen and nitrogen were desorbed in this sequence from the molecular sieve and eluted through the chromatographic column. The heights of the corresponding peaks in the chromatograph were used for the concentration determinations.

Calibration

For rapid calibration, known volumes of hydrogen, nitrogen and oxygen were injected through rubber cap b_1 while absorption tube b was at liquid nitrogen temperature. After removal of the liquid nitrogen the gases were desorbed and measured as described above.

For more precise determinations of hydrogen and oxygen, known amounts of these gases were generated coulometrically in a 0.5 *M* potassium sulfate solution[11] in a stripping chamber equipped with platinum electrodes. The stripping procedure mentioned was then applied.

For the determinations of hydrogen and nitrogen, these gases were generated coulometrically in a 0.1 *M* hydrazine sulfate solution[12].

DISCUSSION

The sensitivity of this method is determined primarily by the sensitivity of the chromatographic detector. In the standard procedure, the detection limit was found to be 2 p.p.b. (by weight) for hydrogen and 10 p.p.b. for nitrogen and oxygen in water samples of 30 ml. The sensitivity can be increased by using larger volumes for stripping. In the concentration range 0.1–1 p.p.m., values with a precision of 10% can be easily obtained.

The walls of the sampling vessel should be perfectly clean: grease stains may cause erroneous results on account of absorption effects. The connection made for sampling between tube a_1 of the sampling vessel and the delivery tube of the vessel with bulk sample should be made of glass or metal; no plastic tubing (causing high oxygen and nitrogen measurements) should be applied here. Sampling is the most critical part of the whole procedure.

A stripping time of 20 min is quite sufficient. If the stripping time is increased considerably, hydrogen may be eluted from the molecular sieve in absorption tube b even at liquid nitrogen temperature, and low hydrogen values may be obtained.

After about one month of use the molecular sieve in the absorption tube should be reactivated by heating at 300° in a helium stream for 4 h.

Traces of carbon monoxide and methane that may be present in the sample can be determined without difficulty in the same run with hydrogen, nitrogen and oxygen, following the general procedure. Carbon dioxide is absorbed irreversibly by the molecular sieve and is not detected. Any argon present in the sample is detected together with oxygen. Argon and oxygen can be separated in an extra column of 150 cm length filled with molecular sieve and held at dry ice–acetone temperatures ($-72°$)[13,14]. This column is placed between the absorption tube (b) and the chromatographic column (chr) in Fig. 3. In this case, nitrogen, carbon monoxide and methane absorbed on the molecular sieve at $-72°$, can be determined in a separate run with the standard equipment without the extra column.

The authors wish to thank Mr. H. A. RUITER for his assistance in this work.

SUMMARY

Traces of hydrogen, nitrogen and oxygen in water can be determined by stripping the gases from water samples of up to 30 ml with a helium stream. The stripped gases are absorbed from the helium on molecular sieve 5A pellets at liquid nitrogen temperature; at room temperature, the gases are desorbed from the molecular sieve and determined by gas chromatography. Carbon monoxide, methane and argon can be determined simultaneously.

RÉSUMÉ

Des traces d'hydrogène, d'azote et d'oxygène dans l'eau peuvent être dosées en "entrainant" ces gaz à l'aide d'un courant d'hélium. Les gaz "strippés" sont absorbés à la température de l'azote liquide et dosés par chromatographie gazeuse. On peut doser simultanément oxyde de carbone, méthane et argon.

ZUSAMMENFASSUNG

Spuren von Wasserstoff, Stickstoff und Sauerstoff können in Wasserproben bis zu 30 ml bestimmt werden, indem sie durch einen Heliumstrom herausgespült werden. Die Gase werden dann mittels eines Molekularsiebes bei der Temperatur des flüssigen Stickstoffs vom Helium abgetrennt und bei Raumtemperatur desorbiert und gaschromatographisch bestimmt. Kohlenstoffmonoxid, Methan und Argon können gleichzeitig bestimmt werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DOSAGE DE DEUX ETATS D'OXYDATION D'ELEMENTS MULTIVALENTS

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(Reçu le 14 juillet, 1968)

Les problèmes analytiques qu'on rencontre généralement en chimie minérale consistent à déterminer la quantité ou la concentration d'un élément donné, le plus souvent mélangé à d'autres éléments, sans se préoccuper de la forme chimique ou de l'état d'oxydation, dans lequel il se trouve. Dans certaines études toutefois, notamment, dans celles des équilibres d'oxydo-réduction, en photochimie, en chimie des radiations ou en sonochimie, c'est le dosage d'un état d'oxydation déterminé ou de deux, parfois de trois états du même élément, qui est exigé. Il s'agit, en effet, de pouvoir suivre quantitativement l'évolution d'un état d'oxydation aux dépens ou au profit d'un autre état, donc de doser, fréquemment, de très faibles quantités ou des concentrations, de l'ordre de 10^{-4} ou 10^{-5} *M*, d'un état en présence d'un grand excès de l'autre ou des autres états. Ces dosages sont, d'autre part, souvent facilités par le fait que les solutions à analyser ne contiennent pas d'éléments étrangers susceptibles d'interférer.

On trouve dans la littérature analytique des renseignements utiles pour de tels dosages, mais ils sont rarement adaptables directement aux problèmes posés. Au cours de recherches radiolytiques étendues sur des composés minéraux variés, nous avons essayé de résoudre ceux-ci, surtout à l'aide de méthodes spectrophotométriques, qui paraissent être les plus rapides et les plus sensibles. Mais dans certains cas, la potentiométrie, la polarographie et même la volumétrie peuvent également fournir des résultats satisfaisants.

Dans ce qui suit, nous allons décrire les procédés spectrophotométriques que nous avons utilisés pour le dosage des états d'oxydation II et IV du platine, et IV et VI du tellure. Nous renvoyons le lecteur à des publications déjà parues sur les méthodes élaborées dans notre laboratoire pour le dosage de quelques autres systèmes*.

APPAREILLAGE

Nous avons utilisé un spectrophotomètre enregistreur Beckman DK-2A pour l'examen préliminaire des spectres et pour le contrôle de leur stabilité, puis un spectrophotomètre Jobin et Yvon du type Maroc, pour la vérification de la loi de Beer de la longueur d'onde choisie et pour les dosages proprement dits. Les cuves étaient en quartz et avaient 1 cm de côté. L'eau utilisée dans ces expériences était

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* Système phosphite–phosphate[1,2]; chromite–chromate[3]; manganite–manganate[4]; ferrocyanure–ferricyanure–pentaferrocyanure[5]; Ru(IV)–ruthénate[6]; OsO_4–états d'oxydation inférieurs d'osmium[7].

tridistillée: la deuxième fois sur permanganate de potassium en solution sulfurique, la troisième sur baryte. Les réactifs étaient d'une haute pureté analytique: Merck, Johnson-Matthey ou Prolabo R.P.

PLATINE(II) — PLATINE(IV)

Les composés les plus caractéristiques de platine bi- et tétravalents en solution aqueuse sont les acides chloroplatineux (H_2PtCl_4) et chloroplatinique (H_2PtCl_6) et leurs sels. Le spectre d'absorption de l'ion chloroplatineux dans l'eau, a été étudié par ORGEL *et al.*[8], qui ont trouvé un pic à 216 nm avec un coefficient d'extinction de 9580 M^{-1} cm^{-1} et 5 autres pics beaucoup moins prononcés. JORGENSEN a étudié[9] le spectre de l'ion chloroplatinique et a établi la présence de trois pics à 453, 353 et 262 nm, le dernier étant de loin le plus important avec $\varepsilon = 24{,}500$ M^{-1} cm^{-1}.

Afin de pouvoir utiliser les pics à 216 et 262 nm pour le dosage respectivement de platine(II) et platine(IV), nous avons examiné l'influence de l'acidité sur leurs coefficients d'extinction et la superposition éventuelle de l'absorption dans les deux états d'oxydation.

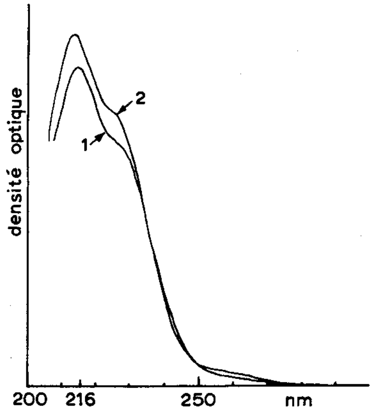
La loi de Beer est vérifiée pour les deux pics dans tout le domaine exploré d'acidité (acide chlorhydrique 0.02 à 0.5 N) et de concentration (de 10^{-5} à $1.2 \cdot 10^{-4}$ M pour 216 nm et de $5 \cdot 10^{-6}$ à $5 \cdot 10^{-5}$ M pour 262 nm).

Comme le montre la Fig. 1, se référant à une solution $4 \cdot 10^{-5}$ M en chloroplatinate de potassium, le maximum à 216 nm est associé à un épaulement à 225 nm et son coefficient d'extinction ε croît avec l'acidité:

HCl 0.02 N $\varepsilon = 8750$ M^{-1} cm^{-1} HCl 0.1 N $\varepsilon = 9800$ M^{-1} cm^{-1}

HCl 0.05 N $\varepsilon = 9500$ M^{-1} cm^{-1} HCl 0.5 N $\varepsilon = 10{,}500$ M^{-1} cm^{-1}

Les solutions de platine(IV) absorbent également à 216 nm (Fig. 2) avec un



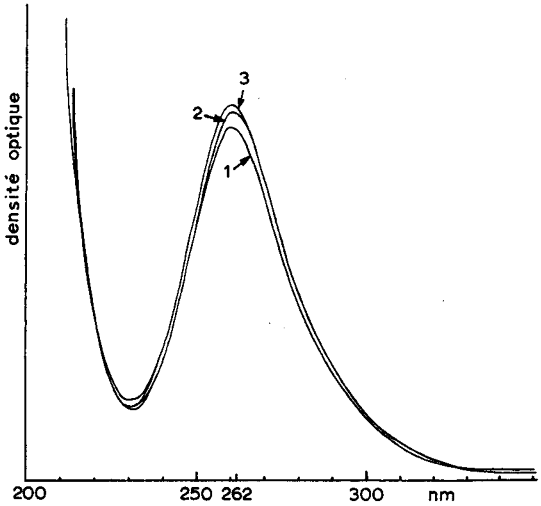


Fig. 1. Variation de l'intensité du maximum à 216 nm avec l'acidité (1) HCl 0.5 N, (2) HCl 0.05 N.

Fig. 2. Variation de l'intensité du maximum à 262 nm avec l'acidité (1) HCl 0.02 N, (2) HCl 0.1 N, (3) HCl 0.5 et 1 N.

coefficient d'extinction encore plus élevé: $\varepsilon = 17{,}000\ M^{-1}\ \mathrm{cm}^{-1}$, pratiquement indépendant de l'acidité. Par contre, la densité optique du pic caractéristique du platine(IV) à 262 nm varie, comme le montre la Fig. 2, avec l'acidité: $\varepsilon_{IV}(262) = 21{,}500$ dans l'acide chlorhydrique 0.02 *N*, ~23,000 en milieu acide chlorhydrique 0.1 *N* et 23,700 $M^{-1}\ \mathrm{cm}^{-1}$ en milieu acide chlorhydrique 0.5 et 1 *N*.

Le chloroplatinite absorbe légèrement à 262 nm avec un coefficient d'extinction croissant avec l'acidité: $\varepsilon_{II}(262) = 450$ en solution acide chlorhydrique 0.02 *N* et 700 $M^{-1}\mathrm{cm}^{-1}$ dans l'acide chlorhydrique 0.5 *N*.

En solution alcaline, les deux maxima à 216 et 262 nm sont très légèrement déplacés, mais surtout leurs modifications ne correspondent pas nécessairement à un changement de l'état d'oxydation, mais à des variations de complexes. C'est ainsi que dans l'hydroxyde de sodium 0.2 *N* et l'ion chloroplatineux 10^{-4} *M*, on observe un pic à 220 nm, dont la densité optique, initialement peu différente de celle qu'on mesure à 216 nm en milieu très faiblement acide, diminue avec l'âge de la solution, de 37% environ après 48 h.

D'autre part, les solutions sodiques de platine(IV) présentent également un pic à 220 nm et un autre à 260 nm, dont l'intensité suit la loi de Beer: $\varepsilon = 21{,}000\ M^{-1}\ \mathrm{cm}^{-1}$. Il présente cependant plusieurs anomalies qui le rendent inutilisable à des fins analytiques.

1. Il n'apparaît pas, même après 72 h, dans les solutions contenant initialement le platine(II) et oxydées en platine(IV) par le peroxyde d'hydrogène ou par un rayonnement ionisant.
2. Il disparaît dans les solutions de platine(IV) sous l'action du rayonnement, bien qu'il soit établi que, dans les conditions choisies, l'état d'oxydation du platine n'est pas modifié[10].
3. Si l'on acidifie les solutions oxydées en (1) en les rendant 0.5 *N* en acide chlorhydrique, le spectre normal du platine(IV) n'apparaît qu'après 2 ou 3 jours.

En conclusion, le platine(IV) peut facilement être dosé par spectrophotométrie en solution acide à 262 nm même en présence de platine(II). Si la concentration du chloroplatinite n'est pas négligeable on peut tenir compte de son absorption à l'aide des relations d'additivité:

$$c = c_{II} + c_{IV} \quad \text{et} \quad d = \varepsilon_{II} c_{II} + \varepsilon_{IV} c_{IV},$$

où *d* est la densité optique et *c* la concentration globale du platine, supposée connue.

D'autre part, le platine(II) peut être mesuré à 216 nm seulement si la concentration en platine(IV) est négligeable; dans le cas contraire, il peut être déterminé par manganimétrie, mais naturellement avec une précision bien moindre. Si le mélange se trouve en solution alcaline, celle-ci doit être acidifiée et l'on attendra 72 h environ avant de doser le platine(IV) à 262 nm. Le dosage spectrophotométrique permet de doser 0.1 μg de platine(IV) et 0.2 μg de platine(II) par ml de solution.

TELLURE(IV) — TELLURE(VI)

Le tellure tétravalent peut être dosé par potentiométrie en l'oxydant en solution alcaline par le permanganate de potassium[11]. HANSON *et al.*[12] qui ont étudié le spectre d'absorption du tellure(IV) en solution acide chlorhydrique 12.9 et 6 *N* ont préconisé son dosage spectrophotométrique au maximum de 376 nm en milieu acide chlorhydrique 9 à 12 N. Le coefficient d'extinction du pic dans l'acide chlorhydrique 12 N est de 2480 M^{-1} cm^{-1} [13]. Les auteurs cités ont trouvé un autre maximum dans ce dernier milieu à 269 nm qui n'apparaîtrait pas en milieu acide chlorhydrique 6 N. En réalité, selon nos propres mesures, ce pic est seulement déplacé (Fig. 3) vers les courtes longueurs d'onde et apparaît à 250 nm. Même en solution acide chlorhydrique 4 N, on observe sur la courbe d'absorption à la même longueur d'onde un point d'inflexion dont l'intensité suit la loi de Beer (entre 10^{-5} et 10^{-4} M). Les opérations avec les solutions très concentrées en acide chlorhydrique étant fastidieuses et nuisibles pour l'appareillage, nous avons préféré doser le tellure(IV) précisément à 250 nm en milieu acide chlorhydrique 4 N; ε_{IV} est alors égal à 9000 M^{-1} cm^{-1}, tandis que $\varepsilon_{\text{VI}}(250)$ est environ de 16 M^{-1} cm^{-1}. Pour doser donc séparément les constituants d'un mélange tellure(IV) + tellure(II) en solution aqueuse on procédera pratiquement ainsi.

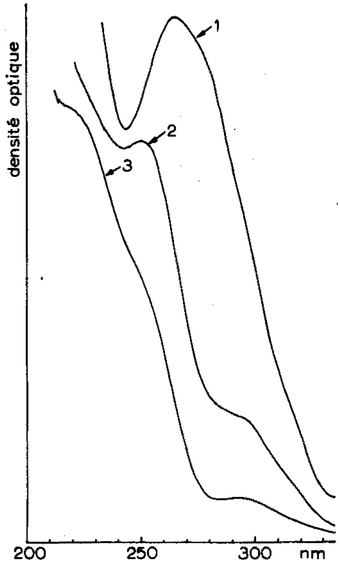


Fig. 3. Effet de l'acidité sur le pic à 269 nm de tellure(IV) (1) HCl 12 N, (2) HCl 6 N, (3) HCl 4 N.

En rendant la solution 4 N en acide chlorhydrique, on dose le tellure(IV) à 250 nm. On sépare ensuite les deux états d'oxydation à l'aide du triphosphate de butyle qui extrait le tellure(IV) en milieu acide chlorhydrique 4 N[14]. On doit au préalable traiter le solvant avec cet acide et le passer à travers un tamis moléculaire (Merck à 4 Å), afin d'éliminer le mono- et le bi-phosphates qui absorbent aussi à 250 nm. L'opération d'extraction est répétée. Le tellure(VI) passe dans la phase aqueuse qu'on évapore sur bain-marie et qu'on reprend avec l'acide chlorhydrique 12 N. Il est alors réduit en tellure(IV). On évapore de nouveau et l'on reprend avec l'acide chlorhydrique 4 N. Ce traitement modifie cependant la valeur du coefficient d'extinction qui devient 9700 M^{-1} cm^{-1}. Connaissant alors la concentration de tellure(VI), on en tient éventuellement compte pour corriger la concentration trouvée pour le tellure(IV).

Ce procédé permet de doser 0.2 μg environ de tellure(IV) par ml de solution.

RÉSUMÉ

Le chloroplatinate en solution très diluée ($\sim 10^{-5}$ M) est dosé spectrophotométriquement à 262 nm même en présence de chloroplatinite. Ce dernier peut être dosé à 216 nm, mais seulement si la concentration en platine(IV) dans la solution est relativement faible. Le tellure(IV) peut être dosé en solution acide chlorhydrique 4 N à 250 nm en présence de tellure(VI), qui peut être déterminé à son tour après extraction du tellure(IV) par le phosphate de tributyle et réduction par l'acide chlorhydrique concentré.

SUMMARY

Chloroplatinate can be determined in very dilute solution ($\sim 10^{-5}$ M) spectrophotometrically at 262 nm even in the presence of platinum(II). The latter can be determined at 216 nm only if the concentration of platinum(IV) in the solution is relatively small. Tellurium(IV) can be determined in 4 N hydrochloric acid solution at 250 nm in the presence of tellurium(VI), which can be also determined after extraction of tellurium(IV) by tributyl phosphate and reduction with concentrated hydrochloric acid.

ZUSAMMENFASSUNG

Chloroplatinat kann in sehr verdünnten Lösungen ($\sim 10^{-5}$ M) spektralphotometrisch bei 262 nm sogar in Gegenwart von Platin(II) bestimmt werden. Das letztere kann bei 216 nm nur bei relativ kleinen Konzentrationen an Platin(IV) bestimmt werden. Tellur(IV) kann in 4 N Salzsäure bei 250 nm in Gegenwart von Tellur(VI) bestimmt werden. Das letztere kann auch nach Extraktion von Tellur(IV) mit Tributylphosphat und Reduktion mit konzentriertem Salzsäure bestimmt werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

PHOTOMETRISCHE OZONBESTIMMUNG BEIM VORHANDENSEIN DER CHLORVERBINDUNGEN

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(Eingegangen den 21. Oktober, 1968)

In der Technologie der Trink- und Nutzwasseraufbereitung verwendet man das Ozon teils zur Liquidation von Balaststoffen teils zur Desinfektion. In einigen Fällen wird das Ozon in der Chlorkombination verwendet. Für die Regelung der Technologie und für die Beschaffenheitskontrolle des aufbereiteten Wassers ist es unerlässlich, die Konzentration des vorhandenen Ozons genau zu kennen.

Bei der Ozonbestimmung bedient man sich heute am häufigsten der titrimetrisch–jodometrischen[1–7] oder kolorimetrischen Mangan–*o*-Tolidin-Methode[1–3,8]. Es wurden noch weitere Methoden für die Ozonbestimmung beschrieben; sie sind aufgebaut z.B. auf der Titration mit Eisen(II)-sulphat[6,9,10], auf der kolorimetrischen Ozonbestimmung mit *o*-Tolidin[11], *p*-Aminodimethylanilin[12], Indigo[4], Fluorescein[13], Tetramethyldiaminodiphenylmethan[14], in wasserfreiem Milieu mit in N-Phenyl-2-Naphthylamin aufgelöstem *o*-Dichlorbenzol[15], der kolorimetrischen Methode unter Nutzbarmachung der Farbreaktion des Jodes mit Stärke[7], der Chemilumineszenz-Methode unter Verwendung der Gallussäure und des Rhodamins B[16], evtl. mittels der direkten spektrophotometrischen Ozonbestimmung im UV-Gebiet[17–20]. In der hydrometrischen Praxis fanden jedoch diese Methoden keine breitere Anwendung.

Keine der heute bekannten Methoden ermöglicht das Ozon neben Chlor und dessen sauerstoffhaltigen Verbindungen zu bestimmen. Um dieses Problem zu lösen, wurde die Aufmerksamkeit einigen Redoxsystemen gewidmet, von denen sich das System des Diphosphatkomplexes des zwei- und dreiwertigen Mangans als das zweckmässigste erwies. Die Ozonreaktion mit dem Diphosphatkomplex des zweiwertigen Mangans wurde in der Literatur bisher noch nicht beschrieben und wurde deshalb in dieser Arbeit ausführlich untersucht. Auf Grund der festgestellten Reaktionsbedingungen wurde eine neue photometrische Methode für die Ozonbestimmung beim Vorhandensein von Chlor und dessen sauerstoffhaltiger Verbindungen ausgearbeitet.

EXPERIMENTELLER TEIL

Geräte

Hilger Spekker Spektrophotometer (Hilger & Watts, Ltd., London) Filter Nr. 605 "spectrum yellow-green", Abs. Max. bei *ca.* 550 nm.

Reagentien

Diphosphatkomplex des zweiwertigen Mangans 0.15 *M* $Na_4[Mn(H_2P_2O_7)_3]$ und 0.45 *M* H_2SO_4 Lösung: 60 ml Lösung 0.75 *M* $Na_2H_2P_2O_7$, 12.5 ml H_2SO_4 (1 +4) und 15 ml Lösung 1 *M* $MnSO_4$ wird mit destilliertem Wasser bis zu 100 ml ergänzt.

Schwefelsäure, verdünnt (1 +24).

Ozonreaktion

Das Ozon reagiert mit dem Diphosphatkomplex des zweiwertigen Mangans im sauren Milieu unter Bildung eines violett gefärbten Diphosphatkomplexes des dreiwertigen Mangans[21]. Die Reaktion verläuft nach der Gleichung:

$$O_3+2[Mn(H_2P_2O_7)_3]^{4-}+2H^+=O_2+2[Mn(H_2P_2O_7)_3]^{3-}+H_2O$$

Die Identität des entstandenen Farb-Komplexes des dreiwertigen Mangans mit dem Komplex in der Zusammensetzung $[Mn(H_2P_2O_7)_3]^{3-}$ wurde durch Vergleich der Absorptionskurve der durch die Oxydation mit Ozon angesetzten Lösung mit der Absorptionskurve der Lösung des Mn(III)-Diphosphatkomplexes festgestellt.

Der Reaktionsverlauf wurde teils beim Einblasen eines Gases mit bestimmter Ozonmenge in die Lösung des Mn(II)-Diphosphatkomplexes, teils bei der Mischung der Ozonlösung von bestimmter Konzentration mit dem Mn(II)-Diphosphatkomplex verfolgt. Weiter wurde der Einfluss verschiedener Konzentrationen von zweiwertigem Mangan und Diphosphat-Ionen und der Einfluss verschiedener Konzentrationen der Schwefelsäure auf den Reaktionsverlauf geprüft.

Zur Konzentrationsermittlung des Mn(III)-Diphosphatkomplexes wurde die photometrische Messung angewendet. Der Mn(III)-Diphosphatkomplex besitzt im sichtbaren Gebiet ein Absorptionsmaximum bei 518–524 nm. Die Eigenschaften dieser Verbindung sind für die Kolorimetrie sehr vorteilhaft, ihre Lösung ändert sich auch während einer langen Zeitperiode nicht und ihre Verfärbung eignet sich für die visuelle Messung.

Die Oxydation des Mn(II)-Diphosphatkomplexes auf Mn(III)-Diphosphatkomplex mit gasförmigem Ozon wurde im Verlauf eines Experimentes verfolgt, bei welchem die Ozonmischung mit Sauerstoff in eine Lösung eingeblasen wurde; die Lösung enthielt Mn(II)-Diphoshatkomplex in Konzentrationen 0.001, 0.002, 0.003, 0.004 und 0.005 *M* und einen Überschuss an $Na_2H_2P_2O_7$ in Konzentrationen 0.45 *M* und 0.45 *M* H_2SO_4. Der Entstehungsverlauf des Mn(III)-Diphosphatkomplexes wurde bei Raumtemperatur gegen destilliertes Wasser photometrisch in einer Küvette der Schichtdicke $l=3.465$ cm verfolgt. Der Versuch wurde so arrangiert, dass sich keine Gasbläschen im Strahlengang des Photometers befanden. Das Ozon zeigte sich unmittelbar nach Beginn der Blasenbildung durch die violette Verfärbung, die sich im Verlauf der weiteren Gaszuführung vertiefte. Nach einer gewissen Zeitdauer der Blasenbildung wurde die Grenze der Verfärbung erreicht, die sich weiterhin nicht mehr änderte. Der Oxydationsverlauf ist in der Abb. 1 dargestellt. Im Diagramm in der Abb. 2 sind die Extinktionen der Grenzfärbungen von Absorptionslösungen in Bezug auf die Konzentration des vorhandenen Mn(II)-Diphosphatkomplexes aufgezeichnet. Die Entstehung der Grenzverfärbung unter den beschriebenen Reaktionsbedingungen und die lineare Abhängigkeit der Grenzverfärbung in Bezug auf die Konzentration des vorhandenen zweiwertigen Mangans beweisen, dass das Ozon sämtliches in der Lösung vorhandene Mangan oxydierte.

Weiter wurde die Reaktion des gelösten Ozons mit der Lösung des Mn(II)-Diphosphatkomplexes geprüft. Es wurde mit Lösungen in Konzentrationen von 2.90 und 4.35 mg O_3/l gearbeitet. Die Ozonlösung wurde zu der Lösung 0.15 *M* $Na_4[Mn(H_2P_2O_7)_3]$ und 0.45 *M* H_2SO_4 in solchem Verhältnis zugegeben dass die resultierenden Konzentrationen der einzelnen Komponenten 0.01 *M* $Na_4[Mn(H_2P_2O_7)_3]$ und 0.05 *M* H_2SO_4 betrügen. Nach dem Vermengen wurden die Lösungen bei Raumtemperatur gegen destilliertes Wasser photometrisch in einer Küvette mit Schichtdicke l = 20.0 cm gemessen. Die Zeitabhängigkeit der Extinktion der entstehenden Verfärbung des Mn(III)-Diphosphatkomplexes in der Abb. 3 zeigt, dass die Reaktion des gelösten Ozons im Laufe von 3 Minuten erfolgt. Die Extinktion der Lösung ändert sich nicht einmal nach Ablauf von 24 Stunden.

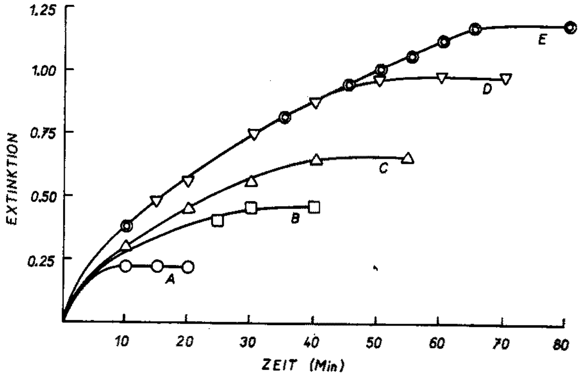

Abb. 1. Zeitverlauf der Oxydation des Mn(II)-Diphosphatkomplexes mit gasförmigem Ozon. Kurve (A) 0.001 *M*; (B) 0.002 *M*; (C) 0.003 *M*; (D) 0.004 *M*; (E) 0.005 *M* Mn(II)-Diphosphatkomplex (Schichtdicke l = 3.465 cm).

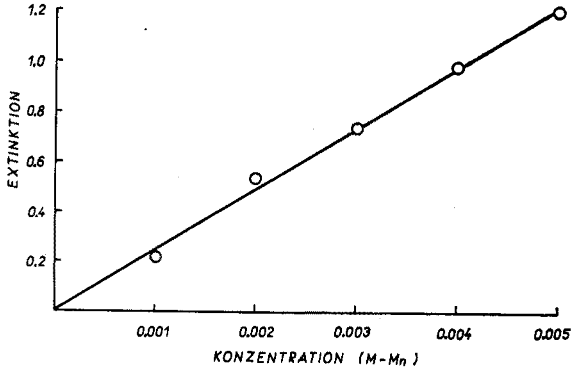

Abb. 2. Extinktionen der Grenzfärbungen des Mn(III)-Diphosphatkomplexes in Abhängigkeit von der Mangankonzentration (Schichtdicke l = 3.465 cm).

Bei weiteren Versuchen wurde die Ozonreaktion mit dem Mn(II)-Diphosphatkomplex in Lösungen bei verschiedenen Konzentrationen der reagierenden Komponenten und weiter in der Gegenwart eines Überschusses von Diphosphat und zweiwertigem Mangan verfolgt. Es wurde festgestellt, dass die Ozonreaktion in einer Lösung, die einen Überschuss des Mn(II)-Diphosphatkomplexes enthält, nach der oben genannten Gleichung verläuft, wobei das Verhältnis von Mangan zum Diphosphat ohne Belang ist. Dies bedeutet, dass es belanglos ist, ob das zweiwertige Mangan oder das Diphosphat im Überschuss vorhanden ist.

Wenn das Ozon mit dem Mn(II)-Diphosphatkomplex in einer Lösung mit Ozonüberschuss reagiert oder wenn das Ozon in die Lösung des Mn(II)-Diphosphatkomplexes in ausreichendem Überschuss zugeführt wird, ist das Konzentrationsverhältnis des zweiwertigen Mangans und des Diphosphats von Bedeutung. Falls das Verhältnis Mn^{2+}: $(H_2P_2O_7)^{2-}$ höher ist als 1:12, verläuft die Reaktion nach dem angeführten Schema. Ist das Verhältnis niedriger, kommt es zu einer tieferen Oxydation des Mangans, das zu MnO_2 und MnO_4^- oxydiert wird.

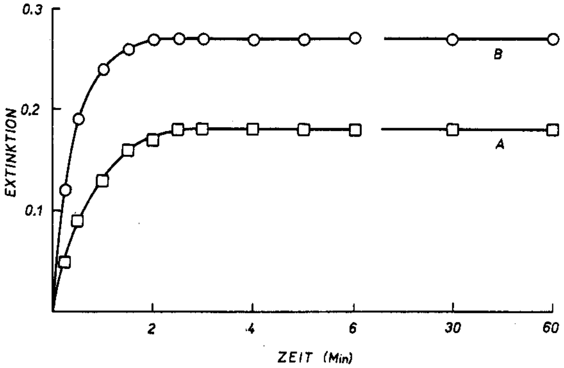

Abb. 3. Zeitverlauf der Oxydation des Mn(II)-Diphosphatkomplexes mit gelöstem Ozon. Kurve (A) 2.90 mg O_3/l; (B) 4.35 mg O_3/l (Schichtdicke l = 20.0 cm).

Bei der Verfolgung der Aziditäts-Verhältnisse wurde experimentell bewiesen, dass die Reaktion im Bereiche 0.005 bis 0.5 *M* H_2SO_4 quantitativ verläuft.

Eichkurve

Die Eichkurve der photometrischen Ozonbestimmung wurde für 0–4.0 mg O_3/l bestimmt. Die in der Küvette mit Schichtdicke l = 20.0 cm gegen destilliertes Wasser festgestellten Extinktionen wurden in einem Diagramm gegen die jodometrisch festgestellten Ozonkonzentration aufgetragen. Die jodometrische Gehaltsbestimmung der für die Eichung verwendeten Ozonlösungen war mit Rücksicht auf ihre Unbeständigkeit nötig. Die lineare Abhängigkeit zeugt von der Gültigkeit des Lambert-Beerschen Gesetzes für dieses Konzentrationsgebiet.

Die zur Aufstellung der Eichkurve angewandte Methode ist schwierig und darüber hinaus ist die massanalytische jodometrische Bestimmung des Ozons in diesen Konzentrationen schon weniger genau. Es wurde deshalb die Verwendungsmöglichkeit stabiler Standardlösungen verfolgt. Eine 0.005 *N* Kaliumdichromatlösung erwies sich als geeignetste. Das Kaliumdichromat reagiert im sauren Milieu mit dem Mn(II)-Diphosphatkomplex unter Bildung des Mn(III)-Diphosphatkomplexes. Es wurden die Extinktionen unter Verwendung von Dichromat Standardlösung gemessen und mit den Eichungskurven für die bei der Ozonkonzentration abgelesenen Extinktionen verglichen.

Eine gute Übereinstimmung zeigen die in der Tabelle I angeführten Ergebnisse. Sie bestätigen von neuem die Einelektronen-Oxydation des Mn(II)-Diphosphatkomplexes mittels Ozon und deuten gleichzeitig die Möglichkeit einer einfachen Methode zur Aufstellung der Eichkurve mit Hilfe der Kaliumdichromat-Standardlösung an.

TABELLE I

ERGEBNISSE DER MESSUNG FÜR ZUSAMMENSTELLUNG DER EICHKURVE

Nr.	*mg O_3/l*	*Extinktion (l = 20.0 cm)*	*N $K_2Cr_2O_7$*	*Extinktion (l = 20.0 cm)*
1	1.20	0.075	0.00005	0.075
2	2.40	0.148	0.00010	0.150
3	3.60	0.222	0.00015	0.220
4	4.80	0.296	0.00020	0.290

Reaktionen der Chlorverbindungen

Es wurde die Reaktion von Chlor und dessen sauerstoffhaltigen Verbindungen mit dem Mn(II)-Diphosphatkomplex im Schwefelsäure-Milieu verfolgt.

Die Reaktion des gasförmigen Chlors und des gasförmigen Chlordioxyds wurde während des Durchblasens von Gas durch die saure Mn(II)-Diphosphatkomplexlösung verfolgt. Das Chlor wurde mit einer Geschwindigkeit von etwa 1 ml/sek 100 ml einer 0.15 *M* Mn(II)-Diphosphatkomplexlösung mit 0.45 *M* H_2SO_4 zugeführt. Auch nach 8-stündigem Zuführen rief das Ozon keine für den Mn(III)-Diphosphatkomplex typische violette Verfärbung hervor.

Das Chlordioxyd wurde unter Einhaltung der gleichen Arbeitsweise wie beim Chlor der Mn(II)-Diphosphatkomplexlösung zugeführt. Nach 8-stündigem Zuführen von ClO_2 wurde die Bildung des Mn(III)-Diphosphatkomplexes festgestellt. Die sehr schwache violette Verfärbung wurde jedoch durch eine grüngelbe Verfärbung des vorhandenen ClO_2 überdeckt. Nach Austreibung von ClO_2 wurde in der Küvette mit Schichtdicke l = 2.0 cm die Extinktion 0.11 gegen destilliertes Wasser gemessen, was von einem sehr langsamen Verlauf der Reaktion des Chlordioxyds mit dem Mn(II)-Diphosphatkomplex zeugt. Dieser Umstand kann unter den üblichen analytischen Bedingungen die Ozonbestimmung nicht stören.

Weiter wurde die Reaktion des Mn(II)-Diphosphatkomplexes mit den Lösungen von Hypochlorit, Chlorit, Chlorat und Perchlorat verfolgt. Zu den Lösungen dieser Verbindungen von je 20 ml 0.05 *M* wurde je 5 ml Lösung in der Konzentration von 0.15 *M* $[Mn(H_2P_2O_7)_3]^{4-}$ und 0.45 *M* H_2SO_4 zugegeben und mit destilliertem Wasser auf 100 ml aufgefüllt. Das Verhalten der Lösungen wurde während 8 Stunden beobachtet. Nach 24 Stunden wurden nicht ausgefärbte Lösungen bis zum Siedepunkt erhitzt und kurz gekocht. Es wurde festgestellt, dass unter den beschriebenen Bedingungen Hypochlorit, Chlorit, Chlorat und Perchlorat mit dem Mn(II)-Diphosphatkomplex nicht reagieren.

Arbeitsvorschrift für die Ozonbestimmung in Wasser und reinen Lösungen

Zu 100.0 ml einer Probe werden unmittelbar nach dessen Entnahme 5.0 ml Lösung des Mn(II)-Diphosphatkomplexes (s. Reagentien) zugegeben; die Lösung wird gut durchgemischt. Nach fünf Minuten wird die Extinktion der Lösung in der Küvette mit Schichtdicke l = 20.0 cm bei Raumtemperatur gemessen. Als Vergleichslösung wird das mit 5.0 ml H_2SO_4 (1 + 24)—auf 100.0 ml der Probe—angesäurte Wassermuster verwendet.

Für die Aufstellung der Eichkurve wird eine künstliche Standardlösung verwendet. In die Messkolben mit einem Inhalt von je 100 ml werden genau 0.00, 1.00, 2.00, 3.00, 6.00 und 9.00 ml 0.005 *N* Lösung des Kaliumdichromats abgemessen und je 5.00 ml Lösung des Mn(II)-Diphosphatkomplexes zugegeben. Nach zehn Minuten Stehen bei Raumtemperatur werden die Messkolben bis zur Marke mit destilliertem Wasser aufgefüllt und in jeden Kolben werden noch 5.00 ml destilliertes Wasser zugegeben. Die bei Raumtemperatur gegen destilliertes Wasser gemessenen Extinktionen werden im Diagramm im Vergleich zu den entsprechenden Ozonkonzentrationen 0.00, 1.20, 2.40, 3.60, 7.20 und 10.80 mg O_3/l aufgezeichnet.

Standardabweichung

Es wurde die Berechnung der Standardabweichung für 10 parallele Experimente mit der Ozonlösung in einer Konzentration von 4.30 mg O_3/l durchgeführt. Die Ergebnisse sind in der Tabelle II angegeben. Die nach der Formel $\tau = \sqrt{\frac{\Sigma \Delta^2}{n-1}}$ berechnete Standardabweichung beträgt ±2.42%.

TABELLE II

STANDARDABWEICHUNG DER ERGEBNISSE DER OZONBESTIMMUNG

Nr.	*Extinktion*[a] *(l = 20.0 cm)*	*Extinktion (Durchschnitt)*	*ΔExt.*	$\tau = \sqrt{\frac{\Sigma \Delta^2}{n-1}}$
1	0.2683		+ 0.0022	
2	0.2633		− 0.0028	
3	0.2683		+ 0.0022	
4	0.2666		+ 0.0005	
5	0.2650	0.2661	− 0.0011	± 0.00643
6	0.2616		− 0.0045	
7	0.2683		+ 0.0022	
8	0.2650		− 0.0011	
9	0.2683		+ 0.0022	
10	0.2666		+ 0.0005	
mg O_3/l		4.30		± 0.104
%				± 2.418

[a] Durchschnitt von 3 Messungen.

Für wertvolle Bemerkungen bei der Experimentalarbeit und die Bewertung der Ergebnisse danken die Autoren dem Herrn Doz. Dr. A. BERKA C.Sc. vom Lehrstuhl für analytische Chemie der Karlsuniversität in Prag.

ZUSAMMENFASSUNG

Ozon reagiert mit dem Mangan(II)diphosphat-Komplex in saurem Medium unter Bildung eines violett gefärbten Komplexes, welcher zur photometrischen Bestimmung von Ozon in Wässern benutzt werden kann. Es werden Verfahren für Konzentrationen von mehr als 1 mg O_3/l im Trink- und industriellen Wässern beschrieben. Für 4.30 mg O_3/l beträgt die Standardabweichung 2.42%. Das Ozon

kann in Gegenwart von Chlor, Chlordioxid, Hypochlorit, Chlorit, Chlorat und Perchlorat bestimmt werden.

SUMMARY

Ozone reacts with the manganese(II) diphosphate complex in acidic media, to form a violet-coloured complex which can be used for the photometric determination of ozone in waters. Procedures for concentrations greater than 1 mg O_3/l in drinking and industrial waters are described; at the 4.30 mg O_3/l level, the standard deviation was 2.42%. Ozone can be determined in the presence of chlorine, chlorine dioxide, hypochlorite, chlorite, chlorate and perchlorate.

RÉSUMÉ

L'ozone réagit avec le complexe de diphosphate de manganèse(II) en milieu acide, en formant un complexe coloré violet qui peut être employé pour la détermination photométrique de l'ozone dans les eaux. On décrit les procédés pour des concentrations supérieures à 1 mg O_3/l dans les eaux potables et industrielles; pour une teneur de 4.30 mg O_3/l, l'écart type fut de 2.42%. L'ozone peut être déterminée en présence de chlore, de dioxyde de chlore, d'hypochlorite, de chlorite, de chlorate et de perchlorate.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE

PART VII. THE ANALYSIS OF IRON ORES AND SLAGS

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(Received October 14th, 1968)

The decomposition–determination technique proposed in the present series of papers has been found applicable to the analysis of iron ores and slags. Methods are given for the determination of silicon, aluminium, magnesium, calcium, titanium and manganese in these materials; in addition, methods for determining sodium and potassium in iron ores, and total iron, chromium and vanadium in slags are given. Methods for other constituents, such as barium, zinc, copper, silver and nickel can be incorporated in the scheme.

It is recommended to attack iron ores and slags by decomposition method 2 (described in Part I of this series[1]).

EXPERIMENTAL

Reagents and solutions

The reagents and solutions required for the present determinations are listed in Part I[1]. The detailed preparation of the primary standard solutions (designated below as metal standard I) is described in Part I, except for the vanadium standard described below. The composition of the secondary standard solutions is given below. Each of the series of secondary standard solutions below is designed for measurement of a definite dilution of the sample solution; this dilution is indicated in each case.

Vanadium standard I (1 mg V_2O_5/ml). Prepare by dissolving 0.5602 g of the metal in a mixture of 15±1 ml of nitric acid and 50±10 ml of water, transfer the solution to a 1-l volumetric flask and dilute to volume with water.

Secondary standard solutions

Silicon (undiluted sample solutions). For the analysis of iron ores, transfer by plastic pipette up to 10 ml, in steps of 1 ml, of silicon standard I to plastic bottles, and add water to a final volume of 100 ml. (Range: up to 10% SiO_2, in steps of 1%.) For the analysis of slags, transfer similarly up to 30 ml, in steps of 2 ml, of the same standard solution, etc. (Range: up to 30% SiO_2, in steps of 2%.)

Aluminium in iron ores (undiluted sample solutions). Dilute aluminium standard I to 0.5 mg Al_2O_3/ml with water. Transfer up to 10 ml, in steps of 1 ml, of this solution to plastic bottles, and add 50 ml of saturated boric acid solution, 5 ml of hydrofluoric acid, and water to a final volume of 100 ml. (Range: up to 2.5% Al_2O_3, in steps of 0.25%.)

Aluminium in slags. Two series of secondary standard solutions are prepared. Prepare Series I by transferring up to 40 ml, in steps of 2 ml, of the above diluted standard solution to plastic bottles, and proceed as described immediately above. If the sample solutions are undiluted, Series I covers the range up to 10% Al_2O_3, in steps of 0.5%. Prepare Series II by transferring 20–40 ml, in steps of 2 ml, of the diluted aluminium standard solution to plastic bottles, and add 25 ml of saturated boric acid solution, 2.5 ml of hydrofluoric acid, and water to a final volume of 100 ml. If the sample solutions are diluted 2 times, Series II covers the range 10–20% Al_2O_3, in steps of 1%.

Total iron in slags (sample solutions diluted 20 times). Dilute iron standard I to 0.1 mg Fe_2O_3/ml with water. Transfer up to 20 ml, in steps of 1 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. (Range: up to 20% Fe_2O_3, in steps of 1%.)

Magnesium in iron ores (sample solutions diluted 20 times). Dilute magnesium standard I to a concentration of 0.01 mg MgO/ml with water. Transfer up to 20 ml, in steps of 2 ml, of this solution to 100-ml volumetric flasks, add 10 ml of potassium reagent solution (10 mg K/ml) and dilute to volume with water. (Range: up to 2% MgO, in steps of 0.2%.)

Magnesium in slags. Transfer up to 16 ml, in steps of 2 ml, of the above diluted standard solution to 100-ml volumetric flasks, and proceed as above. If the sample solutions are diluted 100 times, this series covers the range up to 8% MgO, in steps of 1%. If the sample solutions are diluted 200 times, the series covers the range up to 16% MgO, in steps of 2%.

Calcium in iron ores (sample solutions diluted 2 times). Dilute calcium standard I to 0.02 mg CaO/ml with water. Transfer up to 50 ml, in steps of 2.5 ml, of this solution to 100-ml volumetric flasks, add 10 ml of potassium reagent solution and dilute to volume with water. (Range: up to 1% CaO, in steps of 0.05%.)

Calcium in slags (sample solutions diluted 625 times). Transfer up to 20 ml, in steps of 1 ml, of the above diluted standard solution to 250-ml volumetric flasks, add 25 ml of potassium reagent solution and dilute to volume with water. (Range: up to 50% CaO, in steps of 2.5%.)

Sodium and potassium in iron ores (undiluted sample solutions). Dilute sodium and potassium standards I with water to a concentration of 0.01 mg Na_2O/ml and 0.01 mg K_2O/ml, respectively. Transfer up to 20 ml, in steps of 2 ml, of each of these solutions to 100-ml volumetric flasks, add 50 ml of saturated boric acid solution to compensate for its content of alkali, and make up to volume with water. (Range: up to 0.1% Na_2O or K_2O, in steps of 0.01%.)

Titanium in iron ores (undiluted sample solutions). Dilute titanium standard I to 0.02 mg TiO_2/ml with water. Transfer up to 40 ml, in steps of 5 ml, of this solution to plastic bottles, and add 50 ml of saturated boric acid solution and 5 ml of hydrofluoric acid. Add a volume of aluminium standard solution, corresponding to the aluminium concentration in the main solution; finally, add water to a volume of 100 ml. (Range: up to 0.4% TiO_2, in steps of 0.05%.)

Titanium in slags. Transfer up to 10 ml, in steps of 1 ml, of titanium standard I to plastic bottles, and proceed exactly as described for the solution prepared for iron ores. If the sample solutions are undiluted, the series covers the range up to 5% TiO_2, in steps of 0.5%. For measurement against sample solutions diluted 2 times, prepare a second series as follows. Transfer 5–10 ml, in steps of 1 ml, of titanium standard I to plastic bottles, and add 25 ml of saturated boric acid solution, 2.5 ml of hydrofluoric acid, a volume of aluminium standard solution corresponding approximately to the content of aluminium in the sample solution, and water to a final volume of 100 ml. This series covers the range 5–10% TiO_2, in steps of 1%.

Manganese in iron ores and slags. Dilute manganese standard I to 0.01 mg MnO/ml with water. Transfer up to 90 ml, in steps of 10 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. With undiluted sample solutions of iron ores, this series covers the range up to 0.45% MnO, in steps of 0.05%. If the sample solutions of slags are diluted 20 times, the series covers the range up to 9% MnO, in steps of 1%.

Chromium in iron ores (undiluted sample solutions). Dilute chromium standard I to 0.05 mg Cr_2O_3/ml with water. Transfer up to 40 ml, in steps of 4 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. (Range: up to 1% Cr_2O_3, in steps of 0.1%.)

Vanadium in iron ores (undiluted sample solutions). Dilute vanadium standard I to a concentration of 0.1 mg V_2O_5/ml with water. Transfer up to 50 ml, in steps of 5 ml, of this solution to 100-ml volumetric flasks, add a volume of phosphate reagent solution (1 mg P_2O_5/ml) corresponding approximately to the content of phosphate in the sample solution and dilute to volume with water. (Range: up to 2.5% V_2O_5, in steps of 0.25%.)

Phosphate reagent solution (1 mg P_2O_5/ml). Prepare from a suitable amount of alkali phosphate or phosphoric acid.

Procedure

Weigh 0.2000 g of the sample, add by glass and plastic pipette 0.75 ml of

TABLE I

ANALYTICAL DATA FOR THE BRITISH CHEMICAL STANDARDS SAMPLE NO. 175/1 (LIBERIAN IRON ORE)[a]

Sample no.	*Si as SiO_2 (%)*	*Al as Al_2O_3 (%)*	*Mg as MgO (%)*	*Ca as CaO (%)*	*Na as Na_2O (%)*	*Ti as TiO_2 (%)*	*Mn as MnO (%)*
1	3.55	1.10	1.41	0.26	0.032	0.144	0.134
2	3.63	1.09	1.40	0.23	0.018	0.149	0.135
3	3.46	1.08	1.42	0.23	0.021	(0.127)[b]	0.133
4	3.56	1.08	1.39	0.23	0.022	0.144	0.138
5	3.79	1.11	1.41	0.21	0.033	0.144	0.134
Averages	3.59	1.09	1.41	0.23	0.025	0.145	0.135
Stand. dev.	0.13	0.01	0.01	0.02	0.007	0.002	0.002
Rel. dev.	3.6	0.9	0.7	7.5	28	1.4	1.5
Certificate value	3.52	1.10	1.49	0.28	Not reported	0.15	0.13

[a] The potassium content was below the limit of detection, *i.e.* < 0.01% K_2O.
[b] Not included in average.

TABLE II

ANALYTICAL DATA FOR THE BRITISH CHEMICAL STANDARDS SAMPLE NO. 174/1 (BASIC SLAG)

Sample no.	*Si as SiO_2 (%)*	*Al as Al_2O_3 (%)*	*Total Fe as Fe_2O_3 (%)*	*Mg as MgO (%)*	*Ca as CaO (%)*	*Ti as TiO_2 (%)*	*Mn as MnO (%)*	*Cr as Cr_2O_3 (%)*	*V as V_2O_5 (%)*
1	14.49	1.86	12.36	7.17	44.09	0.685	5.14	0.274	1.27
2	14.49	1.80	12.00	7.18	44.43	0.674	5.10	0.272	1.26
3	14.58	1.79	12.27	7.14	44.36	0.679	5.04	0.273	1.23
4	14.43	1.80	12.21	7.11	44.25	0.665	5.02	0.268	1.25
5	14.52	1.81	12.29	7.18	44.23	0.686	4.98	0.272	1.25
Averages	14.50	1.81	12.23	7.15	44.34	0.678	5.06	0.271	1.25
Stand. dev.	0.06	0.03	0.14	0.03	0.15	0.007	0.07	0.003	0.02
Rel. dev.	0.41	1.7	1.1	0.42	0.34	1.0	1.4	0.89	1.6
Certificate value	14.69	1.72	12.10	7.13	44.83	0.70	5.11	0.26	1.20

hydrochloric acid, 0.25 ml of nitric acid and 5 ml of hydrofluoric acid, and decompose by method 2. Many iron ores and slags succumb to heating for about 30 min at 110°.

For the analysis of iron ores, determine silicon, aluminium, sodium, potassium, titanium and manganese in the main solution. Determine calcium after pipetting 50 ml of the main solution into a 100-ml volumetric flask, add 10 ml of potassium reagent solution (10 mg K/ml), dilute to volume with water and transfer at once to a plastic bottle. Determine magnesium after transferring 10 ml of the latter solution into a 100-ml volumetric flask, add 9 ml of potassium reagent solution, dilute to volume with water and transfer to a plastic bottle.

For the analysis of slags, use the main solution for determining up to 30% SiO_2, 10% Al_2O_3, 5% TiO_2, 1% Cr_2O_3 and 2.5% V_2O_5. Determine concentrations in the range 30–60% SiO_2, 10–20% Al_2O_3 and 5–10% TiO_2 in a solution prepared by pipetting 50 ml of the main solution into a 100-ml volumetric flask and diluting to volume with water. Determine iron and manganese in a solution prepared by pipetting 5 ml of the main solution into a 100-ml volumetric flask and diluting to volume with water. For the determination of up to 8% MgO, transfer 10 ml of the main solution into a 100-ml volumetric flask and dilute to the mark with water. Pipette 10 ml of this solution into another 100-ml volumetric flask, add 10 ml of potassium reagent solution (10 mg K/ml) and make up to volume with water.

If the concentration of magnesium is above 8% (as MgO), pipette 5 ml of the solution diluted 10 times into a 100-ml volumetric flask, add 10 ml of potassium reagent solution and dilute to volume with water. For the determination of calcium, pipette 10 ml of the main solution into a 250-ml volumetric flask and dilute to volume with water. Transfer 10 ml of this solution into another 250-ml volumetric flask, add 25 ml of potassium reagent solution and make up to volume with water.

Determine iron, sodium, potassium and manganese with an acetylene–air flame; determine the other components with an acetylene–nitrous oxide flame.

Make the measurements and calculations as described in Part I.

Applications

The scheme was tested by analyzing the British Chemical Standards samples No. 175/1 (Liberian iron ore) and No. 174/1 (basic slag). The analytical results and the certificate values are listed in Tables I and II.

The present work was made possible by grants from the Royal Norwegian Council for Scientific and Industrial Research.

SUMMARY

A scheme is described for the analysis of iron ores and slags by atomic absorption spectrophotometry. Methods are given for the determination of silicon, aluminium, magnesium, calcium, titanium and manganese in both materials; methods for determining sodium and potassium in iron ores, and total iron, chromium and vanadium in slags are also given. The samples are decomposed by a mixture of hydrofluoric, hydrochloric and nitric acids. Analytical data for standard samples are given.

RÉSUMÉ

Un schéma est décrit pour l'analyse de minerais de fer et de scories au moyen de la spectrophotométrie par absorption atomique. On donne des méthodes pour la détermination du silicium, de l'aluminium, du magnésium, du calcium, du titane et du manganèse dans ces deux matériaux. On fournit également des méthodes pour déterminer le sodium et le potassium dans les minerais de fer ainsi que le fer total, le chrome et le vanadium dans les scories. Les échantillons sont attaqués et décomposés au moyen d'un mélange d'acides fluorhydrique, chlorhydrique et nitrique. Des valeurs analytiques sont données pour des échantillons étalons.

ZUSAMMENFASSUNG

Es wird gezeigt, dass sich die in früheren Veröffentlichungen beschriebene Zersetzungstechnik für die Bestimmung von Elementen bei der Atomabsorptionsanalyse auch für Eisenerze und Schlacken eignet. Es wird die Bestimmung geringer Anteile von Silicium, Aluminium, Magnesium, Calcium, Titan und Mangan in diesen Materialien beschrieben; ferner die Bestimmung von Natrium und Kalium in Eisenerzen und das Gesamteisen, Chrom und Vanadin in Schlacken. Auch die Bestimmung von Barium, Zink, Kupfer, Silber und Nickel können in dieses Schema mit einbezogen werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ELECTRONICALLY MODULATED MICROWAVE-EXCITED ELECTRODELESS DISCHARGE TUBES AS SOURCES IN ATOMIC ABSORPTION SPECTROSCOPY

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(Received November 25th, 1968)

The interest in microwave-excited electrodeless discharge tubes has largely centred on their use as high-intensity line sources for use in atomic fluorescence spectroscopy[1,2]. In this technique, the profile of the atomic line and the nature of the spectral region surrounding it are of considerably less importance than in atomic absorption spectroscopy because the source is not directly viewed by the detector. However, the "purity" of the emission from these discharge tubes, because of the absence of carrier gas spectrum, the suppression of ion lines and the elimination of lines of extraneous elements present in electrode materials, appears to make such sources very suitable for atomic absorption measurements[3].

Previously, these electrodeless tubes have been used in conjunction with d.c. amplification systems or their radiation has been mechanically chopped to match the a.c. amplification of the flame spectrometer for both atomic absorption and atomic fluorescence spectroscopy[4]. Obviously, electronic modulation, tuned to the frequency of the a.c. detecting system, greatly simplifies the experimental arrangement, especially in atomic fluorescence spectroscopy where mechanical choppers physically prevent radiation from reaching the atom reservoir, and greatly facilitates their application to atomic absorption measurements.

In this paper, electronic modulation of electrodeless discharge tubes is discussed, and the spectra emitted from several modulated sources and the sensitivity attainable by using them in atomic absorption spectroscopy are described. The discharge tubes used (lead, mercury, silver, thallium and tin) were operated in resonant cavities with microwaves of frequency 2450 ± 25 MHz and with superimposed electronic modulation at 50 Hz. Their properties were compared with those of the correspondingly modulated hollow-cathode lamps. Special attention was given to features liable to affect the precision of absorption measurements made with electrodeless discharge tubes as line sources. In all cases, their performance, modulated and unmodulated, was found to be comparable with, or better than, the respective hollow-cathode lamp under optimised running conditions.

EXPERIMENTAL

Apparatus

Quantitative comparisons of spectral intensities, stabilities, warm-up times and signal-to-noise levels for both hollow-cathode lamps and electrodeless discharge tubes were made on a Perkin-Elmer 290 atomic absorption spectrometer fitted with a flame emission accessory allowing variable backing off and switched time constants from zero to 10 sec. Signals were recorded on a Servoscribe recorder with output ranges from 2 mV to 5 V.

The hollow-cathode lamps used were all from the Perkin-Elmer Intensitron series except for the mercury hollow-cathode which was manufactured by the Westinghouse Corporation. All were run from the internal power supply of the instrument (square-wave pulsed at 50 Hz). The electrodeless discharge tubes were operated in approximately the same position in the lamp compartment as the cathode of a hollow-cathode lamp and, when run on the unmodulated microwave supply, their output was mechanically chopped within the lamp compartment at 50 Hz.

When the electrodeless discharge tubes were operated with electronic modulation at 50 Hz, the internal electronic chopper of the atomic absorption instrument amplifier was run from the 6.3 V supply incorporated for this purpose in the modulator unit. The microwave generator, modulation accessory and cavities used in this study were all manufactured by Electro-Medical Supplies Ltd (209B Great Portland Street, London). The Microtron 200 generator and cavities ($\frac{3}{4}$ wave [type 210L] and $\frac{1}{4}$ wave [type 214L]) have been described elsewhere for both atomic absorption and atomic fluorescence purposes in the d.c. mode of operation[5]. The power output from the Microtron 200 is normally controlled by varying the anode voltage of the magnetron valve. When the generator is used in its modulated mode, as in this study at 50 Hz, a modulation signal is introduced into the anode circuit of the magnetron by means of a modulation transformer, the primary of which is supplied from the mains by a variable transformer. This superimposes a 50-Hz component on the d.c. potential of the anode. The d.c. supply of the magnetron incorporates a smoothing circuit and, to prevent the modulation signal from being shunted by this, it is isolated from the circuit by a filter consisting of a choke and a capacitor in the anode circuit of the magnetron.

The modulation unit also supplies a low-voltage a.c. signal whose phase relationship with the "mains" supply may be altered by a bridge network and which is then power-amplified in order to drive the electronic chopper of the a.c. amplifier. This allows correct phasing of the detector with the modulated discharge tube.

Spectral plots of the tin and lead electrodeless discharge tubes and hollow-cathode lamps around the region of their resonance lines at 224.6 nm and 217.0 nm respectively were made on a Unicam SP 900 A spectrophotometer because this provided better sensitivity in the low ultraviolet region. For this purpose, all the sources were operated without modulation in conjunction with the Unicam SP 900 A spectrometer in its "emission" mode.

Preparation of electrodeless discharge tubes

The preparative conditions for tin[3], mercury[6], thallium[6] and silver[7] electrodeless discharge tubes have already been described.

The most intense and stable lead tubes made contained lead iodide in the presence of a very slight excess of metallic lead. About 1 mg of analytical-grade lead powder was introduced into a degassed quartz tube 3–4 cm long and of 0.8-mm internal diameter. Under vacuum (*ca.* 0.1 torr), most of the lead was volatilised out of the bulb with a micro-burner. About 5 mg of lead iodide (general-purpose reagent) were then added and the tube was gently warmed while the system was flushed out twice with argon to remove traces of moisture. The tube was finally sealed under an argon pressure of 3–5 torr.

Tubes may also be prepared from lead chloride sealed under *ca.* 6 torr of argon in the absence of excess of lead; however, these have a less favourable signal : background ratio than the iodide tubes.

RESULTS AND DISCUSSION

Spectral characteristics of electronically modulated electrodeless discharge tubes

The operating conditions of the discharge tubes were chosen to fit the criterion of maximum light output compatible with stability and prevention of overheating of the tubes. Initially, the conditions were optimized with the source powered in the usual way (*i.e.* unmodulated) with a mechanical chopper. Then the percentage electronic modulation, phase shift and running power required to produce the same signal on the recorder were found (all other variables such as wavelength, amplifier gain, slit width and source position remaining unchanged). For this purpose, the phase shift and percentage modulation controls were arbitrarily calibrated into ten equal divisions. These settings, together with the power requirements (the power absorbed by the source being the difference between the output and reflected powers, neglecting losses in the coaxial cables) for each of the discharge tubes examined are shown in Table I.

TABLE I

OPERATING CONDITIONS FOR ELECTRODELESS DISCHARGE TUBES

Element	*Unmodulated*		*Modulated*			
	Power (W)	*R.P.*[a]	*Power (W)*	*R.P.*	*%Mod.*[b]	*P.S.*[c]
Tin[d]	50	6	40	7	3·5	3
Lead[e]	70	14	70	8	3	3
Thallium[e]	50	3	55	5	3	1.5
Mercury[d]	20	8	25	12	5	4
Silver[e]	70	20	70	20	5	3

[a] Reflected power.
[b] Percentage modulation control setting.
[c] Phase shift control setting.
[d] Tubes operated with 214L ($\frac{1}{4}$ wave) cavity.
[e] Tubes operated with 210L ($\frac{3}{4}$ wave) cavity.

The mercury and tin tube were run in the $\frac{1}{4}$ wave [214L] cavity, with forced air cooling the whole of the mercury tube, but only the base of the tin tube. The lead, thallium and silver sources were run uncooled in the $\frac{3}{4}$ wave [210L] cavity. The operating conditions quoted give a measure of what is required rather than a precise definition, and some tolerance is permissible. However, any appreciable alteration in these conditions may lead to instability, decreased intensity or a longer warm-up time.

Various source characteristics for hollow-cathode lamps and the modulated and unmodulated electrodeless discharge tubes are shown in Table II. The electrodeless discharge tubes are generally superior to the hollow-cathode lamps. The results show that electronic modulation has little effect on the behaviour of the electrodeless dis-

TABLE II

SOURCE CHARACTERISTICS

Element	*Wave length (nm)*	*Warm-up time*[a] *(min)*			*Noise level on signal (%)*[f]			*Av. drift rate (%h^{-1})*			*Reproducibility of output (%)*[g]		
		H.C.L.[b]	*E.D.T.*[c]		*H.C.L.*	*E.D.T.*		*H.C.L.*	*E.D.T.*		*H.C.L.*	*E.D.T.*	
			M.[d]	*U.M.*[e]		*M.*	*U.M.*		*M.*	*U.M.*		*M.*	*U.M*
Tin	224.6	15	3	3	0.5	1	0.5	8	1	3	6	2	3
Lead	217.0	12	10	10	1	0.5	0.5	3	3	5	4	1	2
Thallium	276.8	12	10	10	1	1	1	3	2	3	5	3	3
Mercury	253.6	12	5	5	1	1	1	4	4	4	5	3	3
Silver	328.1	6	6	4	0.5	0.5	0.5	3	1	1	6	2	2

[a] Time taken for recorder to reach an equilibrium value.
[b] Hollow-cathode lamp.
[c] Electrodeless discharge tube.
[d] Electronically modulated.
[e] Unmodulated.
[f] With no external damping on the system.
[g] Reproducibility of output on re-initiation 15 min after being switched off.

TABLE III

COMPARISON OF INTENSITIES OF HOLLOW-CATHODE TUBES AND ELECTRODELESS DISCHARGE TUBES

Element	*Wavelength (nm)*	*H.C.L. current*[a] *(mA)*	*Relative intensities*[b]	
			H.C.L.	*E.D.T.*
Tin	224.6	12	1	820
	286.3	12	220	275,000
Lead	217.0	15	1	80
	283.3	15	3,200	120,000
Thallium	276.8	10	1	60
	377.5	10	4	380
Mercury	253.6	7	1	910
Silver	328.1	8	1	1

[a] Maximum recommended operating current.
[b] Intensities are uncorrected for the spectral response characteristics of instrument and are taken relative to the weakest absorption line from the hollow-cathode lamp in those instances in which more than one resonance line is used for atomic absorption.

charge tubes except that it appears to improve the stability of their emissions. Modulation also appears to inhibit migration of material within the tube and it is this which is probably the major cause of drift in output when some tubes are operated without modulation.

The relative intensities of the electrodeless discharge tubes and hollow-cathode lamps at the wavelengths most sensitive for atomic absorption spectroscopy (Table III) show the electrodeless discharge tubes to be between 60 and 1250 times more intense than the corresponding hollow-cathode lamps (operated at their maximal recommended currents); this is in accordance with previous observations[3]. Silver is exceptional in this respect because of the involatility of the silver chloride used in the preparation of the discharge tube; combined with the unusually high brightness of the silver hollow-cathode lamp, this leads to the low intensity ratio shown here. Nevertheless, this tube is more than adequate for atomic absorption spectroscopy and is sufficiently bright to obtain appreciable atomic resonance fluorescence signals.

Most resonance lines from both hollow-cathode lamps and electrodeless discharge tubes showed a sufficiently high signal : background ratio, so that a more detailed study was not merited. However, the lines most sensitive for the atomic absorption determination of tin and lead (at 224.65 nm and 217.00 nm respectively) are rather weakly emitted by the sources in comparison to other lines, and the continuous background emission found in the hollow-cathode lamps at these wavelengths becomes significant for the sensitivity of determination.

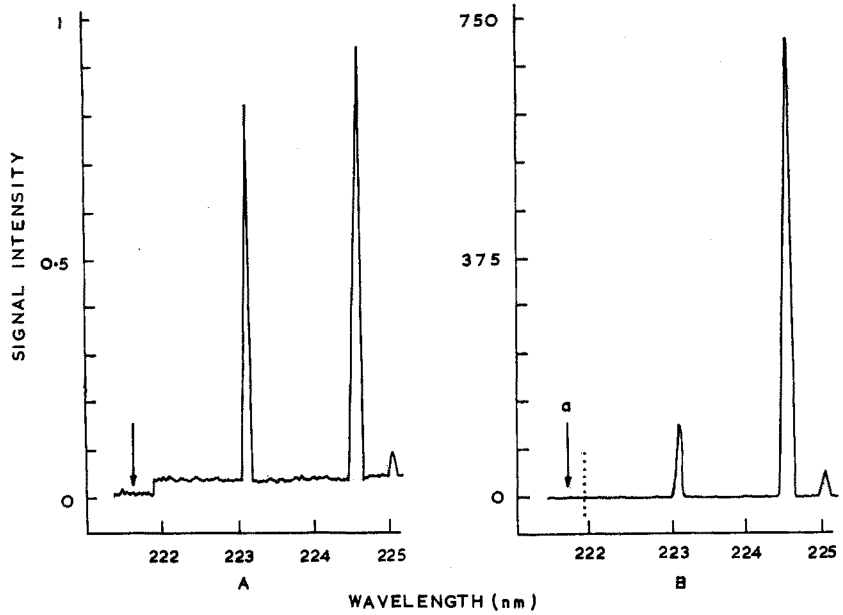

Fig. 1. Spectral plot of tin sources. (A) Hollow cathode lamp; (B) electrodeless discharge tube; (a) shutter closed, showing level of continuous background.

A comparison of the operation of the two tin sources (Fig. 1), near the line at 224.65 nm shows that the hollow-cathode lamp (plot A) has a signal : background ratio at 224.65 nm of only 36:1 compared with the electrodeless discharge tube (plot B) of >150:1. Both show a weak line at 225.12 nm (ratio λ 224.65 : λ 225.12 is 12:1 for the discharge tube and 16:1 for the hollow-cathode lamp), but the tin line at 223.17 nm is much stronger in the hollow-cathode lamp than in the discharge tube (ratio for λ 224.65 : λ 223.17 is 1.1:1 in the hollow-cathode lamp and 6.1:1 in the discharge tube). This indicates that the spectrum of the tin discharge tube resembles the arc spectrum and that of the hollow-cathode lamp more closely resembles the spark spectrum.

This is of particular importance with elements such as cobalt and nickel in which the spectra show unresolvable and non-absorbing lines close to the most absorbing spectral line.

The signal-to-background ratio of the lead electrodeless discharge tube (Fig. 2 B) at 217.00 nm is 140:1 and is again superior to that of the hollow-cathode lamp at 18.5:1. Furthermore, the hollow-cathode lamp shows two lines at 216.7 nm and 217.9

nm whose wavelengths and relative intensities appear to correspond to part of the iron spark spectrum[8]. Other lines at longer wavelengths were found which could also only be attributed to iron impurity in the cathode material. Such lines, when close to the major absorbing line, would add to the general background radiation observed in hollow-cathode lamps and would cause poor sensitivity, particularly insofar as many commercial atomic absorption spectrometers contain monochromators of low resolution.

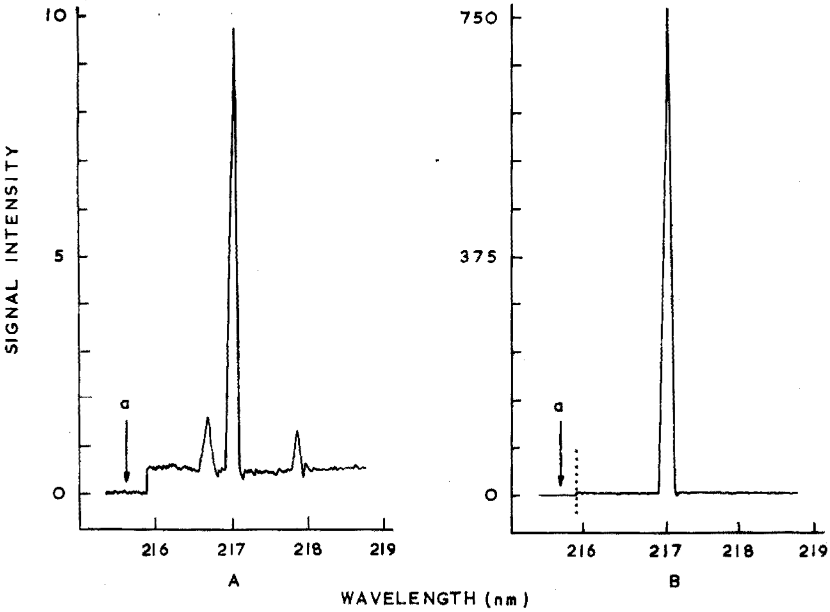

Fig. 2. Spectral plot of lead sources. (A) Hollow cathode lamp; (B) electrodeless discharge tube; (a) shutter closed, showing level of continuous background.

Applications in atomic absorption spectroscopy

Analytical absorption curves were prepared for lead, mercury, silver, thallium and tin in order to evaluate the performance of the electronically modulated and mechanically modulated (unmodulated plus mechanical chopper) electrodeless discharge tubes, and the corresponding hollow-cathode lamps under practical operating conditions. The discharge tubes gave identical results irrespective of the method of modulation. Also, for silver and thallium there was, as expected, no difference in the sensitivity, detection limit or linearity of the analytical curve, whether the discharge tubes or hollow-cathode lamps were used. In an air–acetylene flame, with a 5 cm × 0.5 mm slot burner at a 0.2-nm band-pass slit setting, the sensitivity for 1% absorption with both the silver and thallium sources was 0.08 p.p.m. at 328.1 nm and 0.7 p.p.m. at 276.8 nm respectively.

However, the analytical curves for tin and lead conformed to those expected from the spectral characteristics of the sources. In the determination of tin at 224.6 nm in a fuel-rich air–hydrogen flame the electrodeless discharge tube provided greater sensitivity and a longer linear working range than the hollow-cathode lamp. This can be attributed directly to the lower background in the electrodeless discharge tube. A 0.2-nm band-pass slit setting gave the highest sensitivity with the electrodeless tube, but the hollow-cathode lamp gave too little radiation at this wavelength to allow a slit with a band-pass narrower than 0.7 nm to be used; this results in a higher percentage of light falling outside the absorption profile of the 224.6-nm line in the flame, but within the band-pass of the monochromator. However, even with a 0.7-nm band-pass slit setting, the electrodeless discharge tube was found to give better sensitivity than the hollow-cathode lamp. With the electrodeless discharge tube, the sensitivity for 1% absorption at 224.6 nm was 2.0 p.p.m. and the detection limit with a four-times scale expansion was 0.75 p.p.m. The figures for the hollow-cathode lamp were 2.6 p.p.m. for 1% absorption and a detection limit of 0.8 p.p.m. The absorption curves at 286.3 nm were identical for both sources.

The same pattern was found with the two sources in the determination of lead at 217.0 nm in an air–acetylene flame. In this case, the influence of a higher background level on the shape of the analytical curves was further investigated by using an electrodeless discharge tube prepared from lead chloride which was of comparable brightness to the lead iodide tube, but which had a signal : background ratio of only 35:1 (*i.e.* intermediate between the lead-iodide discharge tube and the hollow-cathode lamp). The absorption curve slope fell between those found with lead-iodide tube and the hollow-cathode lamp. With the electrodeless discharge tubes, a 0.2-nm band-pass slit setting was again used, but, as before, the hollow-cathode lamp required the use of a slit with a band-pass greater than 0.7 nm. This allows the non-absorbing line at 216.7 nm to be passed, which causes further losses in sensitivity. With the electrodeless discharge tube, the sensitivity for 1% absorption at 217.0 nm was 0.5 p.p.m. and the detection limit with a four-times scale expansion was 0.1 p.p.m. The hollow-cathode lamp gave a sensitivity for 1% absorption of 0.9 p.p.m. and a detection limit of 0.5 p.p.m. Identical absorption curves were obtained with both sources at 283.3 nm.

The analytical curves for the atomic absorption of mercury(II) in an air–acetylene flame at 253.67 nm again show greater linearity and a higher sensitivity with the electrodeless discharge tube than with the hollow-cathode lamp. As the signal:background ratio in both sources is high ($>$100:1), it is likely that the hollow-cathode lamp in this instance exhibits some self-reversal. With a 0.2-nm band-pass for both sources, the electrodeless discharge tube gave a sensitivity for 1% absorption of 12 p.p.m. with a detection limit of 1.5 p.p.m.; the hollow-cathode lamp gave a sensitivity for 1% absorption of 16 p.p.m. with a detection limit of 2.5 p.p.m.

CONCLUSIONS

It would appear that electrodeless discharge tubes can be operated with electronic modulation at 50 Hz without difficulty and with no alteration in the usual methods of preparation. This development considerably enhances their application in atomic fluorescence and atomic absorption spectroscopy, because it is not always a simple task to mount mechanical choppers in position in many currently available spectrophotometers; also it is not always easy to achieve the modulation frequency required by many instruments in this way.

Although electrodeless discharge tubes have been used before in atomic absorption measurements, mainly the advantages associated with their high intensity in the short wavelength regions, *e.g.* sources for arsenic, selenium, etc.[3], have been demonstrated. However, because of the very high radiative flux and the absence of background radiation near the major resonance lines, and because of the elimination or suppression of other lines which may be present in other sources, the discharge tubes can give rise, in some cases, to considerable increases in sensitivity and a wider working range, compared with hollow-cathode lamps[9]. The mercury electrodeless discharge tube demonstrates the further advantage of reduced self-reversal in such sources. In this case, a greater sensitivity and a wider working range are given by the discharge tube, because of the better spectral profile of the emitted resonance line compared with that from a hollow-cathode lamp.

We thank the Perkin-Elmer Corporation for the loan of the apparatus and hollow-cathode lamps and also for technical assistance received. We also thank the Science Research Council for the award of a research studentship (Cooperative Award in Pure Science) to R.F.B.

SUMMARY

Electronic modulation of a selected range of electrodeless discharge tubes is achieved by superimposing a 50 Hz component on the d.c. potential of the anode of the magnetron valve. The effect of modulation is favourable and the usual methods of tube preparation are satisfactory. The source spectra for lead, mercury, silver, thallium and tin are compared with those for the corresponding hollow-cathode lamps and the analytical atomic absorption working curves obtained with the various sources are compared. The sources for lead and tin give considerably higher sensitivity and a wider working range than the hollow-cathode lamps because of the absence of continuous background or non-absorbing lines near the resonance line. The mercury source behaves similarly, probably because of less self-reversal.

RÉSUMÉ

On propose des tubes à décharge sans électrodes électroniquement modulés, comme sources en spectroscopie par absorption atomique. Les spectres du plomb, du mercure, de l'argent, du thallium et de l'étain sont comparés avec ceux obtenus avec les lampes correspondantes à cathode creuse. On compare également les courbes obtenues par analyse par absorption atomique avec les diverses sources. Les sources du plomb et de l'étain fournissent une sensibilité considérablement plus élevée et un champ de travail plus étendu que les lampes à cathode creuse en raison de l'absence de bruit de fonds continu ou de lignes non-absorbantes au voisinage de la ligne de résonance. La source de mercure se comporte de la même façon.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

An investigation of the solubility of some fluorides in 38.5% hydrofluoric acid

The decomposition of inorganic materials by 38–40% hydrofluoric acid frequently results in the formation of slightly soluble fluorides. Various authors[1–5] have discussed the composition of the solid phase resulting from the decomposition of silicate rocks. A survey of the literature on the solubility of fluorides in the hydrofluoric acid solvent system showed that comprehensive studies[6] had been made with hydrogen fluoride as solvent, while only few and scattered data were found on the solubility in the analytically important 38–40% acid.

The present work was started with the general purpose of procuring some solubility data, and with the special intention of ascertaining whether any of the main constituents of silicate rocks are quantitatively precipitated during the decomposition.

Experimental

Equipment. For the syntheses, analyses and solubility experiments, plastic apparatus was used. Special filter crucibles were made from polytetrafluoroethylene (PTFE), the porous disk (Gachot, France; porosity 5–15 μ) also being made of PTFE. Platinum dishes were used for removing hydrofluoric acid by evaporation.

Up to six 50-ml plastic bottles containing the reaction mixtures were fastened radially by clips to a circular disk, which was rotated slowly (about 24 r.p.m.) in a thermostatically controlled water bath maintained at $25.0 \pm 0.1°$.

Reagents. The 38–40% hydrofluoric acid (Merck, Germany), the fluorides and the majority of the other chemicals were of reagent-grade quality. The strontium fluoride was of a less pure quality. The concentration of the acid was determined titrimetrically and was found to be 38.5%.

Syntheses and analyses. The compounds $MgAlF_5 \cdot 2.7\ H_2O$ and $NaAlF_4 \cdot 1.4\ H_2O$ were synthesized and analyzed as described in the literature[5].

Solubility experiments. About 50 g of 38.5% acid were weighed in each of six 50-ml plastic bottles with screw closure, and 0.75–1.00 g of the fluoride to be studied was weighed and transferred to the bottles. After periods of 2, 4 and 8 days in the thermostat, sets of two bottles were removed. The content of a bottle was transferred as quickly as possible to the filter crucible, and the filtrate was collected in a weighed platinum crucible. The hydrofluoric acid was removed by evaporation and the residue was dried or ignited to constant weight. If the results indicated that equilibrium conditions had not been reached, additional experiments were run for prolonged periods (10–24 days) until the results were consistent.

Results

The results are listed in Table I. It is of interest to compare the present data with those for water and hydrogen fluoride. However, for a number of fluorides a direct comparison is difficult, because the measurements have been made at different temperatures and the solubilities reported in different ways. The solubilities in 38.5% hydrofluoric acid of the fluorides of the alkali or alkaline earth metals are about the same, or slightly higher, than those reported for water. In hydrogen fluoride the solubilities are considerably higher than in water or 38.5% acid.

The compounds ($NaAlF_4 \cdot 1.4\ H_2O$ and $MgAlF_5 \cdot 2.7\ H_2O$) detected in precipitates from decompositions of silicate rocks have relatively low solubilities; however, neither aluminium nor magnesium is quantitatively precipitated.

TABLE I

SOLUBILITIES AT 25.0° OF SOME FLUORIDES IN 38.5% HYDROFLUORIC ACID

Compound	*Solubility (g/100 g of acid)*	*Residue dried and/or ignited at (°)*
LiF	0.305	800
NaF	4.66	900
KF	49.6	750
RbF[a]	146	700
CsF[a]	391	600
BeF_2[b]	51	650
MgF_2	0.0147	110 and 900
CaF_2	0.0052	110 and 900
SrF_2	0.102	900
BaF_2	0.327	900
CeF_3	0.193	900
Na_3AlF_6	1.06	110 and 900
$NaAlF_4 \cdot 1.4\ H_2O$	0.764	110
$MgAlF_5 \cdot 2.7\ H_2O$	0.0318	110

[a] The high price and the high solubility of these salts made it necessary to reduce the number of experiments and the volume of hydrofluoric acid; of each salt only two solutions, in 6–12 g of acid, were prepared. These were run for 8 and 14 days.

[b] Only four experiments, with 9–18 g of acid, were run.

The present data confirm the observation[5] that, in the presence of aluminium, magnesium is precipitated as $MgAlF_5 \cdot x\ H_2O$, and not as magnesium fluoride. It is further interesting to note that $NaAlF_4 \cdot 1.4\ H_2O$ is less soluble than Na_3AlF_6.

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(Received October 2nd, 1968)

The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique. Part V. The analysis of ferrosilicon

The production of ferrosilicon is normally controlled by determining the content of silicon, aluminium, calcium and phosphorus; in addition, it is of importance to know the concentration of a number of minor and trace metals. The present scheme contains methods for the determination of silicon, aluminium, magnesium, calcium, titanium, manganese, chromium, copper, nickel, cobalt, lead and tin. It is highly probable that the principles of the present scheme, with proper modifications, would be applicable to the analysis of other ferrous alloys.

Samples of ferrosilicon are attacked according to decomposition method 2 (described in Part I of this series[1]).

Reagents and solutions

Analytical results for ferrosilicon are usually reported, not as oxides, but as elements. Routine analyses of this material are therefore conveniently made with a special series of primary standards (designated below as metal standard I). The composition of the secondary standard solutions is also given below. Each of these series of standards is designed for measurement of a definite dilution of the sample solution; this dilution is indicated in each case.

Silicon. Weigh 0.1070 g of silicon dioxide and prepare silicon standard I (0.5 mg Si/ml) as described in Part I. Transfer 9–37 ml, in steps of 1 ml, of this solution to plastic bottles and add water to a volume of 100 ml. If the sample solutions are diluted 10 times, the series covers the range 22.5–92.5% Si, in steps of 2.5%.

Aluminium. Weigh 1.0000 g of the metal and prepare aluminium standard I (1 mg Al/ml) as described in Part I. Dilute standard I with water to give a concentration of 0.2 mg Al/ml. Transfer up to 30 ml, in steps of 2.5 ml, of this solution to plastic bottles, add 50 ml of saturated boric acid solution, 5 ml of hydrofluoric acid, and water to a final volume of 100 ml. If the sample solutions are undiluted, the series covers the range up to 3% Al, in steps of 0.25%.

Magnesium. Weigh 0.1658 g of magnesium oxide and prepare magnesium standard I (0.1 mg Mg/ml) as described in Part I. Dilute standard I with water to a concentration of 0.005 mg Mg/ml. Transfer up to 20 ml, in steps of 2 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. If the sample solutions are undiluted, the series covers the range up to 0.05% Mg, in steps of 0.005%.

Calcium. Weigh 0.2497 g of calcium carbonate and prepare calcium standard I as described in Part I. Dilute standard I with water to give a solution containing 0.01 mg Ca/ml. Transfer up to 40 ml, in steps of 5 ml, of this solution to 100-ml volumetric flasks, add 100 ml of potassium reagent solution (10 mg K/ml) and dilute to the mark with water. If the sample solutions are diluted 10 times, the series covers the range up to 2% Ca, in steps of 0.25%.

Titanium. Weigh 1.0000 g of the metal and prepare standard I as described in Part I. Dilute standard I with water to a concentration of 0.1 mg Ti/ml. Transfer up to 20 ml, in steps of 2 ml, of this solution to plastic bottles, add 50 ml of boric acid solution, 5 ml of hydrofluoric acid and a volume of aluminium standard solution

TABLE I

ANALYTICAL DATA FOR THE BRITISH CHEMICAL STANDARDS SAMPLE NO. 305 (FERROSILICON)

Sample no.	*Si* (%)	*Al* (%)	*Mg* (%)	*Ca* (%)	*Ti* (%)	*Mn* (%)	*Cr* (%)	*Cu* (%)	*Ni* (%)	*Co* (%)	*Sn* (%)	*Pb)* (%
1	75·9	1.26	0.012	0.59	0.071	0.131	0.090	0.102	0.078	Below detection limit, *i.e.* below about 0.01% Co	0.189	0.020
2	75·7	1.24	0.012	0.57	0.090	0.129	0.095	0.104	0.080		0.184	0.019
3	75.8	1.25	0.013	0.56	0.094	0.128	0.097	0.100	0.079		0.184	0.020
4	75·5	1.21	0.013	0.57	0.093	0.126	0.095	0.098	0.081		0.186	0.014
5	75.8	1.24	0.013	0.54	0.078	0.127	0.095	0.097	0.079		0.192	0.016
Averages	75·7	1.24	0.013	0.56	0.085	0.128	0.095	0.100	0.079	—	0.187	0.018
Stand. dev.	0.16	0.02	0.001	0.02	0.010	0.002	0.0026	0.003	0.0013	—	0.004	0.0026
Rel. dev.	0.21	1.6	4·9	3·6	11	1.6	2·7	3·0	1.6	—	2.1	14
Certificate value	76.0	1.25	—[a]	0.56	—[a]	—[a]	—[a]	0.10	—[a]	—[a]	—[a]	—[a]

[a] Not reported.

corresponding approximately to the amount of aluminium present in the sample solution; finally, add water to a volume of 100 ml. If the sample solutions are undiluted, the series covers the range up to 1.0% Ti, in steps of 0.1%.

Manganese. Weigh 1.0000 g of the metal and prepare standard I as described in Part I. Dilute standard I with water to give a solution containing 0.01 mg Mn/ml. Transfer up to 60 ml, in steps of 10 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. If sample solutions are undiluted, the series covers the range up to 0.3% Mn, in steps of 0.05%.

Chromium. Weigh 1.0000 g of the metal and prepare standard I as described in Part I. Dilute standard I with water to a concentration of 0.01 mg Cr/ml. Transfer up to 80 ml, in steps of 10 ml, of this solution to 100-ml volumetric flasks and make up to volume with water. If sample solutions are undiluted, the series covers the range up to 0.4% Cr, in steps of 0.05%.

Copper. Prepare copper standard I by dissolving 1.0000 g of the metal in a mixture of 50 ± 5 ml of water and 20 ± 1 ml of nitric acid; transfer the solution to a 1-l volumetric flask and dilute to volume with water. Dilute standard I with water to a concentration of 0.01 mg Cu/ml. Transfer up to 80 ml, in steps of 5 ml, of this solution to 100-ml volumetric flasks and make up to the mark with water. When measured against undiluted sample solutions, the series covers the range up to 0.4% Cu, in steps of 0.025%.

Nickel. Prepare nickel standard I as described for copper. Dilute nickel standard I with water to give a solution containing 0.01 mg Ni/ml. Transfer up to 80 ml, in steps of 10 ml, to 100-ml volumetric flasks and dilute to volume with water. If the sample solutions are undiluted, the series covers the range up to 0.4% Ni, in steps of 0.05%.

Cobalt. Prepare cobalt standard I as described above for the preparation of copper standard I. Dilute cobalt standard I with water to a concentration of 0.02 mg Co/ml. Transfer up to 50 ml, in steps of 5 ml, of this solution to 100-ml volumetric flasks and dilute to the mark with water. With undiluted sample solutions, the series covers the range up to 0.5% Co, in steps of 0.05%.

Lead. Weigh 2.0000 g of lead (purity not less than 99.9%) and transfer to a beaker. Add 50 ± 10 ml of water and 25 ± 1 ml of nitric acid, cover the beaker and heat the solution until the metal has dissolved. Transfer the cooled solution to a 1-l volumetric flask and dilute to volume with water. Dilute this solution with water to a concentration of 0.01 mg Pb/ml. Transfer up to 20 ml, in steps of 2 ml, of the diluted solution to 100-ml volumetric flasks and dilute to volume with water. With undiluted sample solutions, the series covers the range up to 0.1% Pb, in steps of 0.01%.

Tin. Weigh 1.0000 g of the metal (purity 99.9%, or better) and transfer to a beaker. Add 500 ± 20 ml of water, 100 ± 5 ml of hydrochloric acid and 2.0 ± 0.2 ml of nitric acid, and proceed as described for the preparation of lead standard I. Dilute tin standard I with water to give a solution containing 0.1 mg Sn/ml. Transfer up to 20 ml, in steps of 5 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. With undiluted sample solutions, the series covers the range up to 1% Sn, in steps of 0.25%.

Procedure

Transfer 0.2000 g of the sample to the decomposition vessel, and add by pipette

5 ml of water and 5 ml of hydrofluoric acid. Cover the vessel and let it stand at room temperature for some minutes. Add by pipette 1 ml of concentrated nitric acid, close the vessel without delay and decompose by method 2 as described in Part I[1]. It is recommended to attack samples of ferrosilicon by heating for 30 min at 110°.

Determine aluminium, magnesium, titanium, manganese, chromium, copper, nickel, cobalt, lead and tin in the main solution. Determine silicon in a solution prepared by diluting the main solution 10 times with water. Determine calcium on the solution obtained by pipetting 10 ml of the main solution into a 100-ml volumetric flask, adding 10 ml of potassium reagent solution (10 mg K/ml) and diluting to volume with water.

Determine silicon, aluminium, magnesium, calcium, titanium and chromium with acetylene–nitrous oxide flames, and the other elements with the acetylene–air flames*. Measure and calculate the results as described in Part I.

Applications

The scheme was tested by analyzing the British Chemical Standards sample No. 305 (ferrosilicon). The analytical results and the certificate values are shown in Table I.

The authors gratefully acknowledge grants from the Royal Norwegian Council for Scientific and Industrial Research.

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(Received October 6th, 1968)

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* According to the literature[2], it is better to determine tin with hydrogen–air flames, but this was not found to be essential.

The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique.

Part VI. The analysis of felspars

The felspars and some related materials, *e.g.* nepheline syenite, are of great importance to the ceramic, glass and other industries. Routine analyses of these materials are normally concentrated upon determining iron and the alkalis. Previous publications[1,2] have described the determinations of iron, magnesium, calcium, sodium, potassium and minor components in felspars. The present scheme describes methods for the determination of silicon, aluminium, total iron, magnesium, calcium, sodium and potassium. Methods for titanium and manganese may be incorporated in the scheme.

The felspars succumb quickly to an attack by hydrofluoric acid; consequently, decomposition method 1 (described in Part I of this series[3]) is applicable.

Reagents and solutions

The reagents required for the present determinations are listed in Part I, and the detailed preparation of the primary standard solutions (designated below as metal standard I) is described in Part I. The compositions of the secondary standard solutions are given below. Each of these series is prepared for measurement of a definite dilution of the sample solution, which is indicated in each case.

Silicon (sample solutions diluted 4 times). Transfer by plastic pipette 10–20 ml, in steps of 0.5 ml, of silicon standard I to plastic bottles and add water to a final volume of 100 ml. (Range: 40–80% SiO_2, in steps of 2%.)

Aluminium (sample solutions diluted 4 times). Dilute aluminium standard I with water to a concentration of 0.5 mg Al_2O_3/ml. Transfer 15–30 ml, in steps of 1 ml, of this solution to plastic bottles, add by plastic pipette 25 ml of the combined boric acid–hydrofluoric acid reagent solution and water to a final volume of 100 ml. (Range: 15–30% Al_2O_3, in steps of 1%.)

Total iron (undiluted sample solutions). Dilute iron standard I with water to give a solution containing 0.01 mg Fe_2O_3/ml. Transfer up to 40 ml, in steps of 4 ml, of this solution to 100-ml volumetric flasks and dilute to volume with water. (Range: up to 0.2% Fe_2O_3, in steps of 0.02%.)

Magnesium (undiluted sample solutions). Dilute magnesium standard I with water to a concentration of 0.01 mg MgO/ml. Transfer up to 50 ml, in steps of 2.5 ml, of this solution to 100-ml volumetric flasks, and dilute to the mark with water. (Range: up to 0.25% MgO, in steps of 0.0125%.)

Calcium. Dilute calcium standard I with water to a concentration of 0.02 mg CaO/ml. Transfer up to 50 ml, in steps of 2.5 ml, of this solution to 100-ml volumetric flasks, add 10 ml of potassium reagent solution (10 mg K/ml) and dilute to volume with water. If sample solutions are diluted 10 times, this series covers the range up to 5% CaO, in steps of 0.25%. If the sample solutions are diluted 100 times, the interval 5–20 ml of the above series covers the range 5–20% CaO, in steps of 2.5%.

Sodium. Dilute sodium standard I with water to a concentration of 0.01 mg Na_2O/ml. Two series of secondary standard solutions are prepared. Prepare Series I by transferring up to 10 ml, in steps of 1 ml, of the diluted standard solution to 100-ml volumetric flasks, add 10 ml of caesium reagent solution (10 mg Cs_2O/ml) and dilute to volume with water. If the sample solutions are diluted 100 times, Series I covers the range up to 5% Na_2O, in steps of 0.5%.

Prepare Series II similarly by transferring 5–12 ml, in steps of 1 ml, of the diluted standard solution to 100-ml volumetric flasks, etc. With 200-fold dilution of the sample solution, Series II covers the range 5–12% Na_2O, in steps of 1%.

Potassium. Dilute potassium standard I with water to give a solution containing 0.01 mg K_2O/ml. Prepare two series of secondary standard solutions. Prepare Series I by transferring up to 24 ml, in steps of 2 ml, of the diluted standard solution to 100-ml volumetric flasks, add 10 ml of caesium reagent solution and make up to the mark with water. If the sample solutions are diluted 50 times, Series I covers the range up to 6% K_2O, in steps of 0.5%.

Prepare Series II in a similar way by transferring 6–18 ml, in steps of 2 ml, of the diluted standard solution to 100-ml volumetric flasks, etc. With 200-fold dilution of the sample solution, Series II covers the range 6–18% K_2O, in steps of 2%.

Procedure

Weigh 0.2000 g of sample and transfer to the decomposition vessel. Moisten with 1 ml of water (added by pipette), add by plastic pipette 5 ml of hydrofluoric acid, and decompose by method 1[1]; heating for *ca.* 15 min on a boiling water bath is normally sufficient to open up samples of felspars and nepheline syenite.

Determine total iron and magnesium in the main solution.

For the determination of silicon and aluminium, pipette 25 ml of the main solution into a dry plastic bottle, add 75 ml of water by pipette and mix.

Determine calcium by pipetting 10 ml of the main solution into a 100-ml volumetric flask, add 10 ml of potassium reagent solution and dilute to volume with water. This solution is suitable for samples containing up to 5% CaO. Higher contents call for a further dilution as follows: transfer by pipette 10 ml of the above diluted solution to a 100-ml volumetric flask, add 9 ml of potassium reagent solution and make up to volume with water.

Determine sodium and potassium as follows. Transfer 10 ml of the main solution into a 100-ml volumetric flask and dilute to volume with water (Solution A). Determine up to 5% Na_2O in a solution prepared by pipetting 10 ml of Solution A to a 100-ml volumetric flask, adding 10 ml of caesium reagent solution and making up to volume with water. Determine 5–12% Na_2O and 6–17% K_2O by transferring 50 ml of the latter solution to a 100-ml volumetric flask, adding 5 ml of caesium reagent solution and diluting to volume with water. Determine up to 6% K_2O by pipetting 20 ml of Solution A to a 100-ml volumetric flask, adding 10 ml of caesium reagent solution and diluting to the mark with water.

Determine silicon, aluminium, magnesium and calcium with acetylene–nitrous oxide flames and the other elements with acetylene–air flames. Measure and calculate the results as described in Part I.

TABLE I

ANALYTICAL DATA FOR U.S. BUREAU OF STANDARDS SAMPLE NO. 99 (SODA FELSPAR)

(Before analysis the sample was dried for 1 h at 105°. The averages and deviations were calculated from the results of five separate determinations)

	Si as SiO_2 (%)	*Al as Al_2O_3 (%)*	*Total Fe as Fe_2O_3 (%)*	*Mg as MgO (%)*	*Ca as CaO (%)*	*Na as Na_2O (%)*	*K as K_2O (%)*
Averages	68.56	19.12	0.083	0.058	0.36	11.00	0.382
Stand. dev.	0.17	0.14	0.004	0.003	0.03	0.20	0.006
Rel. dev.	0.24	0.73	4.8	5.2	0.83	1.8	1.6
Certificate value	68.66	19.06	0.067	0.053	0.36	10.73	0.41

TABLE II

ANALYTICAL DATA FOR A SAMPLE OF NEPHELINE SYENITE

(The averages and deviations were calculated from the results of ten separate determinations)

	Si *as* SiO_2 (%)	*Al* *as* Al_2O_3 (%)	*Total Fe* *as* Fe_2O_3 (%)	*Mg* *as MgO* (%)	*Ca* *as CaO* (%)	*Na* *as* Na_2O (%)	*K* *as* K_2O (%)
Averages	55.17	25.26	0.102	0.0144	1.37	8.49	8.78
Stand. dev.	0.32	0.14	0.0007	0.0004	0.034	0.10	0.18
Rel. dev.	0.58	0.56	0.69	2.6	2.5	1.2	2.0

Applications

The methods were tested by analyzing the U.S. Bureau of Standards sample No. 99 (soda felspar) and a sample of nepheline syenite. The analytical results, certificate values and some statistical data are given in Tables I and II.

The present work was supported by the Royal Norwegian Council for Scientific and Industrial Research.

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(Received October 6th, 1968)

Precision determination of gadolinium in cadmium fluoride by neutron activation analysis

The determination of trace rare earths in cadmium fluoride by thermal neutron activation analysis presents several problems. Nondestructive analysis in many cases (*e.g.*, gadolinium) is impossible due to the high level of activity produced from the cadmium. ^{115}Cd ($T_{\frac{1}{2}}=2.3$ d), ^{107}Cd ($T_{\frac{1}{2}}=6.5$ h) and ^{117}Cd ($T_{\frac{1}{2}}=2.5$ h) are the primary isotopes which interfere with the determination of ^{159}Gd ($T_{\frac{1}{2}}=18$ h). Irradiation for 1 h of 100 mg of cadmium fluoride in a flux of $1.5\cdot10^{13}$ n cm^{-2} sec^{-1} will produce millicurie amounts of activity from the cadmium.

Radiochemical separation can be employed, but there exists the problem of neutron shielding from the ^{113}Cd and ^{157}Gd which have capture cross-sections of

$2 \cdot 10^4$ and $2.4 \cdot 10^5$ barns, respectively. Because of the shielding caused by these isotopes, precise standards are difficult to prepare. Ball-milled mixed powders would not suffice because of the different environments of the isotopes in the standard and sample. Attempts to produce standard melts and to analyze them by a radiochemical separation gave poor precision, probably because of the loss in sensitivity caused by the neutron shielding.

MASSART AND HOSTE[1] have used a preseparation step for the determination of rare earths in minerals which employed the addition of ^{153}Gd tracer for a yield determination. These authors have also used a comparator method with cobalt as a flux monitor. Although good precision was obtained, there exists the necessity of reproducing counting positions, and making yield determinations.

To circumvent the difficulties of neutron shielding and yield determinations, it was decided to employ a separation of the cadmium before irradiation combined with an internal standard technique.

Reagents and equipment

Except for 99.9% pure Gd_2O_3 and Sm_2O_3 from Michigan Chemical Company, all reagents used are common to the analytical laboratory. The pulse-height analyzer was a Nuclear Data 2200 with a digital spectrum stabilizer coupled to an Ortec cooled Ge(Li) detector. The detector was semicoaxial with a sensitive volume of 24.4 cm^3 and a resolution of 3.1 keV for the 1.3-MeV ^{60}Co γ-ray.

Standard solutions of gadolinium and samarium were prepared from their oxides by dissolving appropriate amounts in small quantities of perchloric acid and diluting with 1:1 nitric acid. These solutions contained *ca.* 0.6 mg/ml of Gd_2O_3 and 1 μg/ml Sm_2O_3. A carrier solution containing *ca.* 1 mg of titanium/ml was prepared by fusing TiO_2 in a small amount of potassium pyrosulfate and diluting with hydrochloric acid which contained a small amount of hydrogen peroxide.

Procedure

Prepare a series of standards by pipetting into a 400-ml beaker 1-ml aliquots of the standard solutions of gadolinium and 10 ml of the titanium carrier solution to give *ca.* 0.6 mg of gadolinium, 1 μg of samarium, and 10 mg of titanium. The amounts of gadolinium and samarium must be accurately known, but the amount of titanium is not critical. Dilute the solution to 200 ml and precipitate the titanium as the hydroxide with an excess of 1:1 ammonium hydroxide. Filter and ignite the precipitates and encapsulate them in small polyethylene vials. The standards are then ready for irradiation.

The sample preparation is more involved because of the presence of cadmium. Accurately weigh 100-mg samples of the cadmium fluoride into 400-ml beakers. Fume off the fluoride with a small amount of perchloric acid and add 10 ml of the titanium carrier solution and 1 ml of the standard samarium solution. Dilute the solution to 300 ml with 1:10 hydrochloric acid. The solution will be yellow in color, owing to the peroxy complex of titanium. Heat the solution almost to boiling and add 1:1 ammonium hydroxide until the yellow color just begins to fade. This occurs just before the titanium begins to precipitate. Add 5 g of solid potassium cyanide, followed rapidly by 100 ml of 1:1 ammonium hydroxide. Filter and ignite the precipitate and encapsulate it in preparation for irradiation.

Irradiate the samples for 2 h in a flux of $1 \cdot 10^{13}$ n cm^{-2} sec^{-1} and cool them for 1 h to allow the titanium activity to decay. Transfer the precipitates to platinum crucibles along with *ca.* 100 mg of cadmium oxide for the sample precipitates. Fuse the mixture in a small amount of potassium or sodium pyrosulfate and dissolve the melt in dilute hydrochloric acid. Make the solution just sufficiently acid to hold the titanium in solution and repeat the precipitation procedure. Filter the precipitates, ignite them, and place them in polyethylene vials for counting.

Count the samples for a sufficient time to obtain good statistics, about 10^4 counts in each of the 360-keV gadolinium and 103-keV samarium peaks.

Background blanks of pure gadolinium and pure samarium oxide should be prepared, irradiated and counted with the standards and samples. It was found that our compounds contained sufficient sodium to require a fusion with radiochemical separation after irradiation.

The background blank spectra are subtracted from the spectra of the samples and standards and the ratios of the counts per gram of gadolinium to counts per gram of samarium in the samples are compared to the average of the ratios for the standards. The percent gadolinium is calculated as follows:

$$\%\mathrm{Gd} = \frac{Y \cdot N_2 \cdot W_1 \cdot 100}{N_1 \cdot W_2}$$

where Y = average ratio of counts per gram of samarium to counts per gram of gadolinium in the standards, N_1 = counts of samarium, N_2 = counts of gadolinium, W_1 = weight of samarium, W_2 = weight of sample.

A computer program to accomplish the subtracting of the background blanks accurately has been briefly described previously[2].

Results and discussion

Typical results are presented in Table I. The effectiveness of the determination depends on the validity of the assumption that the samarium and gadolinium behave similarly so that any loss of one will be exactly parallelled by loss of the other. Although there is no direct proof that this assumption is valid, the precision obtained

TABLE I

DETERMINATION OF GADOLINIUM IN CdF_2

c.p.g. Sm/c.p.g. Gd	*Standard deviation*	*Percent average deviation*
480 485 483 473		
481 Average	5.1	0.77
% Gd		
0.040 0.038 0.040 0.038		
0.039 Average	0.0012	2.5
0.042 0.044 0.041 0.043		
0.043 Average	0.0014	2.7

in the counts per g of gadolinium to counts per g of samarium ratios is good evidence that it is correct to at least the degree necessary for this purpose.

The purpose of the post-irradiation separation is primarily to remove sodium which is a trace contaminant in the titanium oxide precipitate, and the last traces of cadmium. This last separation can be eliminated, however, if one is willing to prepare, irradiate, count and subtract out pure cadmium and sodium spectra from the gadolinium and samarium spectra. Only a minor loss in precision is obtained.

Titanium was chosen as a carrier because of the short half-life of ^{51}Ti and the low yield of fast neutron induced radioactive nuclides. The sodium-24 contamination present, probably produced from the absorbed sodium in the reagents used, proved to be considerably less than the sodium-24 produced from the (n, α) reaction on 10 mg of aluminum after a 2-h irradiation in the core of the reactor. However, the radiochemical separation will remove most of the sodium interference and aluminum can be used as the carrier.

The authors believe that not only is the basic technique presented applicable to the determination of most rare earths in cadmium fluoride, but, because an hydroxide precipitation with a nonisotopic carrier is employed, may prove to be applicable to the determination of many other trace constituents in cadmium fluoride which form insoluble hydroxides in ammoniacal solution and which do not form cyanide complexes. Although the chemistry is time-consuming, the gain in accuracy and precision by avoiding neutron shielding effects, irradiation and counting geometry considerations, and yield determinations warrants the effort. Provided that standards are accurately prepared and internal standards accurately added, the technique is inherently accurate. The primary source of error probably arises from the handling of small quantities and/or very dilute standard solutions.

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(Received October 7th, 1968)

A study of the mechanism of the adsorption on columns of salts
The sorption of europium on cadmium oxalate*

Adsorption chromatography has been little studied as a technique for the separation of metal cations since 1955. The discovery of the ion-exchange properties and the selectivity of inorganic materials, such as zirconium phosphate or zirconium oxide, has, however, caused a revival of interest in this type of stationary phase and has led several authors to investigate typical adsorption chromatographic techniques. Most of the recent studies of simple salts as column materials have been concerned with the development of selective radiochemical separations.

In this context the research effected by GIRARDI[1] should be mentioned. This author has examined systematically the sorption characteristics of columns of simple salts and has completed studies of, among others, cadmium sulfide and copper sulfide, copper chloride and lead fluoride; several interesting separations are possible. Other examples are the sorption of halides such as iodide, on silver bromide as studied by ECKHARDT *et al.*[2], and the separation of americium(VI) from curium(III) on calcium fluoride as examined by HOLCOMB[3]. The sorption of several metal cations on metal sulfides has been studied carefully by PHILLIPS AND KRAUS[4], who concluded that the exchange reactions between the metal ions in the stationary phase and mobile phase occur through metatheses such as:

$$\overline{M_1X} + M_2 \rightarrow \overline{M_2X} + M_1 \qquad (1)$$

where M_1 and M_2 represent cations and a bar represents the stationary phase.

In an investigation of the possibility of using oxalates as the stationary phase for radiochemical column separations, the mechanism of the sorption on such materials, and especially the sorption of europium on cadmium oxalate were investigated.

Experimental

Cadmium oxalate was prepared in 30–50-g batches by precipitation of a 3% oxalic acid solution with a stoichiometric quantity of the metal ion ("stoichiometric" oxalate) or with a 10% excess ("non-stoichiometric" oxalate). The precipitates were washed twice by decantation with water, filtered off on porous glass filters, washed with *ca.* 50 ml of water and dried overnight at 75–80°.

Batch experiments were performed to determine sorption percentages or distribution coefficients under completely equilibrium conditions. Column experiments were performed in glass columns with an internal diameter of 8 mm. The distribution of europium was followed with ^{152m}Eu, prepared by neutron activation in the Thetis reactor of this Institute.

Results and discussion

Influence of the quantity of europium. Figure 1 shows the percentage of europium adsorbed on equilibration with 100 mg of cadmium oxalate in 0.1 *M* nitric acid. On "stoichiometric" cadmium oxalate, a nearly complete sorption occurs for quantities of europium between 0.75 mg and 10 mg. While the increasing loss of

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* Communicated in part to the Vth Symposium on Chromatography and Electrophoresis, Brussels, 1968.

sorption power at higher quantities is expected, the losses at low loading cannot be easily explained on the basis of a metathesis reaction. The behaviour of "non-stoichiometric" cadmium oxalate is still more complicated. It is identical with "stoichiometric" cadmium oxalate at medium and higher loading. At low loading, the sorption decreases with decreasing loading until the range 10–20 μg of europium is reached. From there on, the sorption power increases again.

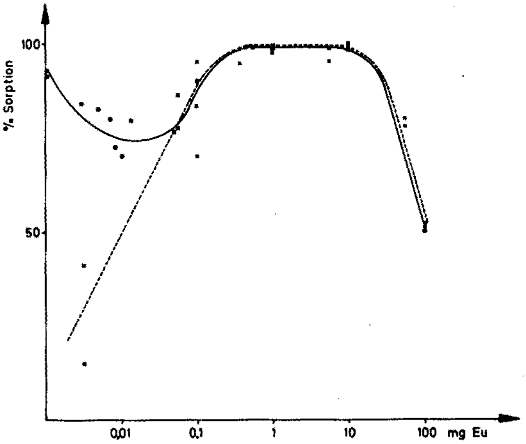

Fig. 1. The adsorption of europium in 0.1 *M* nitric acid on cadmium oxalate as a function of the amount of Eu carrier. (-----) stoichiometric product; (——) non-stoichiometric product.

The behaviour of "stoichiometric" cadmium oxalate can be explained if one postulates that the sorption of europium on cadmium oxalate (and probably on many other oxalates since the same effects were noted on lead oxalate) does not occur through metathesis, but through precipitation with the oxalate anion in solution. This is represented by the following reaction scheme:

$$\overline{M_1X} \rightleftarrows M_1 + X \quad (2)$$

$$M_2 + X \rightleftarrows \overline{M_2X} \quad (3)$$

According to this scheme, reaction (3) would take place only when the solubility product for M_2X is exceeded.

The behaviour of europium at very low loading on "non-stoichiometric" cadmium oxalate can be explained by a secondary process. When a salt is precipitated in the presence of an excess of one of the constituent ions, this ion is adsorbed on the surface. This ion, a cadmium(II) ion in this case, can probably be exchanged against the europium(III) cation which forms a less soluble compound with the oxalate. This is certainly the case for cadmium oxalate, precipitated with a 10% excess of oxalate anion, with which exactly the same sorption results are obtained as with the so-called "non-stoichiometric" cadmium oxalate. As has been shown by KOLTHOFF[5], the negative charge on the surface is in such a case compensated by the adsorption of positive ions. According to the Paneth–Fajans–Hahn rule, the ion which forms the lesser dissociated compound with the anion is preferentially adsorbed, which in this case will lead to the adsorption of europium(III). Because it is a surface phenomenon, however, the capacity as determined by this reaction alone is very low.

Influence of the quantity of cadmium oxalate. When "stoichiometric" cadmium oxalate is equilibrated in 0.1 *N* nitric acid with 1 mg or 1 μg of europium, it was found that over the range of 100 mg to 2 g of stationary phase the quantity of stationary phase has no influence on the percentage sorption. The quantity sorbed appears thus to be determined only by the quantity of free oxalate in solution. The same result was obtained for the sorption of 1 mg of europium on "non-stoichiometric" cadmium oxalate but not for the sorption of 1-μg quantities.

Table I summarizes the results obtained for the sorption of 1 and 10 μg of europium in 0.1 *N* nitric acid on 100 mg or 500 mg of cadmium oxalate expressed as % Eu in solution.

TABLE I

SORPTION LOSSES (%) ON "NON-STOICHIOMETRIC" CADMIUM OXALATE

		100 mg	*500 mg*
1 μg Eu	A	77.7	52.4
10 μg Eu		87.0	65.2
1 μg Eu	B	65.0	19.5
10 μg Eu		79.5	43.4

The fact that the sorption of microgram quantities of europium on "non-stoichiometric" cadmium oxalate is dependent on the quantity of stationary phase can be explained by considering that, if the sorption of small quantities of cadmium oxalate is caused by an exchange with adsorbed ions, the extent of the sorption depends on the total quantity of exchangeable cations present.

Group A represents a set of experiments in which the mobile phase was added one week before the equilibration and group B another set in which the equilibration with europium was carried out immediately after addition of the mobile phase. It is clear that the sorption is better for group B. This is ascribed to a recrystallization process which leads to a decrease in surface area (Ostwald ripening).

Chromatography. The foregoing results were all obtained by batch equilibration. Since chromatography is a process of repeated equilibration, the precipitation phenomena discussed do not appear so clearly in column operation. However, it was found that "stoichiometric" cadmium oxalate is an irreproducible column material for the sorption of microgram quantities of europium. The following sorption percentages were obtained for 2 μg of europium on 1 g of cadmium oxalate in 0.1 *N* nitric acid: 95.2%, 88.0%, 77.5%, 62.2%, 17.8%. "Non-stoichiometric" cadmium oxalate yielded much better results since in a series of 10 experiments no sorption percentage under 99.5% was obtained.

It was also found that the preparation of "non-stoichiometric" columns a long time before use leads to a decrease in efficiency for the sorption of microgram quantities of europium (10 to 20% for a preparation one week before use).

Cadmium oxalate presents two favourable characteristics as a column material. The capacity, for example, for the rare earths is very high. On a column of 500 mg of cadmium oxalate, 129 mg of samarium were sorbed (*i.e.* 50% of the column was converted to the samarium form) before break-through occurred. Furthermore, the attainment of equilibrium is fast so that flow rates of 1 ml/cm^2·min were possible.

Conclusion

The demonstration of many phenomena characteristic of precipitation, indicates that the exchange mechanism is represented by reactions (2) and (3). This mechanism exists probably in many cases where replacement reactions on salts occur, but is not always easy to demonstrate. In the case of the sulfides, for example, it is difficult to obtain stoichiometric salts and furthermore since they are much less soluble than the oxalate discussed here, there would be no measurable downward trend in sorption power at low loading.

The author thanks Prof. Dr. J. Hoste for the interest shown in this work and Mr. L. Mees for his skillful experimental assistance.

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(Received November 9th, 1968)

On analytical curves and limits of detection in phosphorimetry

The shapes of analytical curves and limits of detection in phosphorescence analysis can be predicted from equations derived by St. John, McCarthy and Winefordner who used a signal-to-noise approach[1,2]. Theory predicts a linear relation between phosphorescence intensity and concentration, *i.e.*, analytical curves should have a slope of one. Negative curvatures are expected at high concentrations where complete absorption occurs and molecular aggregation and quenching may be significant. Positive curvatures near the limit of detection are a consequence of luminescent impurities in the solvent. Experimentally, it is difficult to apply signal-to-noise theory in determining phosphorescence limits of detection because of the variable background encountered under most experimental conditions. Winefordner, McCarthy and St. John have recommended an extrapolation procedure to estimate limits of detection[3]. In this case, the limit of detection is defined as the concentration corresponding to the intersection of a line drawn through several background points with the extension of the linear portion of the analytical curve–(log–log plot). A simplification of this procedure which might give a rapid estimation of the limit of detection would be determination of a single analytical point and extrapolation of a line of slope one through this point to background. This procedure of course depends on the accuracy of the measured point and the validity of the assumption of a slope of one for the analytical curve. If one accepts a slope of one, the imprecision in estimating a limit of detection should be essentially that of measuring the point, *i.e.* 5–10%[3,4]. In order to check the validity of the above assumption, we examined the slopes of the analytical curves of a large number of compounds which had been determined in this laboratory over the past few years. We felt that this would be useful in checking how well experimental systems conformed to the theory and in addition would provide the basis for a simple, rapid means of estimating how sensitive phosphorimetry might be for determination of a compound for which little analytical phosphorescence data were available. The purpose of this note is to report the results of this examination.

All the phosphorescence analytical curves examined were determined with an Aminco-Bowman Spectrophotofluorimeter and a phosphoroscope attachment using standard procedures. Data were collected for over 100 organic compounds of widely different structures and functional groups*. Analytical curves were in all cases determined on solutions of the pure compound. The data are the results of 8 different analysts and were obtained over a period of five years with three different Aminco-Bowman instruments. Since more than 95% of the compounds resulted in analytical working curves with slopes of 1.0±0.1, the limiting detectable concentration of a compound in phosphorimetry can be estimated by the extrapolation technique described above. It should be mentioned that most of the compounds which yielded slopes differing from 1.0±0.1 were also compounds which gave linear analytical curve regions of less than two decades, *i.e.*, in such cases the limiting detectable compound concentration is quite high (*e.g.* $> 10^{-5}$ *M*), and in such cases the extrapolation method would not be expected to give reliable results.

This research was carried out as part of a study on the phosphorimetric analysis of drugs in blood and urine supported by a U.S. Public Health Service Grant (GM-11373-05).

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(Received October 29th, 1968)

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Selective estimation of beryllium with morin crayon on the ring oven

The relatively great increase in the use of beryllium and beryllium salts has focussed attention on illness attributed to such compounds. As berylliosis may prove fatal, new and reliable methods to determine beryllium in air and in water are of vital interest.

The rapid, semiquantitative procedures by the ring oven method are generally characterized by simplicity and reliability. The method for the semiquantitative estimation of beryllium presented here is a continuation of another ring oven study[1]. The aim was to improve the sensitivity by changing a color reaction to a highly sensitive fluorescence change, and to free the method from various interferences.

Preparation of the reagent crayon

Glyceryl stearate (3.5 g) was mixed in a test tube with 1.5 g of paraffin wax. The mixture was heated in a boiling-water bath until it became transparent and homogeneous; 50 mg of morin (K and K Laboratories) was dissolved in the hot mixture and poured into a waxed-paper straw. Upon cooling, the crayon may be exposed as needed by peeling off the protective paper and is used by rubbing its tip on the deposit in the ring.

Equipment

Capillary pipets calibrated at 1–20 μl.

F. H. Munkteils Swedish filter paper No. 1F, 55 mm diameter.

Procedure

Place the filter paper on the Weisz ring oven (National Appliance Co., Portland, Oregon) maintained at 90–95°, and fix the paper in position with the retainer ring. Add the sample drop followed by 10 μl of 0.1 *M* EDTA solution, and wash out to the ring zone with twice-distilled water, taking care to avoid flooding the ring. Remove the dry paper from the oven, and rub the test area with the reagent crayon. Expose the paper to a current of hot air from a hair drier until the wax melts and makes intimate contact with the deposited beryllium. Then soak in a bath (1:1 conc. ammonia and methanol) for about 5 min. Finally, dry the paper and examine under a UV lamp fitted with a magnifier glass. Bright yellow fluorescent rings, the intensities of which depend on the concentration of beryllium, appear against a pale yellow background. The yellow fluorescent ring of a positive beryllium reaction is then matched against standard rings under the UV lamp.

To prepare a standard scale, a standard solution containing 0.01 mg of beryllium per ml is convenient. By using 1, 2, 5, 10, 15, and 20 μl of the standard solution, rings containing 0.01, 0.02, 0.05, 0.1, 0.15 and 0.2 μg of beryllium are obtained.

Three rings made from different volumes of solution are sufficient for each unknown sample. The intensity of the fluorescence of each of the 3 rings is matched visually with the standard scale, and it is decided whether it matches one of the rings or if it falls between two rings. The quotient obtained by dividing the total number of μl of the three standards by the sum of the numbers of μl drops of the three rings made from the unknown solution, multiplied by the concentration of the standard solution gives the concentration of the unknown.

Discussion

Beryllium ions give an extremely sensitive yellow-green fluorescent product with morin (3,5,7,2′,4′-pentahydroxyflavone)[2]. Aluminum, scandium, gallium, thorium and indium ions also give fluorescent inner complexes of similar structure, but a far more important interference was recorded by many heavy metal ions, the presence of which masked the fluorescence of beryllium with morin. Some of these metals, like iron and chromium, are important in air or water pollution analysis, hence their elimination was vital. Masking with ethylenediaminetetraacetate[3] proved satisfactory for avoiding the effect of the active interfering group (aluminum, thorium) as well as the negative effect of the heavy metal group. EDTA reacts with most of the metal ions, including beryllium, to produce water-soluble chelate compounds with inner complex anions. These products are resistant to ammonia, except for the Be–EDTA complex, which decomposes in ammonia forming $Be(OH)_2$, which successively forms a green-yellow fluorescent product with morin. The exceptional instability of the beryllium ethylenediaminetetraacetate complex is the basis of this highly selective determination.

The use of the reagent crayon proved very effective in obtaining sharp rings. The reagent in the crayon seems to be stable and the fluorescent rings are stable for at least two months.

The treatment in the bath after the reagent crayon was rubbed in was necessary for three reasons: (1) the beryllium ethylenediaminetetraacetate complex was exposed to ammonia and decomposed; (2) the soluble metal–EDTA complexes were washed out; and (3) most of the excess of the reagent crayon was removed.

The lower limit for the determination of beryllium was found to be 0.01 μg. The upper limit for accurate estimation was 0.2 μg of beryllium. Above this upper limit visual comparison was difficult.

Interferences

The effect of foreign ions was investigated by developing 2 rings for each species, as in the above procedure. The first ring contained 5 μg of the foreign ion, while the second ring contained 5 μg of the foreign ion and 0.05 μg of beryllium. Non-interference was recorded for all cases when the first ring gave no reaction, and the second matched a ring containing 0.05 μg beryllium, when judged visually.

The following ions were found not to interfere: Li^+, Na^+, K^+, Ag^+, Tl^+, Cu^{2+}, Hg^+, Hg^{2+}, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, BO_2^-, Al^{3+}, Ga^{3+}, Ce^{3+}, Ce^{4+}, CO_3^{2-}, SiO_3^{3-} GeO_3^{3-}, Zr^{4+}, Sn^{2+}, Sn^{4+}, Pb^{2+}, Th^{4+}, NH_4^+, NO_2^-, NO_3^-, HPO_4^{2-}, VO_3^-, AsO_3^{3-}, AsO_4^{3-}, Sb^{3+}, Sb^{5+}, Bi^{3+}, S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, SeO_3^{2-}, SeO_4^{2-}, TeO_3^{2-}, TeO_4^{2-}, Cr^{3+}, CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, WO_4^{2-}, ReO_4^-, NO_2^{2+}, F^-, Cl^-, Mn^{2+}, Br^-, I^-, Fe^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Ru^{3+} and Pt^{4+}.

It is interesting to note that aluminum, thorium and gallium, which normally yield fluorescent compounds with the reagent under the given treatment do not show any interference. The possible interference of indium and scandium, which under ordinary circumstances form fluorescent products with morin, was not investigated. The presence of these elements in technical analyses of this type is extremely unlikely. The non-interference of fluoride ions in the beryllium analysis is also of practical significance.

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(Received October 23rd, 1968)

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Determination of sulphite ion (or sulphur dioxide) by atomic absorption spectroscopy

The advantages of atomic absorption spectroscopy in chemical analysis are well recognized. The literature on the determination of metals is growing at a striking rate, but little work has been done on the determination of non-metals. The idea of expanding the technique to technically important non-metals provided the basis of the present work. Sulphur dioxide is one of the most significant inorganic pollutants in the atmosphere. Its determination is done in most laboratories by the familiar WEST–GAEKE colorimetric method[1], by the titrimetric hydrogen peroxide method[2], by conductometry[3], or by turbidimetry with barium sulphate[4]. Except for the colorimetric method, these are all subject to interference from other acidic or basic gases or solids such as: sulphur trioxide, sulphuric acid, ammonia or calcium oxide, and even with the colorimetric method, the relative concentration of nitrogen dioxide in the gas sample is restricted.

The present approach to the indirect determination of sulphite ion (or sulphur dioxide) by the atomic absorption technique is based on the very high stability of the $[Hg(SO_3)_2]^{2-}$ complex. Addition of sulphite ions to a mercury(II) oxide suspension causes the transference of mercury from the solid state to the soluble complex. This produces a proportional increase of atomic absorption of the mercury in the supernatant fluid, indicative of the sulphite content.

Reagent

pH 11 buffer solution.

Apparatus

Perkin-Elmer Model 303 atomic absorption spectrophotometer with a mercury hollow-cathode lamp and a three-slot burner.

Calibration curve

Nearly equal amounts of red mercury(II) oxide (May and Baker laboratory reagent) were weighed in 10-ml volumetric flasks. Approximately equal amounts of this compound can be weighed relatively quickly. Portions of freshly prepared aqueous sodium sulphite solution were then added to each flask, the pH was adjusted to 11 with ammoniacal buffer pH 11, and the mixtures were diluted with triple distilled water to the mark. The flasks were shaken for 1 h and centrifuged, and the atomic absorption of mercury in the supernatant fluid was measured.

The instrument settings were as follows: wavelength, 2537 Å; source, 15 mA; acetylene flow, 9.0; air flow, 9.0; scale expansion, 1.

In order to plot the sulphite concentration *versus* the absorbance, the absorbance of the blank (all the reagent system with no sulphite) had to be deducted from the absorbances of the different sulphite-containing samples. The sulphite standard solutions were prepared by weighing anhydrous sodium sulphite (Baker), and standardized with iodine solution. Such solutions were prepared freshly each day. For example, 0.0208 g of anhydrous sodium sulphite was weighed into a 100-ml volumetric flask, yielding a solution of 119 p.p.m. of sulphite (found by standardization with iodine solution); 1–7 ml of this standard solution was then added to 10-ml volumetric flasks into which mercury(II) oxide had previously been weighed (Table I). The calibration graph was found to be linear over the range mentioned.

Interferences

Except for the obvious interference of mercury(II) ions, similar reactions to that of sulphite ion were expected from chemical species (mostly anions), which also form stable complexes with mercury(II) ion. The problem was, which of these materials act to dissolve mercury(II) oxide under the same conditions.

TABLE I

PREPARATION OF CALIBRATION CURVE

No.	*HgO weighed (g)*	*SO_3^{2-} content (p.p.m.)*	*SO_2 content (p.p.m.)*	*% Absorption*	*Absorbance*	*A_S-A_B*[a]
Blank A	0.1192	Nil	Nil	3.55	0.0157	—
Blank B	0.1180	Nil	Nil	3.60	0.0159	—
Blank C	0.1340	Nil	Nil	3.60	0.0159	—
1	0.1171	11.9	9.55	4.40	0.0195	0.0036
2	0.1213	23.8	19.10	5.10	0.0227	0.0068
3	0.1123	35.7	28.65	5.85	0.0261	0.0102
4	0.1223	47.6	38.20	6.50	0.0292	0.0133
5	0.1126	59.5	47.75	7.25	0.0327	0.0168
6	0.1192	71.4	57.30	8.05	0.0364	0.0205
7	0.1150	83.3	66.85	8.80	0.0400	0.0241

[a] Absorbance of the sample minus absorbance of the blank.

The influence on the reaction system of ammonia, sulphate, nitrite, thiosulphate, bromide, iodide, thiocyanate and cyanide were measured. Of these compounds, iodide, thiosulphate and thiocyanate behaved similarly to sulphite ion, whereas the remainder had no influence whatsoever.

Application

This method would appear to be useful for air pollution analysis. Although the reaction on which the determination is based is not specific, the interfering ions have little if any significance in air pollution. Sulphur dioxide is conveniently absorbed in alkaline impingers, and the proposed determination is carried out also in an alkaline medium. The technique appears to be sensitive enough for air pollution work, especially in view of the possibility of scale expansion.

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(Received October 23rd, 1968)

Anal. Chim. Acta, 45 (1969) 190–192

Solvent extraction of thallium(I) with hexanoic acid

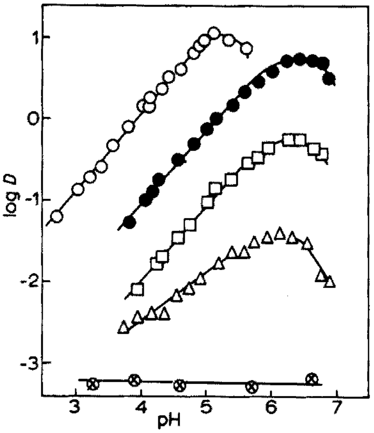
No work has been reported on extraction systems that utilize monocarboxylic acids to remove thallium(I) from aqueous media into immiscible organic phases[1]. The present study was undertaken to ascertain if thallium(I) could be extracted by such procedures. Hexanoic acid was chosen as a representative monocarboxylic acid and several organic solvents were selected to determine the variations produced by solvent alteration.

Experimental procedures

Thallium-204 in dilute nitric acid (U.S. Nuclear Corporation) was converted to the perchlorate by successive evaporations with perchloric acid. All other reagents were either reagent grade or were purified to reagent standards by distillation or crystallization procedures. The water employed was doubly distilled from alkaline permanganate solution.

Samples of 7.0 ml of aqueous phase plus 7.0 ml of organic phase were placed in 20-ml glass bottles and were tumbled at 27.0 ± 0.5° for at least 24 h, this time being sufficient for equilibration. The aqueous phase consisted of a 0.1 *M* sodium perchlorate solution containing a known amount of ^{204}Tl-labelled thallium perchlorate. The pH value of this phase was adjusted with solutions of perchloric acid and sodium hydroxide after the phase had been placed in contact with the organic phase. The organic phase consisted of the organic solvent containing a known concentration of hexanoic acid, or in some cases, it was pure hexanoic acid.

After equilibration, samples were centrifuged, pH measurements were made on the aqueous phase, and then samples were withdrawn from each phase. These



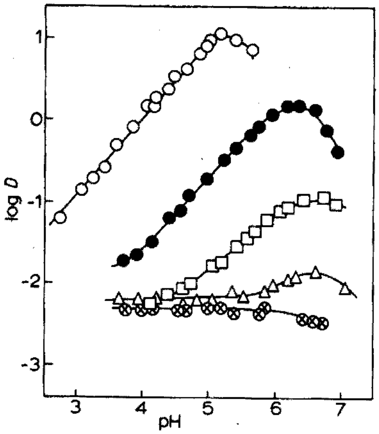


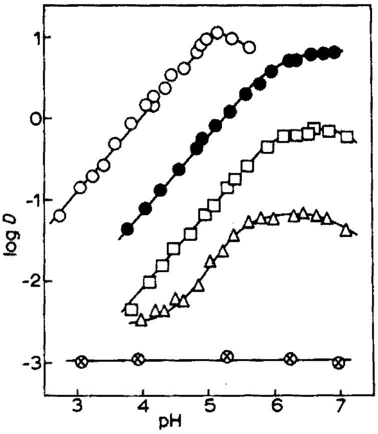
Fig. 1. Extraction of thallium(I) into benzene containing hexanoic acid at various concentrations. (○) Pure acid, (●) 3.0 *M*, (□) 1.0 *M*, (△) 0.3 *M*, (⊗) 0.0 *M*.

Fig. 2. Extraction of thallium(I) into chloroform containing hexanoic acid at various concentrations. (○) Pure acid, (●) 3.0 *M*, (□) 1.0 *M*, (△) 0.3 *M*, (⊗) 0.0 *M*.

samples were placed on planchets, dried, and were counted with standard β-radioactivity detection equipment. From the counting results, values of D (the concentration of total metal in the organic phase divided by the concentration of total metal in the aqueous phase) were determined.

Results

Figures 1, 2, 3, and 4 present data for the extraction of $10^{-7.0}$ *M* thallium(I) into benzene, chloroform, 4-methyl-2-pentanone, and nitrobenzene containing



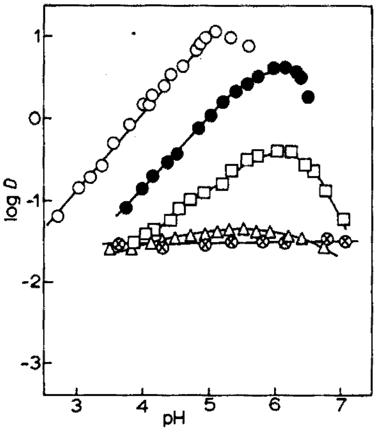


Fig. 3. Extraction of thallium(I) into 4-methyl-2-pentanone containing hexanoic acid at various concentrations. (○) Pure acid, (●) 3.0 *M*, (□) 1.0 *M*, (△) 0.3 *M*, (⊗) 0.0 *M*.

Fig. 4. Extraction of thallium(I) into nitrobenzene containing hexanoic acid at various concentrations. (○) Pure acid, (●) 3.0 *M*, (□) 1.0 *M*, (△) 0.3 *M*, (⊗) 0.0 *M*.

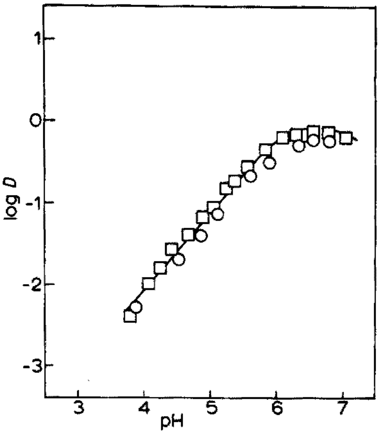


Fig. 5. Extraction of thallium(I) at various concentrations into chloroform containing 1.0 *M* hexanoic acid. (□) $10^{-7.0}$ *M* thallium, (○) $10^{-3.0}$ *M* thallium.

various concentrations of hexanoic acid. It should be noted that the uppermost curve in each figure (circles) presents data for pure hexanoic acid and the lowest curve (crossed circles) presents data for the pure solvent (no hexanoic acid).

Polymerization of the thallium-containing species in the organic or aqueous phase can usually be detected by observing the influence of the thallium concentration on the extraction. Figure 5 presents data for the extraction of $10^{-7.0}$ and $10^{-3.0}$ *M* thallium in the chloroform system. Only very slight dependence on concentration is noted. Similar results were obtained in the other three solvents.

Interpretation

Before the data of Figs. 1–4 could be analyzed for possible species, the extraction curves of these figures were adjusted for the effect of the solvents. As can be seen, the extraction data for the pure solvents 4-methyl-2-pentanone and nitrobenzene show considerable extraction. In all cases, *D* values for the pure solvent were subtracted from the *D* values for the solvent containing 3.0, 1.0, and 0.3 *M* hexanoic acid. The resulting curves were then replotted.

For the benzene systems, all replotted curves and the pure acid curve show rising slopes of 1.0 and then level off to a slope of 0.0. By means of these curves, graphs of log *D* against log $[HR]_o$ (where $[HR]_o$ is the concentration of the hexanoic acid monomer in the organic phase) were made. A dimerization constant of $10^{2.2}$, a partition constant of $10^{0.5}$, and an association constant of $10^{4.9}$ for hexanoic acid were employed in accordance with determinations by SAWHNEY[2]. From these procedures[3], it was discovered that the following equation $D^{-1}=10^{1.0}[H][HR]_o^{-4}+10^{-4.5}[H][HR]_o^{-3}$ fits the experimental curves quite well. In this expression, [H] indicates the hydrogen ion activity. This equation can be rationalized if one assumes the extracting organic species to be $TlR(HR)_3$ (where R is the hexanoate ion and HR hexanoic acid) and the aqueous species to be Tl^+ and TlR.

For the chloroform systems, a similar treatment employing a dimerization constant of $10^{1.6}$ and a distribution constant of $10^{0.9}$ leads to the equation $D^{-1}=$

$10^{3.1}[H][HR]_o^{-3}+10^{-3.5}[HR]^{-3}$ as an adequate expression of the data. This relation would fit very well if one considers the extracting organic species to be $TlR(HR)_3$ and the aqueous species to be $Tl(HR)^+$ and TlR. This $Tl(HR)^+$ species appears to be somewhat odd, but it has been invoked previously to rationalize data on the extraction of thallium(I) with a number of substituted xanthic acids[4]. Whether this species has an actual existence or not cannot be said; however, its postulation seems to fit the data quite well.

The 4-methyl-2-pentanone systems, after correction for extraction into the pure solvent, showed log D *vs.* pH curves with rising slopes of about 1.0 and plateau slopes of 0.0. With a partition constant of $10^{1.6}$ and an association constant of $10^{4.9}$, plots of log D against log $[HR]_o$ were made. These plots gave slopes of 2.0 in all pH regions between 4.0 and 6.5. The best simple description of the data was obtained by the relation $D^{-1}=10^{6.9}[H][HR]_o^{-2}+10^{-0.6}[HR]_o^{-2}$, although the fit was not nearly as good as those obtained in the two previous solvents. This equation corresponds to an extracting organic species $TlR(HR)_2$ and aqueous species $Tl(HR)^+$ and TlR.

The nitrobenzene results were treated in a manner similar to that employed for the 4-methyl-2-pentanone data. A dimerization constant of $10^{1.1}$ and a partition constant of $10^{0.8}$ were employed. A curve giving a good fit to the data was $D^{-1}=10^{3.0}[H][HR]_o^{-4}+10^{-3.8}[HR]_o^{-4}+10^{-10.5}[H]^{-1}[HR]_o^{-3}$. This indicates a possible extracting organic species of $TlR(HR)_4$ and aqueous species $Tl(HR)^+$, TlR, and TlR_2^-.

In all these systems the extracting species appears to be $TlR(HR)_a$ where a equals 2 in 4-methyl-2-pentanone, 3 in benzene and chloroform, and 4 in nitrobenzene. It is quite likely that solvent molecules are also attached to the 4-methyl-2-pentanone species.

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(Received October 29th, 1968)

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Spectrophotometric determination of iron(III) with bithionol

ADAMS[1] has shown that bithionol, bis-(2-hydroxy-3,5-dichlorophenyl)sulphide, acts as a tridentate ligand to form complexes with several metals. ADAMS made a semi-quantitative investigation of metal complexes of bithionol potentiometrically and colorimetrically as a means of demonstrating that the pharmacological action of bithionol may involve complexation of trace metals. Solid complexes of bithionol have been prepared by ADAMS and by NAGASAWA *et al.*[2].

Bithionol is used extensively as a bacteriostat, and, for this reason, could be made readily available as an analytical reagent. To date, no analytical applications of bithionol have been proposed. A potentiometric study has been made of a number of metal complexes of bithionol in 3+1 ethanol–water solution; their stability constants will be reported later. During this study, bithionol was observed to form an intense brown-red coloured complex with iron(III) whereas the other metal ions studied formed either a colourless or a weakly coloured complex. The present communication describes an investigation of the iron(III)–bithionol reaction as a spectrophotometric method of determining iron(III).

A commercial sample of bithionol (Cyclo Chemicals Limited; m.p. 188–190°, lit. value 186–189° [3]) was shown by potentiometric titration with sodium hydroxide to contain 98.5% bithionol.

The formation of the iron(III)–bithionol complexes was studied initially by potentiometric titration with standard carbonate-free sodium hydroxide solution, as described by IRVING AND ROSSOTTI[4]. Since bithionol is insoluble in water, the measurements were made in 3+1 ethanol–water solutions. The titration data indicated that, under the solution conditions used, the 1:2 iron(III)–bithionol complex is formed completely in solutions of apparent pH (pH meter reading) above about 5.0. Precipitation of iron(III) hydroxide was observed in solutions of apparent pH greater than 7.0.

Spectrophotometric measurements were made on 3+1 ethanol–water solutions buffered with an equimolar acetic acid/sodium acetate buffer which gave an apparent pH of 5.9. The spectrum of the iron(III)–bithionol complex was found to have a single broad absorption band in the visible region with a maximum at 484 nm. Bithionol itself is colourless.

The composition of the complex was confirmed by the method of continuous variations[5], absorbance measurements being made on the iron(III)–bithionol solutions at 450, 484 and 550 nm. The position of the maxima of the curves obtained at these wavelengths confirmed that a 1:2 iron(III)–bithionol complex is formed.

In making the stability constant measurements referred to above, the solutions used were made 0.005 *M* with respect to bithionol. To avoid precipitation of bithionol at this concentration, it was necessary to make the measurements on 3+1 ethanol–water solutions. Pretreatment of iron-containing samples, however, will usually yield an aqueous solution, and, thus, if maximum sensitivity is to be attained with the method, it is essential that the amount of ethanol added be minimised. It was found that 1+1 ethanol–water solutions which were 0.001 *M* with respect to bithionol remained clear; this concentration of bithionol is a sufficient excess for the determination of iron. The spectrum of the iron(III)–bithionol complex and its molar absorptivity at 484 nm were unchanged at this lower ethanol concentration The molar absorptivity of the complex at 484 nm was found to be 5,600, and Beer's law was obeyed in the range 0–8 p.p.m. of iron(III) with 1-cm cells.

Reagents

Bithionol solution. 0.4% (w/v) in ethanol.

Buffer solution. 1 *M* with respect to both acetic acid and sodium acetate. This solution buffers aqueous solutions at pH 4.6, but the apparent pH of the 1+1 ethanol–water solutions is 5.6.

Standard iron(III) solution (0.1 mg of iron(III)/ml). Dissolve analytical-reagent-grade iron(III) ammonium sulphate (0.864 g) in water, add concentrated hydrochloric acid (10 ml) and dilute to 1 l[6]. Alternatively, other iron(III) standards may be used[7].

Procedure

Pipette an aliquot of the standard iron(III) solution (or of a weakly acid sample solution) containing up to 0.4 mg of iron(III) into a 50-ml volumetric flask. Add 5 ml of buffer solution, 20 ml of ethanol and 5 ml of 0.4% (w/v) bithionol solution in ethanol. Dilute to volume with water and mix thoroughly. Measure the absorbance of the solution against water at 484 nm in 1-cm glass cells. Deduct the absorbance of a blank solution, containing the reagents but no iron(III), also measured against water.

The calibration curve obtained with the above procedure was linear, and the mean absorbance value of ten solutions containing 0.23 mg of iron(III) was 0.466 with a standard deviation of 0.001.

Interferences

When iron(II) salts are treated by the above procedure, the iron(III)–bithionol complex is formed; this oxidation reaction was shown to be quantitative up to 0.4 mg of iron(II). When the iron(II) and reagent solutions are deoxygenated by bubbling nitrogen through them before mixing, however, no oxidation occurs and a colourless solution is obtained; obviously, dissolved oxygen is responsible for the oxidation of the iron(II). The addition of hydroxylamine salts does not prevent the oxidation.

No interference (*i.e.* an effect less than 1%) was observed at the 0.23 mg of iron(III) level in the presence of 25 mg of iodide, chloride, sulphate, tetraborate, bromide, nitrate or acetate, 5 mg of zinc, cobalt, nickel, magnesium, manganese(II) or aluminium ions, 1 mg of fluoride, 0.3 mg of copper(II) ion or 0.15 mg of dichromate ion. Severe interference was observed at this level of iron from an equal amount of mercury(II), chromium(III), tartrate, oxalate or citrate ions. Mercury(II) forms a precipitate with the reagent and the other ions cause the colour intensity of the solution to be reduced.

Determination of iron in aluminium

The method was applied to the determination of iron in two high-silicon aluminium alloys (British Aluminium Company Limited). Suitable quantities of the samples (0.2–0.5 g) were dissolved in 10 ml of 1+1 hydrochloric acid. Most of the excess of acid was boiled off and the solutions were diluted to 100 ml in volumetric flasks. Aliquots (5 ml) of these solutions were treated, after neutralisation to Congo red (pH 3–5), by the procedure described above. Further aliquots (5 ml) of these sample solutions were treated by the *o*-phenanthroline method described by FURMAN[8]. The results (Table I) show excellent agreement between the colorimetric procedures.

Discussion

Bithionol is a stable, white, crystalline solid, which is produced commercially in a relatively pure form at reasonable cost. Its solutions in ethanol are colourless and are stable if they are stored in the dark. Bithionol could, therefore, become an extremely useful and modestly priced reagent.

TABLE I

DETERMINATION OF IRON IN ALUMINIUM ALLOYS

Sample no.	*Soln. no.*	*Iron found (%, w/w)*		
		Bithionol method	*o-Phenanthroline method*	*Spectrographic result*[a]
1	1	0.24_{2}	0.24_{3}	0.26
	2	0.24_{9}	0.25_{0}	
2	1	0.89_{2}	0.89_{9}	0.91
	2	0.87_{2}	0.87_{2}	

[a] Values supplied by British Aluminium Company.

The proposed determination of iron(III) is fairly selective, and the coloured solutions produced have been shown to be stable for a week. The sensitivity of the method is similar to that of the *o*-phenanthroline method, and the reagent is very considerably cheaper.

Further applications of bithionol and related compounds as analytical reagents are being investigated.

One of us (A.G.) is indebted to the S.R.C. for financial support. We thank Cyclo Chemicals Limited and the British Aluminium Company Limited for the supply of samples of bithionol and aluminium alloys respectively, and Professor R. F. PHILLIPS for his continued encouragement.

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(Received October 21st, 1968)

Colorimetric determination of periodate with benzhydrazide

The determination of periodate has gained considerable significance during the last few years. Gravimetric methods based on precipitation with tetraphenylarsonium or tetraphenylphosphonium chloride are available[1], and infrared[2] and ultraviolet[3] spectrophotometry have also been used quantitatively. A photometric method for its determination in the presence of other oxidizing agents has been described[4]. A colorimetric method after extraction with crystal violet in benzene has also been devised[5]. Benzoylhydrazine or benzhydrazide has been used[6] in titrating periodate in very dilute sulfuric acid media.

In the present communication the use of benzhydrazide as a colorimetric reagent for the determination of periodate is described.

Reagents

Potassium periodate (Mallinckrodt Chemical Works). A 0.01 *M* solution in 0.125 *M* sulfuric acid was prepared.

Benzhydrazide. This was prepared from ethyl benzoate and hydrazine hydrate. An aqueous 0.1 *M* stock solution of the reagent was prepared, and more dilute solutions were prepared by dilution.

All other reagents used in this study were of analytical grade.

Apparatus

Beckman Spectrophotometer Model DBG and 1-cm silica cells; Coleman pH meter Model 7; Bausch and Lomb Spectronic 20.

Determination of absorption spectrum

Figure 1 shows the absorption spectrum for a solution containing $2.0 \cdot 10^{-3}$ *M* potassium periodate in 95% ethanol obtained against a reagent blank.

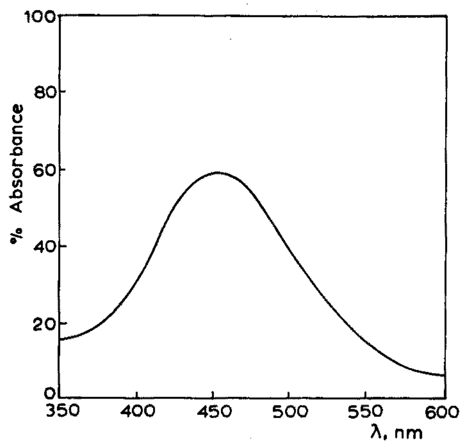
Effect of pH and time on absorbance

To determine the effect of different pH values on the absorbance measurements, several solutions containing 5.0 ml of 0.01 *M* potassium periodate, 2.0 ml of 0.10 *M* potassium hydrogen phthalate and 10.0 ml of 0.01 *M* benzhydrazide were placed in separate flasks. The pH values of the solutions were varied between 0.5 and 3.1 with 3 *M* sulfuric acid and 1 *M* potassium hydroxide; the solutions were not diluted further. The plot of absorbance *versus* pH measured against a reagent blank is shown in Fig. 2.

To study the effect of time, solutions were prepared as above with a pH of 1.0. The change in absorbance was noted at 1-min intervals for 40 min. A similar solution after dilution to 50.0 ml with 95% ethanol was also observed. When ethanol was absent, the absorbance decreased quite rapidly with time over 40 min; in the presence of ethanol, the initial absorbance reading was less, but after 10 min, the decrease in absorbance with time was only gradual. For convenience, a time of 12 min was selected.

Preparation of calibration curve

Different volumes of 0.01 *M* potassium periodate were pipetted into 50.0-ml volumetric flasks. Then 2 ml of 0.1 *M* potassium hydrogen phthalate and 10.0 ml of



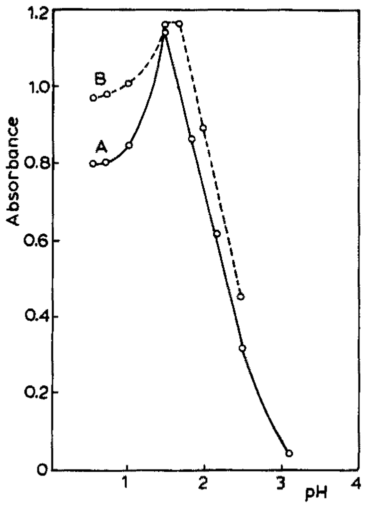


Fig. 1. Absorption spectrum of periodate–benzhydrazide mixture. 10.0 ml of 0.01 *M* KIO_4, 2.0 ml of 0.10 *M* $KHC_8H_4O_4$, 10.0 ml of 0.01 *M* benzhydrazide, 95% ethanol for dilution to 50.0 ml.

Fig. 2. Effect of pH on absorbance. (A) After 12 min; (B) after 15 min.

TABLE I

EFFECT OF DIVERSE IONS ON THE DETERMINATION OF PERIODATE

Ions[a]	*Tolerance*[b] *(mole ratio*[c]*)*	*Ions*	*Tolerance*[b] *(mole ratio*[c]*)*
IO_3^-	14.3	Cr^{3+}	5.7
BrO_3^-	2.57	Zn^{2+}	5.7
ClO_3^-	>14.3	Mn^{2+}	5.7
$C_2H_3O_2^-$	>14.3	Al^{3+}	2.86
CO_3^{2-}	2.86	Cd^{2+}	8.57
$Fe(CN)_6^{4-}$	0.13	Cu^{2+}	1.43
$Fe(CN)_6^{3-}$	0.014	Sn^{2+}	CI
CrO_4^{2-}	0.014	Sn^{4+}	1.43
NO_2^-	14.3	Ca^{2+}	5.7
SCN^-	8.57	Mg^{2+}	5.7
Cl^-	5.7	Hg^{2+}	CI
Cl^-	2.86	Hg_2^{2+}	0.014
I^-	0.21	Pb^{2+}	0.014
Br^-	>14.3	Ag^+	CI
ClO_4^-	2.85	Bi^{3+}	CI
NO_3^-	>71.0	$C_2O_4^{2-}$	5.7
S^{2-}	0.03	MoO_4^{2-}	2.86
SO_3^{2-}	>14.3	SO_4^{2-}	14.3
SO_4^{2-}	14.3		
$S_2O_3^{2-}$	CI[d]		
AsO_3^{2-}	CI		
AsO_4^{2-}	23.0		
PO_4^{3-}	14.3		

[a] Anions were added as their sodium, potassium or ammonium salt, and cations as their chloride or nitrate salt.

[b] Error of 2% tolerated.

[c] Mole ratio of salt added to KIO_4 present.

[d] Complete interference.

0.01 M benzhydrazide were added and the mixture was diluted to the mark with 95% ethanol. The absorbances of the solutions were read at 450 nm in 1-cm silica cells exactly 12 min after the addition of benzhydrazide. A linear calibration was found over the range $6.0–14.0 \cdot 10^{-4}$ M periodate in the final solution; zero absorbance was found for $5 \cdot 10^{-4}$ M periodate.

Effect of diverse ions on the determination of periodate

The effect of interfering ions on the determination of periodate was investigated. The mixtures contained 13.8 mg of potassium periodate and varying amounts of salts in excess of the periodate, and were treated by the above method. The results are given in Table I.

RESULTS AND DISCUSSION

The addition of potassium hydrogen phthalate to the periodate–benzhydrazide mixture helped to stabilize the color. The best pH for color stability was between 1.0 and 1.5; above pH 3.10 the color disappeared. Complete color development was obtained within a few minutes after the addition of benzhydrazide at room temperature. The absorbance read at 450 nm, the wavelength of maximum absorption, decreased rapidly before dilution with 95% ethanol; the rate of decrease was slower after dilution.

We wish to thank Dr. CHARLES WALKER for the preparation of benzhydrazide.

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(Received September 5th, 1968)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BOOK REVIEWS

GILBERT H. AYRES, *Quantitative Chemical Analysis, 2nd Edn*, Harper & Row, Ltd, New York, 1968, x+710 pp., price 102s 6d.

The first edition of this book was published in 1958 and the reviewer regarded it as being in the first rank as a teaching text. Since that time many new analytical techniques and instrumental methods of high sophistication have appeared; like many other authors faced with a revision Dr. AYRES has had to become very selective. The alternative would be a multi-volume work.

Dr. AYRES has clearly been guided by his own philosophical leanings and has come whole-heartedly on the side of chemistry. This does not mean that instrumentation is ignored: in fact it is treated more effectively than in many text-books written by enthusiastic machinists. But chemistry predominates as it should if one is using analytical chemistry as a means of teaching chemical reactions. It is a curious fact that teaching texts either (*a*) do not treat solvent extraction or (*b*) if they do, carefully avoid to describe a practical exercise for students. This is one of only two texts known to the reviewer which provides a student exercise and the one in the other text is hopeless in student hands.

This is an excellent book and the revised text has kept pace with the times in an admirable manner.

R. BELCHER (Birmingham)

Anal. Chim. Acta, 45 (1969) 202

H. J. V. TYRRELL AND A. E. BEEZER, *Thermometric Titrimetry*, Chapman and Hall, London; Barnes and Noble, New York, 1968, vii+207 pp., price 48 s.

Of the many physical methods of chemical analysis now available, thermometric titrimetry must rank among the simplest, yet it is only in comparatively recent years that the technique has achieved any degree of popularity. This is undoubtedly the result of advances in the instrumentation of temperature measurement and the availability of suitable commercial equipment for the analyst to try out the technique.

The present authors have recognised the need for a separate text which can deal with the three main aspects of thermometric titrimetry — principles, measuring equipment and analytical applications, all of which are discussed in sufficient detail for the analyst to acquire an appreciation of the range and limitations of the technique. As the first monograph on the subject, this text will be of use not only to the practising analyst who may wish to apply thermometric methods, but also to the student of analytical chemistry who is anxious to extend his knowledge of this still novel technique.

W. I. STEPHEN (Birmingham)

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ANNOUNCEMENT

GESELLSCHAFT DEUTSCHER CHEMIKER

PROGRAMME FOR 1969

10–15/3/1969	Symposium of the Mass Spectrometry Working Group, Atomic and Molecular Impact Processes Section, together with the Plasma Physics and Short Time Physics Divisions, Heidelberg
8–12/4/1969	Meeting on Analytical Chemistry, prepared by the Division for Analytical Chemistry of the GDCh
15–18/4/1969	3rd International Protactinium Conference organized by the Gesellschaft Deutscher Chemiker in Cooperation with GDCh-Fachgruppe "Kern-, Radio- und Strahlenchemie", Schloss Elmau, near Mittenwald. (The number of participants is limited to 100 persons)
22–26/4/1969	EUCHEM conference "Metal Proteids", Isle of Heligoland. (The number of participants is limited to 100 persons)
7–10/5/1969	Meeting of the Division for Coatings and Pigments of the GDCh, Bad Ems
13–14/5/1969	Annual Meeting of the Division for Water Chemistry of the GDCh, Bad Dürrheim (Black Forest)
15–20/9/1969	General Assembly of the Gesellschaft Deutscher Chemiker in Hamburg Meetings of Divisions on the Occasion of the General Assembly of the GDCh: Analytical Chemistry Division Coatings and Pigments Division Independent Chemists Division History of Chemistry Division Industrial Judicial Protection Division Semiconductor Chemistry Division Nuclear-, Radio- and Radiation Chemistry Division Food Chemistry and Forensic Chemistry Division Marcomolecular Chemistry Division
6–8/10/1969	Meeting of the Division of Applied Electrochemistry of the GDCh on "Organic Electrosynthesis", Bonn

Details of the above-mentioned events may be obtained from Gesellschaft Deutscher Chemiker, 6000 Frankfurt (M), Postfach 119075, Germany.

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5e RÉUNION INTERNATIONALE SUR LES MÉTHODES DE SÉPARATION:

CHROMATOGRAPHIE SUR COLONNE

5. INTERNATIONALE TAGUNG ÜBER TRENNMETHODEN:

SÄULENCHROMATOGRAPHIE

5th INTERNATIONAL SYMPOSIUM ON SEPARATION METHODS:

COLUMN CHROMATOGRAPHY

7–10 October 1969
Lausanne

The 5th meeting held under the patronage of the "Groupement pour l'avancement des méthodes spectrographiques" (GAMS) is being organized by the Association of Swiss Chemists.

Eight Plenary Lectures will be given and the remainder of the programme will be devoted to short original papers (10 minutes maximum). The number of participants is limited to 550.

Short communications should be submitted to the Scientific Committee by not later than 31th of May 1969. Manuscripts should be in a state ready to be printed. The proofs of the accepted papers will be sent to all participants one month before the conference. Prepared contributions to the main lectures (maximal 5 minutes) should be submitted to the committee by 20th of September 1969.

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VOL. 45 NO. 1 ANALYTICA CHIMICA ACTA MARCH 1969

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Short Communications

PRINTED IN THE NETHERLANDS