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International monthly devoted to all branches of analytical chemistry
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Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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Anal. Chim. Acta, Vol. 50, No. 1, 1–180, April 1970
Published monthly

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Papers should be sent to: Prof. Philip W. West, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. 70803 (U.S.A.) or to

Dr. A. M. G. Macdonald, Department of Chemistry, The University, P.O. Box 363, Birmingham 15 (Great Britain)

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Authors should submit two copies in double-spaced type with adequate margins on pages of uniform size. Acknowledgements, summary and references should be placed at the end of the paper.

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

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

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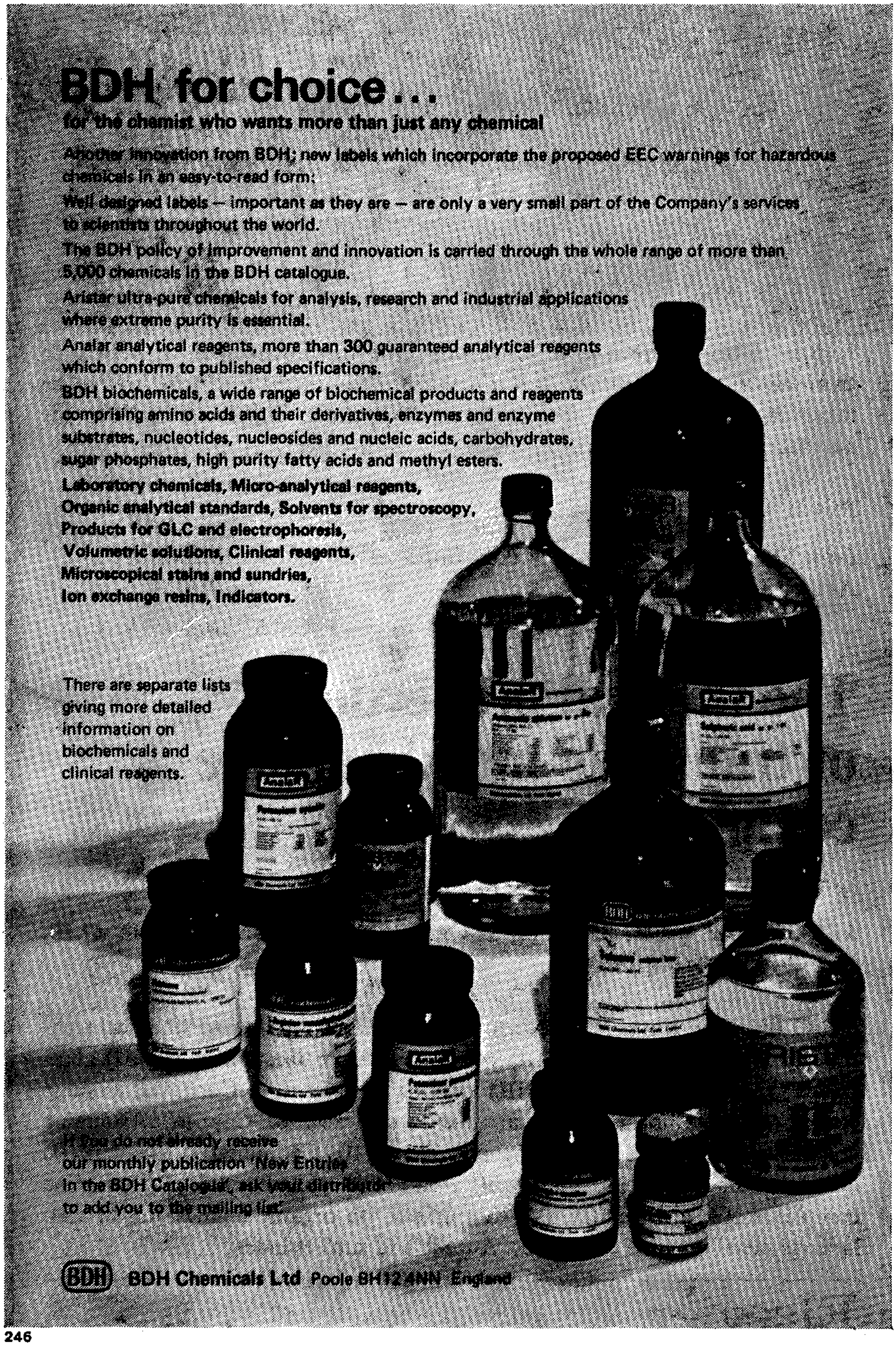

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6-84: The thermolysis curves of compounds of the individual elements.
Author and subject index.

The thermal properties of transition-metal ammine complexes

by W. W. WENDLANDT AND J. P. SMITH

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edited by **JEAN TRANCHANT,**
Laboratoire Central des Poudres, Paris

authors: J. Buzon, N. Guichard, J. Lebbe, A. Prévôt, J. Serpinet, J. Tranchant
6 x 9", xix + 387 pages, 13 tables, 133 illus., 1611 lit. refs., 1969, Dfl. 85.00, £ 10.0.0,
SBN 444-40677-8

The amount of literature that has appeared in recent years on the development and application of gas chromatography bears witness to the power and flexibility of the technique. All modern laboratories will at one time or another have had occasion to use it.

The present book has been written to assist not only those who already use gas chromatography in their work, but also those who are contemplating using it in the future. Emphasis has therefore been given to specific topics in the practical execution of gas chromatographic analyses so that the laboratory technician will be able to cope with the various analytical problems that are presented to him. The detailed information, examples of particular applications and advice on techniques to be found in every chapter have been drawn from the authors' own practical experience of the difficulties likely to be encountered.

Great attention has been paid to the selection of representative references from the literature so that the user will immediately be able to obtain more information on any point he considers to be of particular interest. In all, more than 1600 such references have been included, and have the special advantage that they have been chosen on a world-wide basis rather than being restricted to any one language area.

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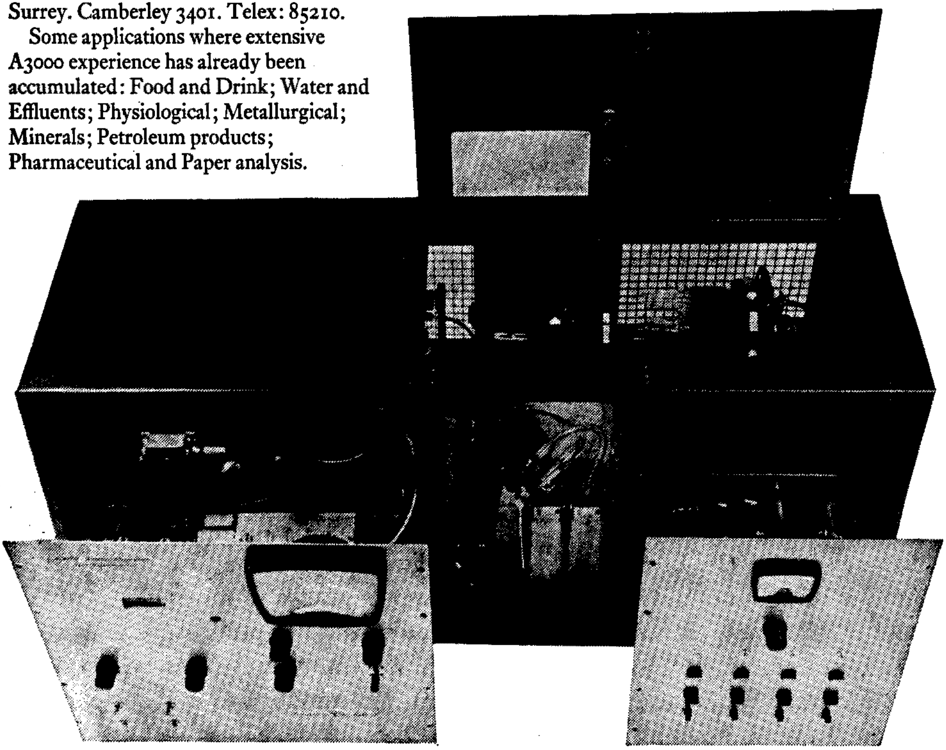

SOUTHERN ANALYTICAL

Inorganic Sulphur Chemistry

edited by GRAHAM NICKLESS, *Department of Inorganic Chemistry, University of Bristol, Great Britain*

7 × 10″, xii + 770 pages, 147 tables, 128 illus., over 4000 lit. refs., 1968
Dfl. 155.00, £18.5.0, SBN 444-40684-0

In recent years, the inorganic chemistry of sulphur has developed very rapidly. Although many specialized reviews on selected topics exist, a complete survey of this branch of chemistry was still lacking. The aim of the present book is to fill this gap, and to provide, for students and research workers alike, a complete reference book on inorganic sulphur chemistry.

The book is divided into two broad sections, the first discussing the various aspects of bonding and methods of investigation in sulphur chemistry, the second describing the latest developments in the inorganic chemistry of the element and its compounds.

CONTENTS: 1. The sulphur atom and its nucleus (G. Nickless). 2. Orbitals in sulphur and its compounds (D. W. J. Cruickshank and B. C. Webster). 3. Stereochemistry of sub-group VIB of the periodic table (W. J. Geary). 4. Mechanisms of sulfur reactions (R. E. Davis). 5. Structural studies on sulphur species (A. J. Banister, L. F. Moore, and J. S. Padley). 6. Analytical chemistry of sulphur compounds (E. Blasius, G. Horn, A. Knöchel, J. Münch, and H. Wagner). 7. Elemental sulphur (B. Meyer). 8. The sulphur cycle (J. R. Postgate). 9. The chemistry of the phosphorus-sulphur bond (D. E. Rogers and G. Nickless). 10. Sulphanes (K. W. C. Burton and P. Machmer). 11. Oxides of sulphur (P. W. Schenk and R. Steudel). 12. Compounds containing sulphur-halogen bonds (H. L. Roberts). 13. The nitrides, nitride-halides, imides and amides of sulphur (H. G. Heal). 14. The lower oxy-acids of sulphur (D. Lyons and G. Nickless). 15. Sulphuric acid: Physico-chemical aspects of manufacture (T .J. P. Pearce). 16. Sulphuric acid as a solvent system (R. J. Gillespie). 17. Fluorosulphuric acid (R. C. Thompson). 18. Amido- and imidosulphonic acids (K.W.C. Burton and G. Nickless). 19. Sulphides (F. Jellinek). Subject index.

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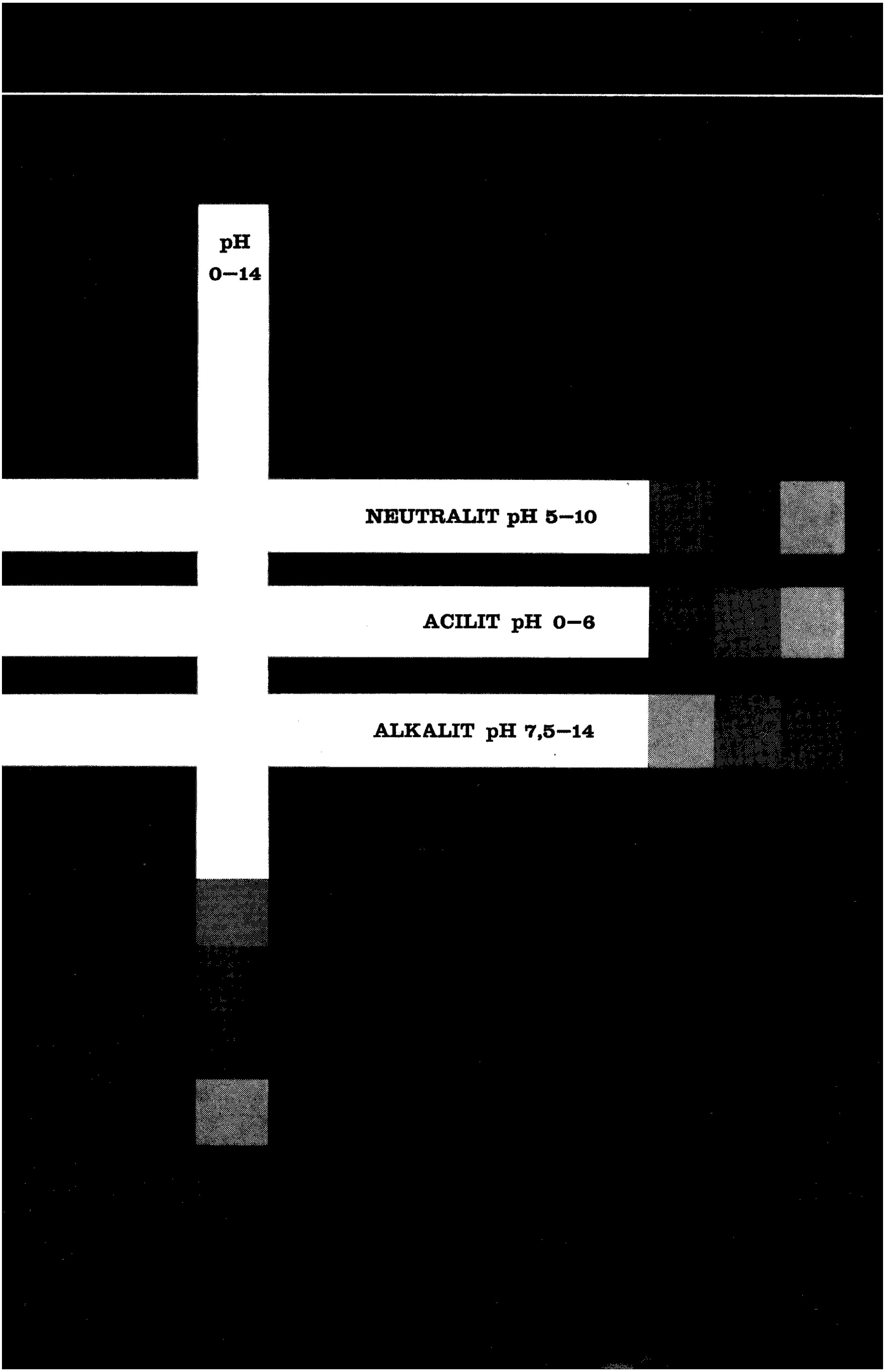
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0–14
NEUTRALIT pH 5–10
ACILIT pH 0–6
ALKALIT pH 7,5–14

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 50, No. 1, April 1970

A NEW COULOMETRIC TITRATION METHOD

APPLICATION TO THE DETERMINATION OF URANIUM

A new coulometric titration technique has been developed which is applicable to substances which undergo reduction or oxidation in at least two stages at potentials that are several tenths of a volt apart. Electrolysis is performed with the potential of the working electrode controlled by a potentiostat at a value sufficient to cause *both* stages of the reduction or oxidation to occur, so that the product of the second stage is produced and reacts in the solution with the initial substance to yield the product of the *first* stage. Instead of carrying the controlled potential electrolysis to exhaustion, the titration is stopped at a discrete end-point (signalled potentiometrically, amperometrically, or by other means) corresponding to the completion of only the *first* stage, and the quantity of substance reacted is evaluated from the number of coulombs required to reach this end-point.

As an example, the titration of +6 uranium to the +4 state, via the +3 uranium produced during reduction of the solution at a mercury cathode, has been studied. In either 0.2 *M* hydrochloric acid or in 0.03 *M* hydrochloric acid plus 0.5 *M* potassium chloride as supporting electrolytes, 15–60 mg quantities of uranium are determinable with an error of +0.4%. Because this error, caused by catalyzed reduction of hydrogen ion, is reproducible, it can be corrected for, to yield results correct to ± 0.1%.

J. J. LINGANE,
Anal. Chim. Acta, 50 (1970) 1–14

A SEMI-AUTOMATIC TITRATOR FOR PRECISION ANALYSIS

A semi-automatic titrator is described which supplies preset increments of titrant and has a direct teletyped read-out system on punched tape suitable for subsequent computer treatment of the titration curve. A total of 45 motor-driven syringe burets can be used for both electrometric and photometric titrations. The use and scope of the titrator in high precision analysis is discussed.

D. JAGNER,
Anal. Chim. Acta, 50 (1970) 15–22

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EFFECT OF CARBOXYLIC ACID BUFFERS ON THE POTENTIOMETRIC TITRATION OF FLUORIDE WITH LANTHANIDE NITRATES AND A LANTHANUM FLUORIDE MEMBRANE ELECTRODE

By means of potentiometric titration of fluoride with lanthanide nitrates in the presence of carboxylate buffers it has been shown that formate, acetate, propionate and n-butyrate (A^-) interfere with the precipitation reaction. Precipitates with the formula $LnF_{3-x}A_x$ (Ln = La, Ce, Pr, Nd, Sm) are formed and the carboxylates cause the lanthanum fluoride membrane electrode to work sluggishly after the titration. Chelating ligands such as lactate, malonate, citrate and acetylacetonate also affect the lanthanum fluoride membrane, and, after titrations in such media, the electrode could be regenerated only by polishing its surface with diamond paste and then immersing it in dilute sodium fluoride saturated with lanthanum fluoride.

T. ANFÄLT AND D. JAGNER,
Anal. Chim. Acta, 50 (1970) 23–30

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

PART V. DESTRUCTIVE AND NON-DESTRUCTIVE DETERMINATION OF MANGANESE, INDIUM AND URANIUM

Manganese, indium and uranium in titanium, titania powder and titania crystals can be determined non-destructively or destructively, by means of solvent extraction with tri-*n*-butyl phosphate. Destructively, the sensitivity for the determinations is enhanced by a factor of 20.

R. NEIRINCKX, F. ADAMS AND J. HOSTE,
Anal. Chim. Acta, 50 (1970) 31–38

THE POSSIBILITY OF ABSOLUTE ATOMIC ABSORPTION AND ATOMIC EMISSION FLAME SPECTROMETRIC ANALYSIS

Complete expressions are given relating the solution concentration of an element with the absolute intensity of a spectral transition emitted in a flame and with the absorbance measured with a line-source of radiation. The variables appearing in the equations are discussed for their significance in analytical flame spectrometry. It is shown that theoretically calculated emission intensities and absorbances agree within a factor of two with experimentally measured values. Although this agreement is insufficient for practical absolute flame spectrometric analysis, it is concluded that the expressions can be used with confidence in further theoretical studies. It is argued that sensitivities form a better criterion for the characterization of flames and burners than limits of detection.

L. DE GALAN AND G. F. SAMAEY,
Anal. Chim. Acta, 50 (1970) 39–50

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Section 6. Oxidation and combustion reactions (2 volumes)
Section 7. Selected elementary reactions (2 volumes)

Other sections are planned on heterogeneous reactions, solid state reactions, and kinetics and technological processes.

DETERMINATION OF SELENIUM IN SULFUR BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Selenium in sulfur can be determined rapidly by atomic absorption spectrophotometry. The sample is decomposed with concentrated nitric acid and bromine. The resultant solution is sprayed into an air–hydrogen flame and the absorbance is measured at 196.0 nm. Sulfur gives a small background absorption to interfere with the atomic absorption measurement of selenium and proper corrections must be made for accurate results. The results were compared with those obtained by the colorimetric 3,3′-diaminobenzidine method.

T. Nakahara, M. Munemori and S. Musha,
Anal. Chim. Acta, 50 (1970) 51–57

A CHEMICAL METHOD FOR THE DETERMINATION OF TRACES OF CHLORINE IN ORGANIC COOLANTS FOR NUCLEAR REACTORS

(in French)

A method for the determination of traces of chlorine in organic coolants is described. The proposed method is based on the combustion of the organic matter in a quartz burner with a flow of oxygen, and final determination of chloride by a null-point potentiometric titration. With a 20-g sample a detection limit of 0.1 p.p.m. is achieved. At the 0.14-p.p.m. level the coefficient of variation is about 12%. The method requires 30 min for one determination.

G. Serrini and W. Leyendecker,
Anal. Chim. Acta, 50 (1970) 59–69

ON THE FISSION TRACK METHOD FOR THE DETERMINATION OF THE URANIUM CONTENT OF WHOLE ROCK SAMPLES

The induced fission track technique in conjunction with internal standard addition has been used for the determination of uranium in geological samples. Convenient aliquots of the sample solution spiked with known amounts of uranium, deposited and dried on "Lexan", were irradiated in CIRUS (thermal flux $2 \cdot 10^{12}$ n cm^{-2} sec^{-1}; irradiation time 40 min). These irradiated "Lexan" pieces were etched with 25% (w/v) sodium hydroxide for 2 min at 200° to reveal the tracks. From a count of track densities in the "Lexan", the uranium contents of the two USGS rock standards G-2 and BCR-1 were determined to be 2.01 and 1.64 p.p.m. of uranium, respectively; these results are in good agreement with the literature values.

A. V. Murali, P. P. Parekh and M. Sankar Das,
Anal. Chim. Acta, 50 (1970) 71–77

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6 x 9″, xxiii + 772 pages, 19 tables, over 2000 lit.refs., 1966, Dfl. 85.00, £10.0.0.

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

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

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

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

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

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

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Bulletin de la Société Chimique de France

... This volume, together with its companion on "Spot Tests in Inorganic Analysis" (5th ed., 1958), is a useful and authoritative source of information not only to analytical chemists but also to organic chemists, pharmaceutical chemists, and biochemists. Advanced students and research workers in analytical chemistry will find these two volumes stimulating and helpful ...

Analytical Chemistry

... As each successive edition of this book appeared, it was greeted with ever increasing praise. It is difficult, therefore, to find adequate superlatives to describe this new, completely revised edition ...
... The astonishing range of applications of the tests makes this book essential for every chemist concerned with organic compounds ...

Chemistry in Britain

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147E

THE THERMAL PROPERTIES OF SOME METAL PYRIDINECARBOXYLATES

The thermal properties of the divalent metal complexes of 2-, 3-, and 4-pyridinecarboxylic acids were determined by TGA, DTA, DSC, high temperature reflectance spectroscopy, and dynamic reflectance spectroscopy. The complexes generally precipitate from solution as the hydrate containing 1–5 moles of water per mole of complex. The decomposition sequence is first the loss of hydrate water followed by the total disruption of the anhydrous complex to yield the metal oxide as the residue. Each dissociation reaction is discussed in terms of the above thermoanalytical techniques.

G. D'Ascenzo and W. W. Wendlandt,
Anal. Chim. Acta, 50 (1970) 79–91

POLAROGRAPHIC ANALYSIS OF SOLUTIONS CONTAINING ADSORBABLE COMPLEXES

The electrolytic reduction of some adsorbable addition complexes was followed by d.c. and a.c. polarography, single-sweep and a.c. oscillographic polarography and chronopotentiometry. The adsorption of the depolarizer leads to an increase in the sensitivity of the analytical determination with different methods to different extents; the highest increase, almost 100-fold, was found with the controlled-current methods.

R. Kalvoda, W. Anstine and M. Heyrovský,
Anal. Chim. Acta, 50 (1970) 93–102

DETERMINATION OF PHOSPHORUS IN NIOBIUM, ZIRCONIUM, TITANIUM AND TUNGSTEN

A method is described for the spectrophotometric determination of up to 0.08% phosphorus in niobium, zirconium, titanium and tungsten and their alloys, based on the extraction of phosphovanadomolybdate by isobutyl methyl ketone. The matrix metals are complexed by fluoride ion and do not interfere in the procedure. The molar absorptivity is 1740 and 3100 at 425 and 400 nm respectively, with a standard deviation of ± 0.5%.

P. Pakalns,
Anal. Chim. Acta, 50 (1970) 103–108

SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM(III) WITH 5,7-DICHLORO-, 5,7-DIBROMO- AND 5,7-DINITRO-8-HYDROXYQUINOLINE N-OXIDE

The deeply coloured 1:1 and 1:2 (metal:ligand) complexes of ruthenium(III) with 5,7-dichloro-8-hydroxyquinoline N-oxide (II), 5,7-dibromo-8-hydroxyquinoline N-oxide (III) and 5,7-dinitro-8-hydroxyquinoline N-oxide (IV) have been investigated spectrophotometrically in 60% acetone medium, and are suggested for the spectrophotometric determination of ruthenium(III) in presence of other platinum metals. The stability constants (log β_1 and log β_2) (determined spectrophotometrically) decrease in the order III > II > IV, which is the same as that of the basicity of the ligands.

R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain,
Anal. Chim. Acta, 50 (1970) 109–116

INORGANIC ELECTRONIC SPECTROSCOPY

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

The first monograph in the series PHYSICAL INORGANIC CHEMISTRY, edited by M. F. LAPPERT

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

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

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

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

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

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

xii + 420 pages, 78 tables, 130 illus., 465 lit. refs., 1968, Dfl. 90.00, £11.10.0.

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ACIDIMETRIC TITRATIONS BY A SIMPLIFIED POTENTIOMETRIC METHOD

THE USE OF ZIRCONIUM AND OTHER METALLIC ELECTRODES

(in French)

The proposed method differs from the classical "dead stop" procedure in that electrodes other than platinum electrodes are used. The simple set-up includes 2 indicating electrodes as cathodes, with a platinum counter electrode. With an applied potential, the method is essentially derivative potentiometry. Zirconium electrodes are given particular attention, and are shown to be particularly effective in the determination of very dilute strong acids. Antimony, bismuth, tungsten and tellurium electrodes are also discussed.

P. DESCHAMPS AND Y. BONNAIRE,
Anal.Chim. Acta, 50 (1970) 117–134

ANALYSIS OF MIXTURES OF AMINES BY DIFFERENTIAL KINETICS

The reaction between salicylaldehyde and primary amines in chloroform is utilised for analysis of binary mixtures of primary amines by the differential rate technique. The method is applicable in the presence of secondary as well as tertiary amines. The difference in the rates of addition of secondary amines to methyl acrylate in methanol is utilised for resolution of binary and ternary mixtures of secondary amines. The method is applicable in the presence of tertiary, but not primary, amines. In either case, the second-order reaction is followed by non-aqueous titration, and the resolution is effected by graphical extrapolation from the usual second-order plots.

I. L. SHRESTA AND M. N. DAS,
Anal.Chim. Acta, 50 (1970) 135–142

DETERMINATION OF SOME FIRST TRANSITION METAL GROUP ELEMENTS BY ELECTRON SPIN RESONANCE

An e.s.r. method is described for the determination of chromium(III), vanadyl(II), and iron(III). The measurement is based on the linear relationship that exists between the peak heights of the spectra of these ions and their concentration. Iron(III) ion has a very broad line in aqueous solution, but in organic solvents its line becomes much narrower, and suitable for analytical purposes. Nickel(II) has no observable spectra in aqueous solution; cobalt(II) has a relatively sensitive signal only in the presence of excess cyanide ion. The reproducibility of the calibration curves is about ± 0.4–0.6%. The accuracy of the determination varies between 2 and 4%. The effect of about 30 different diverse substances (anions and ligands) on the peak heights was studied. The maximum concentrations of these ions that have no effect on the e.s.r. spectra are summarized.

T. MEISEL AND G. G. GUILBAULT,
Anal. Chim. Acta, 50 (1970) 143–150

THE MASS SPECTRA OF ORGANIC MOLECULES

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

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

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

MASS SPECTROMETRIC ANALYSIS OF SOLIDS

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

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

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

ATOMIC-ABSORPTION SPECTROSCOPY

and Analysis by Atomic-Absorption Flame Photometry

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

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

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

Still available:

MASS SPECTROMETRY AND ITS APPLICATIONS TO ORGANIC CHEMISTRY

by J. H. Beynon

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

TABLE OF META-STABLE TRANSITIONS FOR USE IN MASS SPECTROMETRY

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

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

MASS AND ABUNDANCE TABLES FOR USE IN MASS SPECTROMETRY

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

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

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SOME SELECTIVE DETERMINATIONS OF IRON GROUP ELEMENTS IN THE PRESENCE OF EACH OTHER BY ELECTRON SPIN RESONANCE METHODS

The selective determination of iron group elements in the presence of each other by e.s.r., without previous separation is described. The method is based on the difference of *g* values that exists, and on the use of specific complexations. For the determination of copper, ethylenediamine is used, which by complexation eliminates the spectra of all the iron group elements except copper. For the selective measurement of vanadyl ion in the presence of different ions, EDTA complexation is successfully used. The only ion, besides vanadyl, with a spectrum after reaction with EDTA is copper, but the spectra are separated by their different *g* values. Some limitations of the measurement methods are shown and discussed.

G. G. Guilbault and T. Meisel,
Anal. Chim. Acta, 50 (1970) 151–156

COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN CARMINIC ACID AND GERMANIUM(IV) OR BORIC ACID

(Short Communication)

R. S. Brown,
Anal. Chim. Acta, 50 (1970) 157–160

DETERMINATION OF ALUMINUM IN ALKYL ALUMINUM COMPOUNDS

PART II. HYDROLYSIS OF THE REACTIVITY TITRATION SOLUTION

(Short Communication)

D. E. Jordan and W. D. Leslie,
Anal. Chim. Acta, 50 (1970) 161–162

THE SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM WITH N,N′-DI(2-NAPHTHYL)-*p*-PHENYLENEDIAMINE

(Short Communication)

F. G. Nasouri and A. S. Witwit,
Anal. Chim. Acta, 50 (1970) 163–164

THE REACTION OF IRON(III) AND CHLOROKOJIC ACID

(Short Communication)

G. F. Atkinson and I. J. Itzkovitch,
Anal. Chim. Acta, 50 (1970) 165–166

Photoluminescence of Solutions

With Applications to Photochemistry and Analytical Chemistry

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

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

Contents: Basic principles, definitions and kinectics of fluorescence, phosphorescence and delayed fluorescence; polarisation; light scattering; monochromators; light sources; filters; photodetectors; actinometry; recording systems; inner filter effects; specimen compartments; correction of spectra; measurement of photoluminescence efficiency and lifetime; purity of materials; parameters of singlet and triplet states; equilibria in the excited state; excited dimers; solvent effects; fluorescence and phosphorescence analysis.

Comprehensive Analytical Chemistry

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

VOLUME IIB: Physical Separation Methods

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

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.

Atomic-Absorption Spectroscopy

and Analysis by Atomic-Absorption Flame Photometry

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

6 × 9″, xii + 493 pages, 23 tables, 156 illus., 950 lit. refs., 1968, Dfl. 80.00, £9.15.0.

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

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CONCENTRATION AND SEPARATION OF URANIUM WITH ION-EXCHANGE RESINS

(Short Communication, in French)

E. JERCAN AND L. DINOIU,
Anal. Chim. Acta, 50 (1970) 166–169

THE DETERMINATION OF IMPURITIES IN HIGH-PURITY CADMIUM BY SPECTROGRAPHY OR POLAROGRAPHY AFTER DISTILLATION OF CADMIUM

(Short Communication)

S. R. RAJIĆ AND S. V. MARKOVIĆ,
Anal. Chim. Acta, 50 (1970) 169–172

THE USE OF OXAZINES IN ANALYSIS

PART III. INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF SILVER WITH NILE BLUE

(Short Communication, in German)

W. LIKUSSAR AND H. RABER,
Anal. Chim. Acta, 50 (1970) 173–175

DETERMINATION OF CHROMATE BY PRECIPITATION OF SILVER CHROMATE FROM HOMOGENEOUS SOLUTION

(Short Communication)

K. VARUGHESE AND V. G. VAIDYA,
Anal. Chim. Acta, 50 (1970) 176–179

Countercurrent Separation Processes

by H. R. C. Pratt

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

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

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

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

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

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

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Third, completely revised edition

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

$6 \times 9''$, viii+774 pages, 155 tables, 400 illus., 227 lit. ref., 1967, Dfl. 32.50, 65s.

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INTRODUCTION TO THE ATOMIC NUCLEUS

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

by **J. G. Cuninghame**

$5\frac{1}{2} \times 8\frac{1}{2}$, xi+220 pages, 3 tables, 58 illus., 170 lit. refs., 1964, Dfl. 15.00, 35s.

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

INTRODUCTION TO NUCLEAR CHEMISTRY

by **D. J. Carswell**

$5\frac{1}{2} \times 8\frac{1}{2}''$, ix+279 pages, 23 tables, 69 illus., 1967, Dfl. 32.50, 70s.

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

RADIOCHEMICAL SURVEY OF THE ELEMENTS

Principal Characteristics and Applications of the Elements and their Isotopes

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

$6 \times 9''$, ix+177 pages, 1965, Dfl. 32.50, 75s.

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

THE STRUCTURE OF INORGANIC RADICALS

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

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

$6 \times 9''$, x+280 pages, 57 tables, 74 illus., 357 lit. refs., 1967, Dfl. 60.00, £7.0.0.

Contents: Introduction. An introduction to electron spin resonance. Formation and trapping of radicals. Trapped and solvated electrons. Atoms and monatomic ions. Diatomic radicals. Triatomic radicals. Tetra-atomic radicals. Penta-atomic radicals. Summary and conclusions.
Appendices: The language of group theory. The spin hamiltonian. Calculation of g-values. Determination of spin-density distribution and bond angles. Analysis of electron spin resonance spectra. Index.

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Inorganic Macromolecules Reviews

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Editors: F.G.R. Gimblett (London, Great Britain)
K.A. Hodd (London, Great Britain)

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H.A. Schroeder (Connecticut, U.S.A.)

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M. Becke-Goehring (Heidelberg, Germany)

Polyelementorganosiloxane formation
K.A. Andrianov (Moscow, U.S.S.R.)

Viscoelasticity in inorganic polymers
A. Eisenberg (Montreal, Canada)

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L. Holliday (London, Great Britain)

Approximately one volume of four issues will be published per year. Subscription price is Dfl. 90.00 plus Dfl. 3.00 postage or equivalent (US$25.00 plus US$0.85 or £10.9.6. plus 7s. at April 1, 1969). The first issue is scheduled for publication in mid-1969.

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Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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Printed in The Netherlands

A NEW COULOMETRIC TITRATION METHOD

APPLICATION TO THE DETERMINATION OF URANIUM

JAMES J. LINGANE
Department of Chemistry, Harvard University, Cambridge, Mass. 02138 (U.S.A.)

(Received December 18th, 1969)

Any coulometric method of analysis requires 100% current efficiency with respect to the desired reaction. As discussed in detail elsewhere[1], 100% current efficiency can be obtained only when there is either direct or indirect control of the potential of the working electrode so that interfering electrode reactions are excluded. The two means of satisfying this requirement have led to the two chief methods of coulometric analysis in common use: *viz., coulometric analysis at controlled potential* and *coulometric titration.*

In the first method the potential of the working electrode against a reference electrode is controlled directly (usually automatically by a potentiostat) at such a value that only the single desired electrode reaction occurs, and the quantity of substance reacted is evaluated from the measured quantity of electricity (coulombs) that results from carrying the electrolysis to exhaustion as indicated by the decay of the current to near zero. This method is highly selective and well suited to the analysis of mixtures[1], but, because of the increasingly slow current decay, the exhaustive electrolysis requires a relatively long time (typically 30 min to 1 h). The accuracy is critically dependent on how reliably one can adduce a correction for the small background current which is almost always present[1,2].

In coulometric titration (as previously practiced) there is no direct control of the working electrode potential, and instead a relatively large concentration of another electroactive substance (reagent precursor) is added to the test solution and this reacts at the electrode to generate a reagent which in turn reacts in the body of the solution in a definite stoichiometric way with the substance being determined. In effect the reaction at the electrode of this reagent precursor *limits* the potential and prevents the occurrence of extraneous reactions. Any of the classical techniques (potentiometric, amperometric, colorimetric, etc.) can be used to recognize the end-point, and when an exactly constant current is used the number of coulombs passed is measurable simply by noting the time required to reach an end-point. Coulometric titration is much faster than controlled-potential coulometric analysis (typically about 5 min), and it is capable of very high precision and accuracy[1].

In the present study a new technique of coulometric titration has been developed, which combines the virtues of the above two methods. This new method is less catholic in application than the previous methods, because it requires that the substance being determined be capable of undergoing stepwise reduction or oxidation in at least two stages at well separated potentials. However, there are more than a few possible applications. The principle of the method is best explained by a specific example, and the determination of uranium by reducing it from the +6 to the +4 oxidation state in an aqueous acidic medium is a typical case.

In acidic aqueous solutions +6 uranium (UO_2^{++}) undergoes stepwise reduction at a mercury cathode first to the +5 state (UO_2^{+}) and then to the +3 state (U^{+++}), and polarographic studies[3] have demonstrated that the potentials of the two stages are separated by 0.70 V. Because the +5 uranium disproportionates more or less rapidly into UO_2^{++} and U^{++++}, depending on both its own concentration and that of hydrogen ion, prolonged electrolysis at a potential between the two stages ultimately produces a solution of +4 uranium. In 0.2 *M* hydrochloric acid the polarographic half-wave potentials of the two stages are +0.062 V and −0.635 V *vs*. N.H.E., and these values define the formal potentials of the UO_2^{++}/UO_2^{+} and U^{++++}/U^{+++} couples respectively.

Consider a solution of +6 uranium in 0.2 *M* hydrochloric acid, under nitrogen, in a cell provided with a stirred mercury pool cathode and a suitable auxiliary electrode in a separate compartment. If, by the customary technique of controlled potential electrolysis with a potentiostat and with a coulometer or equivalent current-time integrator in series with the cell to measure the number of coulombs passed, electrolysis is performed with the potential of the mercury cathode controlled at a potential of, say, −0.70 V *vs*. N.H.E. (more cathodic than the potential of the U^{++++}/U^{+++} couple but less cathodic than the potential at which hydrogen ion is reduced) then the primary product of the electrode reaction is U^{+++}. However, as it is transferred by the stirring from the electrode surface back into the bulk of the solution, the U^{+++} rapidly reduces the +6 uranium to the +5 state and then to the +4 state. The redox potential of the solution (indicated by a separate mercury indicator electrode) undergoes a very sharp decrease of about 0.6 V when the original +6 uranium has been reduced to the +4 state, and this large abrupt potential change serves precisely to signal an "end-point". This end-point can also be detected amperometrically and, in principle, by various other means.

Thus, the +6 uranium is titrated under conditions which retain the virtue of selectivity inherent in controlled potential electrolysis, and without the necessity of adding a "reagent precursor" as in ordinary constant-current coulometric titration. In effect, in this case the +4 uranium plays the role of reagent precursor, via its transient reduction to the +3 state.

The electrolysis current decays exponentially during the controlled potential electrolysis[1], but in the above case it is still about one-third of its relatively large initial value when the 2-electron end-point is reached. Consequently, the time required to reach the end-point (typically 6–10 min) is about as short as in an ordinary constant-current coulometric titration, and, of course, is only a small fraction of the time required for an exhaustive controlled-potential electrolysis. This is an obvious convenience, and furthermore the cumulative error caused by any background current is also decreased proportionately.

A logical name for this new technique is *controlled-potential coulometric titration*, because the potential of the working electrode is controlled *directly* and yet it is truly a *titration* in the sense that the result is based on measuring the quantity of electricity (coulombs) required to reach a sharply defined stoichiometric equivalence point. Some authors have loosely applied this same name to the ordinary technique of *coulometric* *analysis at controlled potential*, but in that case the electrolysis is exhaustive with no discrete end-point, so that such nomenclature is a violation of the accepted definition of "titration".

EXPERIMENTAL TECHNIQUE

The H-type glass cell used is shown in Fig. 1. The volume of test solution was 100 cm^3, and dissolved air was removed from both compartments with high-purity nitrogen. The area of the mercury cathode was about 20 cm^2, and it was stirred efficiently by the magnetic stirring bar which floated in it. Care was taken to remove dissolved air from the test solution before introducing the mercury, because dissolved oxygen is quickly reduced by mercury in an acidic chloride solution to produce mercury(I) chloride and hydrogen peroxide, both of which would be interferences. The mercury was used repeatedly, but between each trial it was washed thoroughly with water and transferred to a separatory funnel from which it was delivered back to the cell, so that any surface impurities were removed.

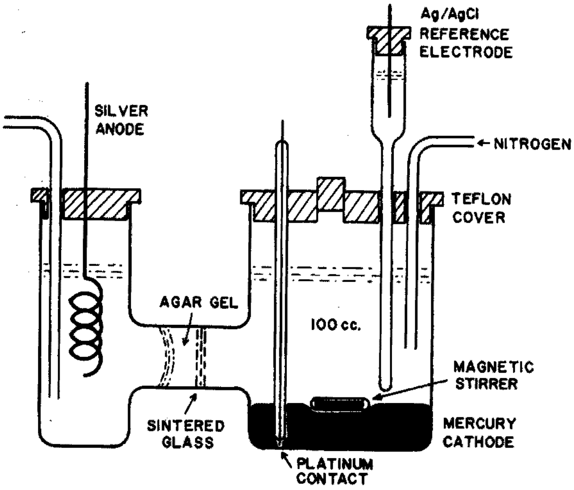


Fig. 1. Controlled potential coulometric titration cell.

A silver–silver chloride–saturated potassium chloride reference electrode was used. The very simple design shown in Fig. 1 is more convenient and reliable than commercially available reference electrodes. A tiny crack in its lower closed end (made by sealing a small *soft* glass bead into the Pyrex tube) constitutes a flowing junction. The smallness of the crack is indicated by the fact that the resistance is of the order of 10,000 ohms, and the outflow rate is so small that the electrode can be used for several months without replenishing the internal saturated potassium chloride solution. The Teflon cover which holds the stout silver wire has a small vent hole, and the silver wire was anodized in a chloride solution before use. The saturated potassium chloride solution was treated with a small amount of silver nitrate to ensure saturation with silver chloride before the reference electrode was assembled.

A coiled silver wire in the left-hand compartment served as the auxiliary electrode (anode). The fine sintered glass disk in the cross arm was augmented by an agar-gel plug to prevent any interflow of the solutions.

A potentiostat was used automatically to control the potential of the mercury cathode during electrolysis. The quantity of electricity passed (coulombs) was measured with an Ether Ltd. (formerly Electro Methods Ltd.) electromechanical integrator provided with a compensating voltage as previously described[4], which insured an integration accuracy of somewhat better than 99.9%.

Standard solutions of +6 uranium were prepared from Mallinckrodt reagent quality uranyl acetate dihydrate. An exactly weighed quantity of the salt was evaporated to dryness twice with excess of concentrated hydrochloric acid to convert it to the chloride. The residue of UO_2Cl_2 was dissolved in water and diluted to a known volume. The uranium content of the solution was then determined carefully by the usual zinc reduction–dichromate titration method. The uranium content thus found corresponded to a purity factor of 99.96±0.04% for the uranyl acetate dihydrate. Volumetric measuring equipment was calibrated, so that the amount of uranium taken for the titrations was known to better than ±0.1%.

In some cases individual samples (100 mg or more) of the previously assayed uranyl acetate dihydrate were weighed out directly, with calibrated weights and a balance sensitive to ±0.01 mg.

PERFORMANCE DATA AND DISCUSSION

Figure 2 demonstrates the behaviour of mercury, gold, and platinum indicator electrodes during the controlled potential reduction of 100 cm³ of 5 m*M* uranyl

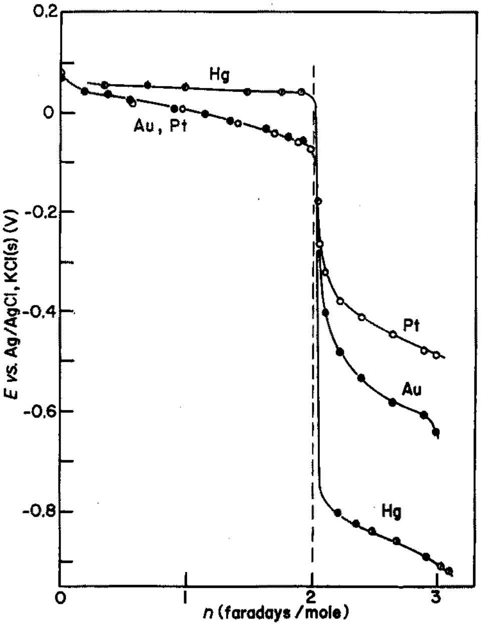


Fig. 2. Titration of 100 cm³ of 5 m*M* UO_2Cl_2 in 1.0 *M* hydrochloric acid with the potential of the mercury cathode controlled at −0.98 V *vs.* Ag/AgCl,KCl (s). The redox potential of the solution was measured with platinum, gold, and mercury indicator electrodes.

chloride in 1.0 *M* hydrochloric acid. The potential of the mercury working electrode was controlled at −0.98 V *vs.* Ag/AgCl,KCl (s) (or −0.78 V *vs.* N.H.E.), which is 0.14 V more cathodic than the formal potential of the U^{++++}/U^{+++} couple in this solution. Thus, U^{+++} was produced at the surface of the mercury cathode and on being stirred into the solution it reduced the UO_2^{++}.

In each case the potential of the indicator electrode was measured with a potentiometer against the same silver–silver chloride reference electrode used for control of the mercury cathode potential. The electrolysis was interrupted while the potential readings were taken. Note that the abscissa units are faradays/mole, symbolized by n, so that $n=1$ corresponds to reduction of the UO_2^{++} to UO_2^{+}, $n=2$ to reduction to U^{++++}, and $n=3$ to complete reduction to U^{+++}.

Although all three electrodes show a sudden large decrease of potential at $n=2$ there are striking differences in the potentials before and beyond this point. A separate small mercury indicator electrode was used in this trial and until just before $n=2$, its potential corresponded to the mercury–mercury(I) chloride half-reaction rather than to any of the uranium couples. In 1.0 *M* hydrochloric acid, and using 0.809 as the activity coefficient of chloride ion, the potential of the Hg/Hg_2Cl_2 half-reaction is +0.076 V *vs.* Ag/AgCl,KCl (s). The observed potential of the mercury indicator electrode (+0.069 V at the start and decreasing only to +0.039 V just before $n=2$) is very close to this value. Evidently, when UO_2^{++} and UO_2^{+} are still present one or the other (or both) of them oxidizes the mercury of the indicator electrode to produce a film of Hg_2Cl_2 on its surface, and the "calomel potential" is established. Close to and beyond $n=2$ the calomel film is reduced and the mercury electrode then indicates the true redox potential of the solution governed by the U^{++++}/U^{+++} couple. At $n=2.5$, corresponding to a 1:1 ratio of U^{++++} and U^{+++}, the observed potential of the mercury indicator electrode is −0.839 V, in good agreement with the observed polarographic half-wave potential of −0.845 V for the reversible reduction of U^{++++} to U^{+++} in 1.0 *M* hydrochloric acid.

Before $n=2$ the platinum and gold indicator electrodes acquire identical potentials, which suggests that they both indicate the true redox potential of the solution. In no case is there any potential change at $n=1$, which no doubt is related to the instability of UO_2^{+} with respect to its disproportionation into UO_2^{++} and U^{++++}. The question then arises "which of the uranium couples controls the potential up to $n=2$?", and the three possibilities are UO_2^{++}/UO_2^{+}, UO_2^{++}/U^{++++}, and UO_2^{+}/U^{++++}.

From the measurements of NELSON AND KRAUS[5], for the disproportionation reaction

$$2UO_2^{+}+4H^{+}=UO_2^{++}+U^{++++}+2H_2O$$

the equilibrium constant at infinite dilution at 25° is $1.7\cdot10^6$, and it increases rapidly with increasing ionic strength (*e.g.*, $480\cdot10^6$ in chloride media at 1 *M* ionic strength). Consequently up to $n=1$ the predominant uranium species is UO_2^{++}, the concentration of U^{++++} is only a little smaller, but the concentration of UO_2^{+} is much smaller.

Even though UO_2^{++} and U^{++++} predominate up to $n=2$, the potential in this region (Fig. 2) apparently is not governed directly by the UO_2^{++}/U^{++++} couple. This couple functions only quasi-reversibly, but studies by several investigators[6–8] do agree in indicating that its formal potential is close to +0.34 V *vs.* N.H.E. or +0.14 V *vs.* Ag/AgCl,KCl (s). Therefore, if this were the potential-determining couple one would expect the potentials of the platinum and gold electrodes in the vicinity of $n=1$ in Fig. 2 to be close to +0.14 V, whereas in fact they are both near 0.00 V.

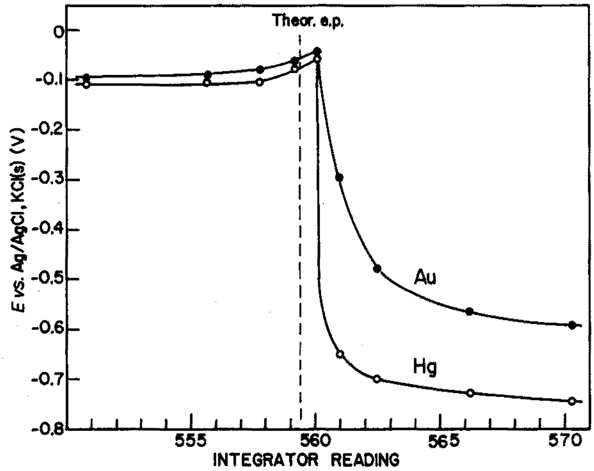
What little is known about the UO_2^+/U^{++++} couple suggests that it also does not function reversibly. On the other hand, it is well established that the UO_2^{++}/UO_2^+ couple does behave reversibly, and there is good agreement from several studies[7,9-11] that its standard potential is +0.062 V *vs.* N.H.E. or −0.135 V *vs.* Ag/AgCl,KCl (s). The observed potentials of the platinum and gold indicator electrodes up to $n=2$ in Fig. 2 agree with the conclusion that the UO_2^{++}/UO_2^+ couple is potential-determining. For example, at $n=1$ the observed potential is +0.005 V, which, when combined with the standard potential of the UO_2^{++}/UO_2^+ couple, indicates a concentration ratio $(UO_2^{++})/(UO_2^+)=234$. In view of the relatively rapid rate of disproportionation of +5 uranium in 1 *M* hydrochloric acid (half-life of 1 m*M* UO_2^+ about 8 sec), this is a plausible value. Further support of this interpretation is the observation that when the hydrochloric acid concentration is decreased to 0.2 *M* the potential in the neighborhood of $n=1$ becomes close to −0.10 V instead of +0.005 V. This is in harmony with a larger proportion of +5 uranium due both to its smaller rate of disproportionation and larger relative concentration at equilibrium as the hydrogen ion concentration is decreased.

The probable reaction sequence during electrolysis is that the U^{+++} produced at the mercury cathode first reduces UO_2^{++} to UO_2^+, and the latter then disproportionates. This interpretation is supported by the fact that after each increment of electrolysis the potential drifts in the positive (more anodic) direction in its approach to constancy, reflecting the disappearance of +5 uranium. In Fig. 2 the potentials were measured only 2–3 min after the electrolysis was interrupted at each point, and, no doubt, they are still somewhat more negative (more cathodic) than the true equilibrium potentials before $n=2$.

Beyond $n=2$ only the mercury electrode indicates the true redox potential. The potentials of the platinum and gold electrodes are less negative than the true potential because *at their surface* there is reduction of U^{+++} by hydrogen ion, $2U^{+++}+2H^+=2U^{++++}+H_2$, and consequently the concentration ratio $(U^{++++})/(U^{+++})$ is larger than in the body of the solution. The exceptionally large hydrogen overpotential on mercury inhibits this reaction at the mercury electrode. The hydrogen overpotential on gold is larger than on platinum, and consequently the gold indicator electrode is less in error than the platinum electrode. Because in either case the potential change is so large, a gold electrode serves almost as well as a mercury electrode for indicating the end-point at $n=2$.

The relative behaviour of gold and mercury indicator electrodes is shown in greater detail in the immediate vicinity of the end-point in Fig. 3. In this case the abscissa units are the integrator reading *N*, proportional to coulombs. The data represent the region within ±2% of the end-point at $n=2$, and with both electrodes the very abrupt decrease in potential occurred 0.14% beyond the theoretical end-point indicated by the vertical dashed line.

Note in Fig. 3 that just before the end-point the potentials of both electrodes show an upward, more positive, trend. The potentials were measured after 2–3 min and thus while the initially formed +5 uranium was still disproportionating. As the end-point is closely approached, the concentration of the remaining +6 uranium becomes very small and the *relative* effect of this disproportionation on the concentration ratio $(UO_2^{++})/(UO_2^{+})$, and consequently on the potential, is enhanced to produce this upward trend. Probably this effect could be eliminated, and a more normal sigmoid curve could be obtained, if one waited long enough for the attainment of disproportionation equilibrium, but this would be tedious. Because of this distortion of the titration curve, the usual method of interpolating to the equivalence point cannot be employed. Consequently, relatively small electrolysis increments must be used as the end-point is approached in order to recognize it precisely.



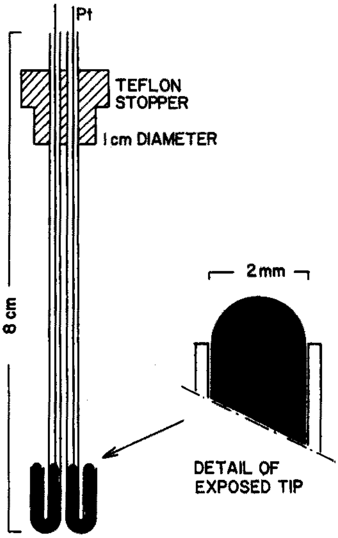


Fig. 3. Behaviour of gold and mercury indicator electrodes in the immediate vicinity of the equivalence point, during the titration of 100 cm³ of 2.50 m*M* UO_2Cl_2 in 0.20 *M* hydrochloric acid with the potential of the mercury cathode controlled at −0.88 V *vs.* Ag/AgCl,KCl (s). The theoretical equivalence point is indicated by the vertical dashed line. One integrator unit corresponds to 0.08606 coulomb.

Fig. 4. Mercury microelectrodes for amperometric titration. The exposed mercury surface of each electrode has an area of about 0.06 cm². The unit is mounted in the cell of Fig. 1 through a 1-cm hole in the Teflon cover which accommodates the Teflon stopper.

However, in virtue of the reversibility of the U^{++++}/U^{+++} couple, and provided a mercury indicator electrode is used, if by accident the end-point is slightly overrun, an accurate correction can be applied from the observed potential for the amount of excess +3 uranium that was generated. For example, if the solution contains 0.20 *M* hydrochloric acid the formal potential of the U^{++++}/U^{+++} couple is −0.832 V *vs.* Ag/AgCl,KCl (s). Consequently, with 0.1, 0.5, and 1% excess +3 uranium the observed potentials are −0.672, −0.714, and −0.732 V. Because the observed potentials beyond the equivalence point are very reproducible (±1 mV) this correction method serves to locate the end-point to well within ±0.1% when the quantity of excess +3 uranium does not exceed about 1%. With larger excesses of +3 uranium the precision of the correction deteriorates rapidly because of the logarithmic nature of the Nernst relation.

The hydrochloric acid concentration for the titration of Fig. 3 was 0.20 *M*, but for the titration shown in Fig. 2, it was 1 M. In the latter case (Fig. 2) the potential does not undergo an upward trend near the end-point, no doubt because of the more rapid disproportionation of the +5 uranium at the larger hydrogen ion concentration, so that the potentials observed after 2–3 min are much closer to the equilibrium values.

KERN AND ORLEMANN[10] found that the rate law for the disproportionation of +5 uranium (during its early stages before the back reaction introduces complications) is

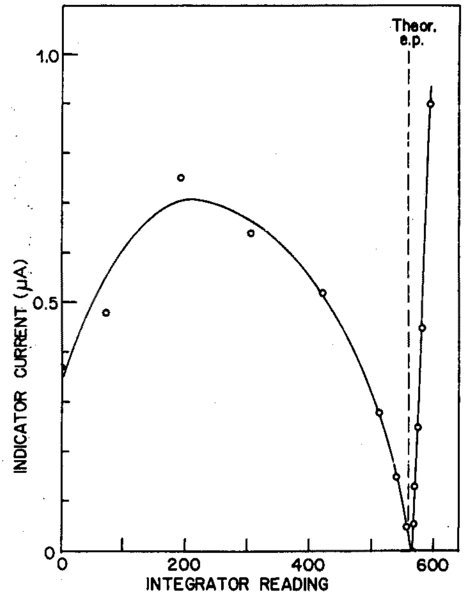
$$\frac{-\mathrm{d}(\mathrm{UO_2}^+)}{\mathrm{d}t} = k(\mathrm{UO_2}^+)^2(\mathrm{H}^+)$$

where $k = 130$ (moles/l)$^{-2}$ sec^{-1} at 25°. Replication of the polarographic measurements of KERN AND ORLEMANN showed a k-value in good agreement with theirs. From this it follows that the half-life of initially 10^{-3} M +5 uranium is about 8 sec at a hydrogen ion concentration of 1 M, and about 40 sec when the hydrogen ion concentration is 0.20 M. For an initially 10^{-5} M solution of +5 uranium, roughly equivalent to the condition near the end-point of the present titrations, the corresponding half-lives are 770 sec and 3900 sec. Evidently, one would have to wait an inordinately long time to observe the true equilibrium potentials just before the end-point.

The equivalence point at $n = 2$ can also be detected precisely by two-electrode amperometry, with two small mercury electrodes subjected to a constant small applied voltage (150 mV), the resulting current being measured with a microammeter. Many abortive attempts were made to use gold microelectrodes for this purpose, but they failed because the overpotential of hydrogen on gold is insufficient to prevent anomalous indicator currents (and even current reversals) at, and just beyond, the equivalence point that result from the catalyzed reduction of hydrogen ion by the +3 uranium at a gold surface.

Figure 4 shows a convenient design of two mercury microelectrodes, held in a Teflon stopper, so that the whole assembly can be easily inserted into the cell through a 1-cm hole in its Teflon cover. The J-form glass tubes were only 2 mm in internal diameter, small enough so that the relatively large mercury–solution interfacial tension stabilized the hemispherical mercury surfaces protruding from their lower ends. Electrical connection was made by platinum wires in the central tubes. It proved easier than expected to adjust the amount of mercury (by first immersing the empty tubes under mercury to fill them and then making small additions of mercury with a medicine dropper) so that the protruding surfaces were approximately hemispherical and thus well exposed to the stirred solution. Although the limitation of two-dimensional representation in Fig. 4 shows the electrodes spread apart the two J-tubes were in fact in parallel alignment to permit their passage through the hole in the cell cover. The exposed area of each electrode was about 0.06 cm^2. The electrolysis must be interrupted for each reading of the indicator current, because spurious readings result when the indicator electrodes are in the electric field (iR gradient) produced by the generating current. As in any amperometric titration, the indicator current depends sensitively on the stirring condition at the electrode surfaces. The electrodes should be positioned in the cell so that they are in a well-stirred region of the solution, and the stirring should be constant. Under this condition, steady-state indicator currents are established within a few seconds.

Figure 5 shows an entire typical amperometric titration curve during the titration of 100 cm^3 of 1.25 mM +6 uranium in 0.20 M hydrochloric acid. The constant voltage applied across the two mercury indicator electrodes was 150 mV, which is small enough compared to the difference in potential (894 mV) between the UO_2^{++}/UO_2^{+} and the U^{++++}/U^{+++} couples to yield a sharp current minimum at the equivalence point and yet is large enough to produce an easily measurable current before and beyond the end-point.



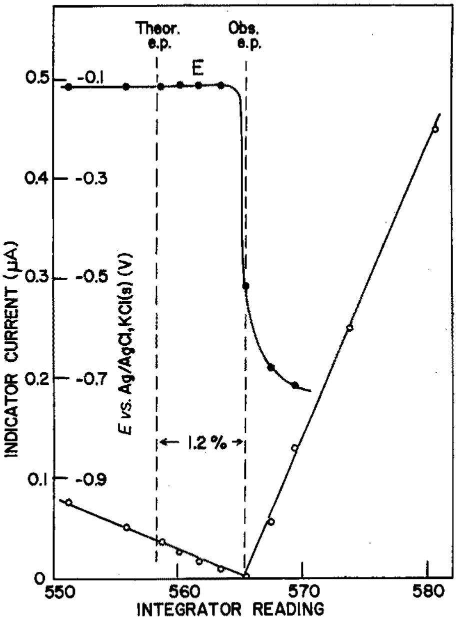


Fig. 5. Amperometric titration curve with two mercury microelectrodes across which a constant voltage of 150 mV was impressed. Titration of 100 cm^3 of 1.25 mM UO_2Cl_2 in 0.20 M hydrochloric acid with the potential of the mercury cathode controlled at −0.88 V *vs.* Ag/AgCl,KCl (s).

Fig. 6. Comparison of amperometric and potentiometric end-point detection (mercury potentiometric indicator electrode). Data from the same titration as Fig. 5 in close proximity to the equivalence point. One integrator unit corresponds to 0.04303 coulomb.

The general shape of the curve corresponds to the case where the titrated and titrant couples both behave reversibly (see Ref. 1, page 280). No doubt, the reactions at the indicator electrodes before the end-point are $UO_2^{++} \rightarrow UO_2^{+}$ at the cathode and $UO_2^{+} \rightarrow UO_2^{++}$ at the anode, and beyond the end-point they are $U^{++++} \rightarrow U^{+++}$ at the cathode and $U^{+++} \rightarrow U^{++++}$ at the anode. During the first half of the titration while +6 uranium predominates, the current is governed by the oxidation of the less predominant +5 uranium at the anode, and it increases as the concentration of the latter increases. In this region the current decays after each electrolysis increment, owing to disproportionation of the +5 uranium, and it depends sensitively on the waiting time before the reading is taken. However, during the later stages of the titration, and especially as the end-point is approached, stable current readings are quickly attained because the rate of disproportionation of the +5 uranium depends on the square of its concentration and thus decreases rapidly as its concentration decreases. At the equivalence point the potential of the indicator cathode is close to the equilibrium potential of the solution (about −0.10 V *vs.* Ag/AgCl,KCl (s)) and consequently, because of the applied voltage of 150 mV, the potential of the indicator anode is close to +0.05 V. Since the concentration of +5 uranium has become vanishingly small, and because this potential is not oxidizing enough to cause oxidation of the mercury to mercury(I) chloride, which would be the next possible anodic reaction, the current falls to zero. Beyond the equivalence point both indicator electrodes are depolarized by the reversible U^{++++}/U^{+++} couple, but because of the much larger concentration of +4 uranium the cathode is most easily depolarized (and thus better poised) and the current increases rapidly and linearly as continued electrolysis produces an increasing concentration of the +3 uranium required to depolarize the indicator anode.

Figure 6 presents a magnified view of the same amperometric titration curve of Fig. 5 but in the immediate vicinity (±3%) of the equivalence point. For comparison the potentiometric titration curve (mercury indicator electrode) is also shown. In this region so close to the equivalence point the two branches of the amperometric titration curve seem to be linear, and their intersection very close to zero current defines an end-point in precise agreement with the abrupt and large potential change that signals the potentiometric end-point. The precision of end-point detection by either method is better than ±0.1%, but the amperometric technique has the advantage of providing a warning as the end-point is approached.

Table I summarizes the results of titrations of 15–118 mg quantities of +6 uranium in a solution volume of 100 cm³, corresponding to a concentration range from about 0.6–5 m*M*. To test the possible effect of hydrogen ion concentration, titrations were performed in 0.20 *M* hydrochloric and also in a supporting electrolyte

TABLE I

TITRATION DATA

(In all cases the solution volume was 100 cm³, and the potential of the mercury cathode was controlled at −0.88 V *vs.* Ag/AgCl,KCl (s). End-points were determined both amperometrically and potentiometrically)

Uranium taken (mg)	*Uranium found (mg)*		*Error (mg)*		*Error (%)*	
	Amp.	*Potent.*	*Amp.*	*Potent.*	*Amp.*	*Potent.*
(A) In 0.20 M HCl						
118.52	122.46	122.59	3.94	4.07	3.33	3.44
117.86	120.82	120.88	2.96	3.02	2.52	2.56
82.95	83.63	83.63	0.68	0.68	0.82	0.82
59.24	59.50	59.54	0.26	0.30	0.44	0.51
59.24	59.56	59.57	0.32	0.33	0.54	0.56
44.45	44.65	44.64	0.20	0.19	0.45	0.42
29.63	29.87	29.87	0.24	0.24	0.81	0.81
29.63	29.86	29.88	0.23	0.25	0.78	0.84
14.82	15.04	15.03	0.22	0.21	1.5	1.4
14.82	15.01	15.03	0.19	0.21	1.3	1.4
(B) In 0.030 M HCl + 0.50 M KCl						
118.52	119.22	119.19	0.70	0.67	0.59	0.57
118.52	119.03	119.19	0.51	0.67	0.43	0.57
59.26	59.61	59.69	0.35	0.43	0.59	0.72
29.63	29.89	29.88	0.26	0.25	0.88	0.86
29.63	29.88	29.91	0.25	0.28	0.84	0.93

containing 0.030 M hydrochloric acid and 0.50 M potassium chloride. In the latter case the concentration of hydrogen ion was only 50% greater than that consumed in the reduction of the largest quantities of uranyl ion.

The potential of the mercury cathode was controlled at -0.88 V *vs.* Ag/AgCl, KCl (s). This is 0.05 V more cathodic than the formal potential of the U^{++++}/U^{+++} couple in 0.20 M hydrochloric acid, and 0.03 V more cathodic in 0.030 M HCl + 0.50 M KCl. A potential of at least -0.98 V would be required for complete reduction of the uranium to the +3 state, but this is not necessary in the present method. To minimize the background current the control potential should not be more cathodic than really is necessary, and nothing is gained by using a value more negative than -0.88 V. Actually the titrations can be performed with a control potential as small as -0.83 V, but the electrolysis current is then considerably smaller and the titration time is increased.

Electrolysis was allowed to proceed uninterruptedly up to about 1% before the equivalence point, which required only 6–7 min in 0.20 M hydrochloric and 8–10 min in 0.030 M HCl + 0.50 M KCl. From then on, short electrolysis increments (0.1–0.2%) were applied and the end-points were detected both amperometrically and potentiometrically (mercury indicator electrodes).

The initial electrolysis currents were directly proportional to the uranium concentration, ranging downward from about 300 to 40 mA. By the time the end-points were approached, the currents had decreased to about one-third their initial values, which is the expected behaviour in a controlled potential electrolysis when the current is governed by the rate of mass transfer to the electrode surface[1].

The data in Table I demonstrate the excellent agreement of amperometric and potentiometric end-point detection; the average discrepancy is less than 0.1% with no evident bias. However, in all cases there is a significant positive error, which is larger than can be accounted for by the small currents observed with the supporting electrolytes alone in the absence of uranium. Note that in 0.20 M hydrochloric acid this error increases very rapidly when more than 60 mg of uranium is titrated, but this sudden increase is not observed with 0.030 M hydrochloric acid plus 0.50 M potassium chloride as supporting electrolyte.

Blank trials were run under the conditions of Table I with both supporting electrolytes. After electrolysis times equal to the times required to reach the end-points in the titrations the accumulated quantity of electricity with 0.20 M hydrochloric acid alone was 0.07 coulomb, which is equivalent to 0.09 mg of uranium. With 0.030 M hydrochloric acid plus 0.50 M potassium chloride the corresponding values were 0.12 coulomb and 0.15 mg of uranium. These values account for only a minor fraction of the total positive errors, and after they are subtracted from the errors listed in Table I significant residual positive errors remain.

In Fig. 7 the residual errors (in mg) remaining after subtracting the above "blank corrections" are plotted against the quantity of uranium titrated. The averaged error of the amperometric and potentiometric end-points, and in most cases of two trials, is represented. The exceptionally large error (3–4 mg) observed with 118 mg of uranium in 0.20 M hydrochloric acid has been omitted, to avoid compressing the ordinate scale so much that all the other data would be obscured. Within the discriminatory capability of the data the residual error increases linearly with the quantity of uranium titrated; the average deviation from the straight line is ±0.03 mg, except for the point corresponding to 83 mg of uranium in 0.20 *M* hydrochloric acid which anticipates the even more aberrant error observed with 118 mg of uranium in this medium.

Most probably the residual errors shown in Fig. 7 are caused by a catalytic or induced reduction of hydrogen ion at the electrode surface via the cyclic reactions

$$2H^+ + 2U^{+++} = H_2 + 2U^{++++}$$
$$U^{++++} + e = U^{+++}$$

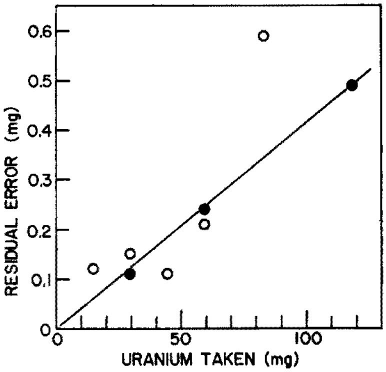


Fig. 7. Residual errors after subtracting blank corrections. Open circles with 0.20 *M* hydrochloric acid as supporting electrolyte and solid circles with 0.030 *M* hydrochloric acid plus 0.50 *M* potassium chloride.

Scarcely anything is known about the kinetics of the reduction of hydrogen ion by +3 uranium, even in homogeneous solution much less at the surface of a mercury electrode. The writer has observed that the anodic polarographic diffusion current of 2 m*M* +3 uranium in 0.20 *M* hydrochloric acid decreased by less than 1% per hour at 25°. From this the rate constant of the *homogeneous* reaction seems to be much too small to cause a significant error during the relatively short times required for the titrations, especially since the concentration of +3 uranium in the body of the solution is exceedingly small until the end-point is passed. However, the titration data indicate that this reaction is catalyzed *at the surface of the mercury cathode*, and the residual errors plotted in Fig. 7 suggest that this catalytic reaction is first order in respect to the concentration of uranium. Because with 60 mg of uranium or less the same residual error is observed with both supporting electrolytes, in spite of their seven-fold difference in hydrogen ion concentration, there is also a temptation to conclude that the hydrogen ion concentration has little or no effect on this catalyzed reduction of hydrogen ion. But this temptation to conclude too much from too little evidence is counteracted by the exceptionally large positive errors observed with more than 60 mg of uranium in 0.20 *M* hydrochloric acid.

Actually the residual error is quite small; the slope of the straight line in Fig. 7 corresponds to a relative error of 0.4%. Because this is reproducible it is justifiable to subtract it as a correction, which should yield results correct to ±0.1%. Alternatively, of course, the total error can be cancelled by calibrating the titration empirically with a known and similar amount of uranium under the same conditions extant in the titration of an unknown.

Several other elements probably can be determined by this method. Among the possibilities suggested by their redox chemistry are +6 molybdenum, +6 tungsten, +5 vanadium, and +2 copper in chloride media.

SUMMARY

A new coulometric titration technique has been developed which is applicable to substances which undergo reduction or oxidation in at least two stages at potentials that are several tenths of a volt apart. Electrolysis is performed with the potential of the working electrode controlled by a potentiostat at a value sufficient to cause *both* stages of the reduction or oxidation to occur, so that the product of the second stage is produced and reacts in the solution with the initial substance to yield the product of the *first* stage. Instead of carrying the controlled potential electrolysis to exhaustion, the titration is stopped at a discrete end-point (signalled potentiometrically, amperometrically, or by other means) corresponding to the completion of only the *first* stage, and the quantity of substance reacted is evaluated from the number of coulombs required to reach this end-point.

As an example, the titration of +6 uranium to the +4 state, via the +3 uranium produced during reduction of the solution at a mercury cathode, has been studied. In either 0.2 *M* hydrochloric acid or in 0.03 *M* hydrochloric acid plus 0.5 *M* potassium chloride as supporting electrolytes, 15–60 mg quantities of uranium are determinable with an error of +0.4%. Because this error, caused by catalyzed reduction of hydrogen ion, is reproducible, it can be corrected for, to yield results correct to ±0.1%.

RÉSUMÉ

Une nouvelle technique de titrage coulométrique est proposée. Le potentiel est controlé à l'aide d'un potentiostat à une valeur permettant d'avoir deux stades de réduction ou d'oxydation; de façon que le produit du second stade puisse réagir avec la substance initiale correspondant au premier stade. Le titrage est stoppé à un point (signalé potentiométriquement, ampérométriquement, etc.) correspondant au premier stade seulement. La quantité de substance ayant réagi est calculée d'après le nombre de coulombs nécessaires pour arriver à ce point final. On a examiné ainsi le titrage de l'uranium+6 en uranium+4, au moyen de l'uranium+3 formé au cours de la réduction à une cathode de mercure. En milieu acide chlorhydrique 0.2 *M* ou 0.03 *M*+chlorure de potassium 0.5 *M* (comme électrolyte de base) il est possible de doser des quantités d'uranium de l'ordre de 15 à 60 mg avec une erreur de+0.4%. Cette erreur, due à la réduction catalysée de l'ion hydrogène, étant reproductible, en peut introduire un facteur de correction et obtenir des résultats à ±0.1% près.

ZUSAMMENFASSUNG

Es wurde ein neues Verfahren der coulometrischen Titration entwickelt, das auf solche Substanzen anwendbar ist, die einer Reduktion oder Oxidation in wenigstens zwei Stufen unterliegen bei Potentialen, die einige Zehntel Volt auseinanderliegen. Das Potential der Arbeitselektrode wird bei der Elektrolyse mit Hilfe eines Potentio-

staten so eingestellt, dass *beide* Stufen der Reduktion oder Oxidation auftreten, so dass das Produkt der zweiten Stufe entsteht und in der Lösung mit der Ausgangssubstanz reagiert, wobei das Produkt der *ersten* Stufe gebildet wird. Anstatt die potentialkontrollierte Elektrolyse bis zur Erschöpfung durchzuführen, wird die Titration bei einem besonderen Endpunkt beendet, der potentiometrisch, amperometrisch oder auf anderem Wege angezeigt wird und sich nur auf die vollständige Bildung der *ersten* Stufe bezieht. Die Menge der Substanz wird aus der Elektrizitätsmenge (in Coulomb) berechnet, die bis zum Erreichen dieses Endpunktes notwendig ist.

Als Beispiel wurde die Titration von Uran von der 6-wertigen zur 4-wertigen Stufe untersucht, die über Uran (III) verläuft, das während der Reduktion der Lösung an einer Quecksilberkathode entsteht. In 0.2 *M* Salzsäure oder in 0.03 *M* Salzsäure und 0.5 *M* Kaliumchlorid als Trägerelektrolyten können Uranmengen von 15–60 mg mit einem Fehler von ±0.4% bestimmt werden. Da dieser Fehler, der durch katalytische Reduktion von Wasserstoffionen hervorgerufen wird, reproduzierbar ist, kann er korrigiert werden; dadurch werden die Ergebnisse bis auf ±0.1% genau.

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A SEMI-AUTOMATIC TITRATOR FOR PRECISION ANALYSIS

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In evaluation of the results of titrimetric analyses in which the demand for precision is high, it is often advantageous to register a large number of points on the titration curve. Since the subsequent treatment of these titration data can often be fairly complicated, much time may be saved by using a computer. Some methods for evaluating titration results with the aid of a computer have been summarised in a textbook by DYRSSEN, JAGNER AND WENGELIN[1] and the use of computers in electroanalytical chemistry has been reviewed by PERRIN *et al.*[2]. The gain in time and precision due to computerisation of the calculations varies considerably from method to method. If the very frequently used method of maximum slope of the titration curve is employed to evaluate the equivalence point, no other advantage is gained from using a computer than that the inflexion point can be located more accurately by means of suitable curve-fitting functions. With this method, however, the risk of systematic errors is appreciable[3]. Furthermore, only a small unbuffered part of the titration curve is exploited. The GRAN method[4] involves an antilogarithmic conversion of the titration data followed by straight line regression. For such methods the gain in time and precision when a computer is used is considerable, while for methods employing computer programs of the type LETAGROP[5] (a least-squares minimizing procedure for non-linear curves) the use of a computer is, of course, imperative. Even if the LETAGROP method has not yet come into common usage in analytical work, it seems likely that it will do so as the ease of access to rapid computers increases.

It is obvious that if a computer method is to be used to evaluate the titration results, a great deal of time can be saved by automation of the titration procedure in such a way that the titration data are obtained directly on punched tape (or punched cards). Moreover, errors caused by manual punching of the data are thereby avoided.

Automatic titrators are by no means new and some of the most common types have been reviewed by PHILIPS[6], while the use of these instruments in automatic volumetric analysis has been summarised by SQUIRRELL[7]. In most of the titrators, however, the read-out system consists of a recording potentiometer and the titrant is added continuously from a syringe buret. The total volume of titrant is thus given by the length of the recorder chart. Even if the recorder and the syringe motors are synchronised, the time-lag from mixing and reaction time will result in a systematic error between the actual volume of titrant and that registered by the recorder. There are several ways of minimizing this time-lag, but it is very difficult to stop the syringe and wait for a steady read-out on the potentiometer.

In this paper a semi-automatic titrator, capable of carrying out several titrations simultaneously, with a read-out system directly on punched tape and key-board, is described. The titrator is designed to fit titrations demanding a high degree of precision, involving the registration of a considerable number of titration points as, for instance, the analysis of the main constituents of sea water. Since in high-precision analysis it is preferable to weigh samples rather than to measure them by volume, and since the automation of the weighing-in process has not yet been solved satisfactorily, samples must be charged manually.

DESCRIPTION OF THE TITRATOR

A block diagram showing the different components of the titrator is given in Figure 1 while their approximate prices are listed in Table I. The various parts are discussed below.

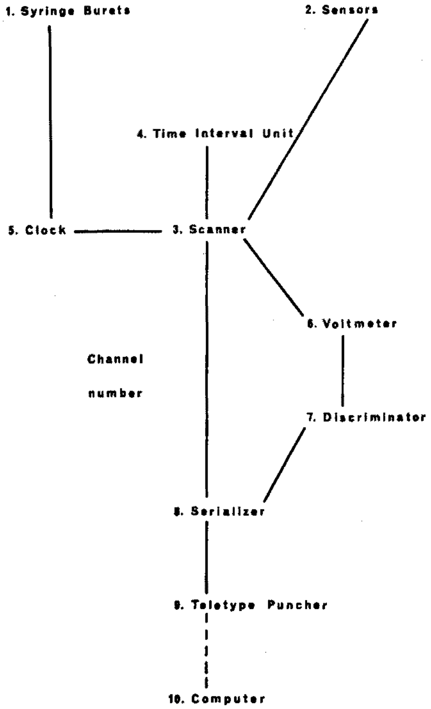

Fig. 1. Block diagram showing the different components of the semi-automatic titrator.

Syringe burets

Although coulometric generation of titrant has proved, in some titrations, to be superior to volumetric addition, the latter method is, without doubt, of more general use, and the titrator was therefore initially built for volumetric addition. The auxiliary equipment needed to convert the instrument into a coulometric titrator is, however, also available (Datametrix AB, Sollentuna, Sweden). The titrant is added from motor-driven syringe burets (Metrohm, Dosimat E 415) of total volumes of

TABLE I

THE DIFFERENT COMPONENTS OF THE SEMI-AUTOMATIC TITRATOR (SEE ALSO FIG. 1)

Component	*Type used*[a]	*Approximate price*	*Other possible uses of the component apart from the titrator*
Modified burets	Mettler E 415	£ 100/buret	General use
Sensors	Various	£ 10–£ 200	General use
Scanner	DS 6001–2	£ 760	Registration of spectra,
Time interval unit	DS 6013	£ 130	chromatograms etc.
Clock	—	£ 100	Different relay functions
Digital voltmeter	DM 2006 mod. D2	£ 1000	pH meter
Discriminator	DS 6020–22	£ 640	Used together
Serializer	DS 6003–9	£ 480	with 3 and 4
Teletype puncher	Teletype mod. 33	£ 750	Programming

[a] DS and DM refer to units from Dynamco Instruments Ltd, England.

either 10 or 20 ml and it is possible to regulate the speed by which titrant is added from each individual buret. Thus, when the burets are triggered, either manually or automatically, with a short-circuiting pulse, they deliver different amounts of titrant to their respective titration vessels. The motor axles of the syringe burets are coupled to helipotentiometers which yield voltages, in the range 0–1 V, proportional to the total volume of titrant added. It is thus possible to use a digital voltmeter to register the buret readings accurately.

As the accuracy in the volume of titrant added is fundamental for the accuracy of the whole titrator, the burets were carefully calibrated with doubly distilled water at 23°. Since increased accuracy is obtained if the major part of the total volume of the buret is used to reach equivalence, only the 10–20 ml volume regions of the buret-cylinders, which had a total capacity of 20 ml, were calibrated. In the calibration procedure, 10 ml (according to buret reading) of doubly distilled water were introduced into a weighed glass vessel which was then sealed and re-weighed. This procedure was repeated for 1-ml portions (according to buret reading) up to a total volume of 20 ml. The drop adhering to the tip of the buret was also transferred to the glass vessel. The weight the water ought to have according to the buret reading (density of water $=0.99760$ g/cm^3 at 23°) was then compared with the measured weight of each volume increment. The total amount of water added according to the buret reading and the measured total weight were also compared in order to estimate the accuracy in the total amount of titrant added. This is obviously an important factor since errors in the total volume of titrant added will, of course, result in a corresponding error in the titration result. A representative calibration for a buret of total volume 20 ml is shown in Table II. From this Table it is seen that the mean deviation in the total volume reading is of the order of magnitude 0.006%, and values greater than 0.01% have seldom been obtained although a large number of calibrations have been performed. It should also be mentioned that, for fairly rapid titration procedures, somewhat greater accuracy is obtained if the buret tip is allowed to dip into the solution. There will then, of course, always be a slight exchange between titrant and titrand but it has proved to be possible to reduce this two-way flow if the density of the titrant is adjusted so that it is of the same order of magnitude as that of the titrand.

TABLE II

WEIGHT CALIBRATION OF A BURET

Volume increment (cm^3)	*Total volume*[a]	*Weight of water in the increment according to buret*	*Total weight of water according to buret*	*Measured weight of water in the increment*	*% Deviation in incremental weight*	*Measured total weight of water*	*% Deviation in total weight*
0–10	10	9.9760	9.9760	9.9733	− 0.027	9.9733	− 0.027
10–11	11	0.99760	10.9736	0.9995	+ 0.19	10.9728	− 0.007
11–12	12	0.99760	11.9712	0.9967	− 0.09	11.9695	− 0.014
12–13	13	0.99760	12.9688	0.9998	+ 0.22	12.9693	+ 0.004
13–14	14	0.99760	13.9664	0.9961	− 0.15	13.9654	− 0.007
14–15	15	0.99760	14.9640	0.9976	± 0.00	14.9630	− 0.007
15–16	16	0.99760	15.9616	0.9976	± 0.00	15.9606	− 0.006
16–17	17	0.99760	16.9592	0.9996	+ 0.20	16.9602	+ 0.006
17–18	18	0.99760	17.9568	0.9974	− 0.02	17.9576	+ 0.007
18–19	19	0.99760	18.9544	0.9972	− 0.04	18.9548	+ 0.002
19–20	20	0.99760	19.9520	0.9980	+ 0.04	19.9528	+ 0.004
					Mean % deviation in total weight		± 0.006

[a] According to the readings of the digital voltmeter.

Sensors

All measuring devices delivering an analog d.c. voltage signal can be used as sensors. Different kinds of electrometric titrations can thus be carried out by the titrator. Many photometric and spectrophotometric devices are also easily adaptable to the titrator, since it is possible to measure output signals, after slight modification, with the digital voltmeter (see below) instead of, for instance, the galvanometer of the instrument. In fact, the galvanometer read-out system is often the least accurate part of such an instrument and a better reading resolution can usually be obtained with the digital voltmeter.

Scanner

The voltage signals from the burets and the sensors enter the scanner (Dynamco Low Level Scanner DS 6001 and Scanner Drive Unit DS 6002) which has ninety channels available for input signals. Since every titration provides at least two signals (*e.g.* buret and sensor) it is thus theoretically possible to handle information from 45 different titration vessels simultaneously. Every signal enters a different channel and is thus associated with a certain channel number (0–89). Since these channel numbers are printed out on the data tape (see below), together with the value of the corresponding channel voltage, they serve as identification tags for the different signals in the subsequent computation of the data. During a scanning the channels are searched in the order of their channel numbers. The voltage signal in the channel is sent forward to the voltmeter and the corresponding channel number to the serializer (see below). The scanning time can be preset to four different values, namely 1, 2, 4 and 10 channels/sec. Moreover, those channels without signals can be skipped during the scanning, although only, however, in blocks of ten at a time, *e.g.* channels 20–29. This will, of course, reduce the time needed for one scanning, which can thus be varied from 1 sec (80 channels skipped, scan-time 10 channels/sec) to 90 sec (no channels skipped, scan-time one channel/sec). In most titration procedures a certain time-lag between the addition of titrant and the reading of the sensor is necessary to ensure proper mixing and attainment of equilibrium. For this reason one scanning seldom takes less than 10 sec.

The last ten channels (number 90–99) of the scanner are reserved for providing short-circuiting pulses to a clock (see below) which in combination with the individual buret speed governs the size of the increments of titrant. The number of such pulses can be preset to be either 1, 2, 3, 4 or 5.

Time interval unit

As mentioned above, the time needed for one scanning, which also includes a new addition of titrant, can be varied from 1 to 90 sec using the scanner. For systems involving slow chemical or electrode equilibria this may, however, be too short a period. For this reason a time interval unit (Dynamco, DS 6013) which allows a pause between the completion of one scanning and the commencement of the next, has been connected to the scanner. The magnitude of this pause can be preset to be 0, 1, 2, 4, 8, 15, 30, 60 or 120 min. If the pause is set to 0 min the scanning will, of course, be continuous. Thus, by adjusting the scanning time, channels/sec, the number of channels scanned and the time interval unit, the time between each new addition of titrant can be varied from 1 sec up to 2 h.

Clock

The short-circuiting pulses coming from channels 90–99 of the scanner trigger a clock, which, in its turn, delivers short-circuiting pulses of preset duration to all burets. The magnitude of the increment of titrant for each individual buret can be adjusted by altering the speed of addition of titrant (see above). By changing the settings of the clock and burets, the magnitudes of the titrant increments can be varied from less than 0.01 ml up to a full buret. The clock can also be adjusted to deliver very long pulses (corresponding to more than 20 ml of titrant) suitable for coulometric generation of reagent.

Voltmeter

The voltage signals leaving the helipotentiometers and sensors are measured with an integrating digital voltmeter (Dynamco, DM 2006) which at the same time acts as an analogue to digital converter. The voltmeter has four measuring ranges namely, 0–0.1 V, 0–1 V, 0–10 V and 0–100 V and the signals are registered with four valid figures. In potentiometric titrations, for instance, a measuring range of 0–1 V is normally used which means that the resolution in the voltage reading is ±0.1 mV. This is more than satisfactory for most titrations. The voltmeter is equipped with an automatic ranging function (Dynamco, Input module D3) which makes it possible to measure signals from different measuring ranges during the same scanning. The input impedance of the instrument is *ca.* 10000 MΩ which is, unfortunately, not sufficient for rapid measurements with a glass electrode (impedance *ca.* 50 MΩ). By inserting a high quality operational amplifier with a high input impedance, *e.g.* Philbrick P2A, as a voltage follower between the glass electrode and the voltmeter, it has, however, been possible to overcome this limitation.

Discriminator

The signals from the voltmeters to the serializer (see below) pass through a signal discriminator (Dynamco, Limit Detector DS 6020 and Limit Selector DS 6022). The discriminator can be programmed for each channel number so that it blocks entry to the serializer if the magnitude of the absolute value of the signal in a specific channel does not exceed a certain preset value. If, for instance, the discriminator for channel No. 10 is set to 89 mV and the measuring range of the voltmeter is 0–1 V, only signals on this channel with an absolute value greater than 89 will pass through to the serializer for subsequent print-out.

The discriminator can be used to prevent print-out of uninteresting parts of a titration curve. It is also used to discriminate punch-out of channel number (*cf*. Fig. 1) and signal magnitude from such channels which are not used for measuring and are switched on during a scanning only in order to adjust the time for one scanning. In such channels small voltages may often build up if the inputs are not carefully short-circuited.

Serializer

Those signals from the voltmeter which pass through the discriminator go to the serializer (Dynamco, Serializer DS 6003 with Punch Output Unit DS 6008).This converts the parallel BCD form signals from the voltmeter to the desired serial format required by the teletype puncher (see below). It also governs the order in which the data are printed out, each voltage value being preceded by the corresponding channel number and every new number either by a sign, a space or a line-feed. Moreover, the line-feed and the space between each line on the teletype puncher are controlled by the serializer, which can, for instance, be adjusted so that a new line is printed before each set of data, one data set comprising: channel number–buret reading channel number–sensor reading (*e.g.* 87 + 1380 88 − 3687).

Teletype puncher

The titration data are printed on punched tape and at the same time typed on paper with a teletype puncher (Teletype Model 33). The teletype puncher, which operates with an 8-level code, is equipped with a tape reader. The key-board of the puncher is equipped with figures, letters and punctuation marks, since, in routine analysis, the titration data for each titration must be preceded by an identifying title which follows the data during the computation and, of course, precedes the results printed out by the computer. If the key-board were equipped with figures only, the amount of information contained in the title would be severely limited. Owing to its wide range of symbols, the puncher can, moreover, be used for programming.

The teletype puncher is, moreover, equipped with a sender unit which would make it possible to have a computer on line.

Computer

Although all components of the titrator have been chosen for their flexibility, the programming facilities of the specific computer contribute, without doubt, most to the versatility of the titrator. Besides providing almost unlimited facilities for calculation, the computer can sort data coming from different input channels and, moreover, "edit" the printing out of the results. By means of a special reading-in program the punched code on the Teletype has been adapted to the IBM 360/65 computer at the Göteborg Universities' Computing Centre.

USE OF THE TITRATOR

When the titrator is to be used for a particular titration procedure, it is, of course, first necessary to determine the optimum time for one scanning, the optimum concentration of titrant, the most suitable magnitude of titrant increments, etc. It is also necessary to decide how many parallel titrations are to be performed. Even if 45 titrations can theoretically be run at the same time, this will probably not be the case in practice. An elementary knowledge of the form of the titration curve is also advantageous in order to be able to discard, by means of the discriminator, those parts of the titration curve which are of little interest in the evaluation of the equivalence point. Once the optimum conditions have been found, it is only necessary to weigh in the samples and to punch manually a suitable title for each sample together with the sample weight or volume, the concentration of titrant, and, if electrode equilibria are involved, the sample temperature. This information is always needed for the calculation of the relevant concentrations. Any further information required by the method chosen to evaluate the equivalence point can also be punched manually.

Once the titrator has been started, the next samples can be weighed in. The titrator is designed so that it can stop after a certain pre-chosen number of titration points or when a certain signal (from, for instance, a buret) exceeds a given pre-chosen value. If it is deemed more practical not to set the titrator to stop automatically, the computer program can, however, easily be modified to neglect less accurately measured parts of the titration curve.

Scope of the titrator

The titrator has, so far, been used for the potentiometric determination of the halide concentration[8] (low-impedance silver electrode) and alkalinity[8] (high-impedance glass electrode) of sea water. The total amount of alkaline earth metals in sea water has been determined by a photometric titration procedure with an EEL photometer[8]. By means of the time interval unit the behaviour of the lanthanum membrane electrode (low impedance) in different buffer systems has been investigated[9].

The author wishes to express his sincere gratitude to the head of the department, Professor D. DYRSSEN, for valuble discussions concerning the construction of the titrator which was worked out in cooperation with Mr. K. A. PETTERSSON, Scantele AB, Sweden. The teletype code was modified for the IBM computer by Mr. O. LINDGREN. Financial support in the form of grants from Carl Tryggers Stiftelse and the Swedish Natural Science Research Council is gratefully acknowledged. The English text of this paper has been revised by Dr. SUSAN JAGNER.

SUMMARY

A semi-automatic titrator is described which supplies preset increments of titrant and has a direct teletyped read-out system on punched tape suitable for subsequent computer treatment of the titration curve. A total of 45 motor-driven syringe burets can be used for both electrometric and photometric titrations. The use and scope of the titrator in high precision analysis is discussed.

RÉSUMÉ

Un titreur semi-automatique est décrit pour des analyses de précision avec traitement au computer de la courbe de titrage. Un total de 45 burettes à moteur peuvent être utilisées pour des titrages électrométriques ou photométriques. Une discussion est présentée sur les possibilités d'utilisation de ce titreur pour des analyses de haute précision.

ZUSAMMENFASSUNG

Es wird ein halbautomatischer Titrierapparat beschrieben, der mit vorherfestgelegten Zugaben des Titrationsmittels arbeitet und die Ergebnisse direkt auf Lochstreifen überträgt, die die nachfolgende Berechnung der Titrationskurve durch einen Computer ermöglichen. Eine Gesamtzahl von 45 motorgetriebenen Büretten kann für sowohl elektrometrische als auch photometrische Titrationen benutzt werden. Die Anwendungsmöglichkeiten des Titrierapparates in der Präzisionsanalyse werden erörtert.

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EFFECT OF CARBOXYLIC ACID BUFFERS ON THE POTENTIOMETRIC TITRATION OF FLUORIDE WITH LANTHANIDE NITRATES USING A LANTHANUM FLUORIDE MEMBRANE ELECTRODE

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The effect of acetate buffer on the potentiometric titration of fluoride with lanthanum nitrate using a lanthanum fluoride membrane electrode has been studied by ANFÄLT AND JAGNER[1]. Acetate ions were found to enter the solid phase during the titration forming precipitates of formula $LaF_{3-x}Ac_x$ ($0 \leq x \leq 1$ depending on the acetate concentration), so that the electrode behaved sluggishly. The effect of other carboxylic acid buffers on the precipitation titration has now been studied with the lanthanum fluoride electrode. In order to ascertain whether or not comparable effects occur for other lanthanide fluorides with crystal structures similar to lanthanum fluoride, their behaviour in potentiometric fluoride titrations has also been investigated.

EXPERIMENTAL

Reagents

All reagents were of analytical grade. Stock fluoride solution was prepared in polyethylene flasks by dissolving the dried sodium salt (Merck) in doubly distilled water. Standard lanthanum and cerium solutions were prepared by dissolving their nitrate hexahydrates (Merck) in doubly distilled water. The remaining lanthanides (Pr, Nd, Sm, Lu) were prepared by dissolving their oxides (L. Light and Co, Ltd) in an equivalent amount of nitric acid. All lanthanide solutions were standardised against the standard fluoride solution and against standard EDTA with xylenol orange as indicator. Stock solutions of carboxylic buffers were prepared by adding sodium hydroxide to the acid until an $[HA]/[A^-]$ molar ratio $= 1$ was obtained.

Apparatus

All titrations were performed in polyethylene beakers at 23°. The fluoride ion activity was followed with fluoride membrane electrodes (Orion, Model 94-06) with saturated calomel electrodes as reference (Radiometer K 401). The titrations were performed with an automatic titrator as described by JAGNER[2], which operates with discrete increments of titrant, it being possible to preset the time between each addition. The read-out system of the titrator is on punched tape and key-board. Several titrations were thus performed at the same time. The solid phases were analysed thermogravimetrically with a Mettler Thermo Analyzer, Serial No. 71.

Systems investigated

Lanthanum–carboxylic acid system. Sodium fluoride solutions (100 ml of 0.0110 M) were titrated with v ml of 0.100 M lanthanum nitrate in the presence of 0.4 M carboxylic acid (HA) + 0.4 M carboxylate (A^-). For each buffer system, three different values of the titrant increment and time between each addition of titrant, namely (*a*) 0.2 ml/1 min, (*b*) 0.1 ml/2 min and (*c*) 0.2 ml/8 min, were employed. Six different carboxylic acids were tested: (1a-c) formic acid, (2a-c) acetic acid, (3a-c) propionic acid, (4a-c) iso-butyric acid, (5a-c) *n*-butyric acid, (6a-c) lactic acid.

For comparison some titrations were also performed with strongly complexing agents namely, malonate, citrate and acetylacetonate.

Lanthanide–acetate system. 100 ml of 0.0030 M sodium fluoride solution were titrated with v ml of c M lanthanide nitrate in the presence of 0.5 M acetic acid + 0.5 M acetate buffer. The titrant increment was 0.2 ml and the time between two successive additions of titrant was 3 min. Six different lanthanides were used as titrants: (7) 0.020 M La, (8) 0.020 M Ce, (9) 0.020 M Pr, (10) 0.020 M Nd, (11) 0.0125 M Sm, (12) 0.0317 M Lu.

RESULTS

The equivalence point, v_{eq}, was evaluated by means of the Gran method[3], using different computer programs. The method of maximum slope could not be used since the point of maximum slope of the $E(v)$ curve does not coincide with the equivalence point in these titrations[4]. The composition of the solid phase formed, $LaF_{3-x}A_x$, was then calculated from v_{eq}, *i.e.*

$$x = \frac{100 \cdot [F^-]_{init}}{v_{eq} \cdot [\text{lanthanide}]_{buret}} \tag{1}$$

Since the accuracy of the value of x obtained from a single determination is relatively low, at least six titrations were performed for each carboxylate buffer and the x values discussed below are the mean values for each set of titrations.

Lanthanum–carboxylic acid system

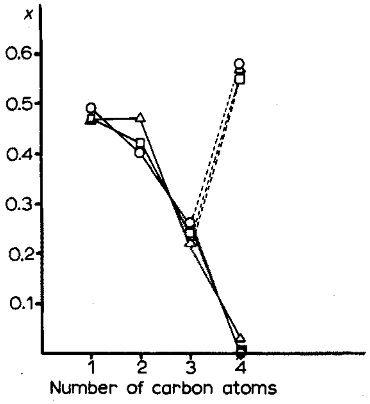
The results are summarised in Table I and Fig. 1. With the exception of *n*-butyrate it is obvious that the x value decreases with increasing number of carbon

TABLE I

VALUES OF x CALCULATED FROM GRAN PLOTS FOR TITRATIONS IN DIFFERENT CARBOXYLIC ACID–CARBOXYLATE BUFFERS

Titration no.	*Buffer system*	*pH*	x			*Estim. error*
			a *1 min/0.2 ml*	*b* *2 min/0.1 ml*	*c* *8 min/0.2 ml*	
1	Formate	3.59	0.49	0.47	0.47	±0.03
2	Acetate	4.72	0.40	0.42	0.47	±0.02
3	Propionate	4.92	0.26	0.24	0.22	±0.02
4	Iso-butyrate	5.58	0	0	0.03	±0.03
5	*n*-Butyrate	5.55	0.58	0.55	0.57	±0.03
6	Lactate	4.07	0.14	0.18	0.11	±0.04

atoms in the carboxylate. The anomalous behaviour of *n*-butyrate can probably be explained in terms of a different crystal structure for the solid phase as a result of the long carbon chain in this ligand. Owing to the slight solubility of unbranched carboxylic acids beyond *n*-butyrate, it was not possible to extend the investigation to higher members of the series.



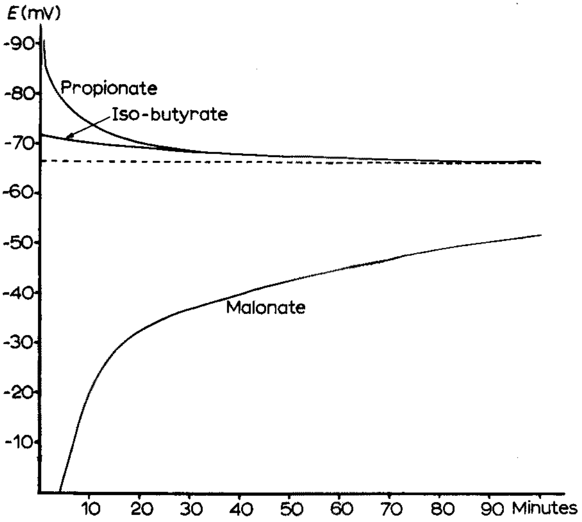


Fig. 1. The composition value x plotted against the total number of carbon atoms in the carboxylic acid–carboxylate buffer for different titrant increments and times between successive increments. (○) 0.2 ml/min, (□) 0.1 ml/2 min, (△) 0.2 ml/8 min.

Fig. 2. Em.f. reading of the electrode in a 0.011 M sodium fluoride solution plotted against time, after the electrode had been used for titration in three different buffer systems for 12 h.

The malonate, citrate and acetylacetonate buffers suppressed the formation of the lanthanum fluoride precipitate making the results difficult to interpret, but the x values appeared to be approximately zero. For lactate, which is only weakly chelating, it was, however, possible to determine $x = 0.14$, which indicated that this ligand, like malonate, citrate and acetylacetonate, has little effect on the stoichiometry of the solid phase.

Effect of titration time

It is reasonable to suppose that the value of x will increase with the duration of the titration. This could, however, not be confirmed with any significance (*cf.* Fig. 1). The effect of titration time on the value of x is, however, of minor importance in comparison with the carboxylate and fluoride concentrations[1].

Effect on the electrode surface

After several hours of titration in carboxylate buffer solutions the membrane electrode was immersed in a 0.011 M standard fluoride solution. A continual drift in the E^0 value was observed. This is illustrated in Fig. 2, in which the potential reading, E (mV), for the electrode in the standard fluoride solution has been plotted against time, after titration in a 0.4 M carboxylic acid + 0.4 M carboxylate buffer for 12 h. Three different types of buffer system are illustrated in Fig. 2. namely malonate (chelating ligand), propionate and iso-butyrate (large and small effects, respectively, on the stoichiometry of the lanthanum trifluoride precipitate). For the buffers with pronounced chelating properties (malonate, citrate and acetylacetonate), the electrode always showed initially too low a fluoride concentration while the opposite was true for those ligands for which x was high (formate, acetate, propionate). For ligands belonging to neither of these groups (lactate and iso-butyrate) there was no pronounced tendency. This shows that the two types of ligand interfere with the electrode membrane in different ways during the titrations. The destroyed electrode surface could be regenerated by polishing with diamond paste (0.25–0.5 μm), washing with ethanol to remove the paste lubrication, and then allowing the electrode to stand in a solution saturated with lanthanum fluoride containing a slight excess of fluoride, for one day. After such a treatment, which may be repeated several times, a constant potential reading was obtained. In this work the surfaces of the electrodes were regenerated before each titration.

It should be stressed that the destruction of the electrode surface is accentuated when the electrode is used to follow titrations. No such effect has been observed for "single-point" measurements in which the electrode is immersed in fluoride solutions buffered with carboxylate, for a short period of time.

Lanthanide–acetate system

Since it might be possible to construct fluoride electrodes from membranes of other lanthanide fluorides[5], it was considered profitable to study the possible interference of carboxylic acid buffers on such electrodes. It was assumed that any interference found to apply to a lanthanide fluoride precipitate ought also to be applicable to a lanthanide fluoride single crystal, as is the case for lanthanum. The results are summarised in Table II, from which it is seen that the interference, expressed in terms of the x value of $LnF_{3-x}Ac_x$, decreases with increasing atomic weight of the lanthanide.

Thermogravimetric analysis

Since the stability of the soluble lanthanide–acetate complexes increases with

TABLE II

VALUES OF x OBTAINED FROM THERMOGRAVIMETRIC ANALYSIS FOR THE LANTHANIDE–ACETATE SYSTEMS

Titration no.	*Lanthanide*	x	pK_{s0}[a]	*log* $\alpha_{Ln(Ac)}$[b]
7	La	0.35(0.91)[c]	17.9	2.43
8	Ce	1.00(0.91)[c]	17.9	2.61
9	Pr	0.26	17.7	2.75
10	Nd	0.06	17.2	2.94
11	Sm	0.05	17.1	3.26
12	Lu	0.00	14.1	—

[a] Evaluated by means of the computer program HALTAFALL[1,6,7] from titrations performed in unbuffered solutions with an ionic strength of approximately 0.01 M.

[b] $\alpha_{Ln(Ac)} = 1 + \beta_{LnAc} \cdot [Ac^-] + \beta_{LnAc_2} \cdot [Ac^-]^2 + \beta_{LnAc_3} \cdot [Ac^-]^3 + \beta_{LnAc_4} \cdot [Ac^-]^4$ for $[Ac^-] = 0.5\ M$.

The stability constants have been taken from SONESSON[8].

[c] Evaluated from the potentiometric titrations.

decreasing ionic radius, whereas the pK_{s0} values decrease (see Table II), it was not possible to interpret the potentiometric titration curves with acceptable accuracy. The solid phases formed during the titrations were therefore analysed thermogravimetrically, with aluminium oxide as reference. The sample was heated in a stream of oxygen at a rate of 8° per min up to 500°. Values of x were calculated from the weight loss commencing at *ca.* 300°, assuming that decomposition occurs according to

$$LnF_{3-x}Ac_x + 2xO_2 \rightarrow \frac{(3-x)}{3} LnF_3 + \frac{x}{6} Ln_2O_3 + \frac{3x}{2} H_2O + 2xCO_2$$

The resulting x values are listed in Table II.

DISCUSSION

Lanthanide trifluorides crystallise either in the hexagonal system (LaF_3 structure) or in the orthorhombic (YF_3 structure)[9,10]. In the hexagonal structure the metal ion is surrounded by five fluoride ions, the next nearest neighbours being a further six fluoride ions. The structure can be considered as consisting of layers of lanthanum(III) and fluoride ions with a layer of fluoride ions on each side of the LaF^{2+} network. In this structure some fluoride ions appear to have a certain amount of mobility as has been indicated by n.m.r.[11] and conductivity[12] measurements. In the orthorhombic structure, however, the metal ion is surrounded by eight fluoride ions and has a further fluoride ion at a slightly longer distance (2.3 and 2.6 Å, respectively, for YF_3). Lanthanide trifluoride crystals with this structure are probably not suitable as fluoride ion electrode membranes. The crystal structures of different lanthanide fluorides, according to ZALKIN AND TEMPLETON[10], have been summarised in Table III, together with the corresponding formula volume for LnF_3 in the crystal.

TABLE III

CRYSTAL STRUCTURES AND FORMULA VOLUMES FOR DIFFERENT LANTHANIDE TRIFLUORIDES

Lanthanide	*Crystal structure*	*Formula volume (Å³)*
La	Hexagonal	54.6
Ce	Hexagonal	53.4
Pr	Hexagonal	52.2
Nd	Hexagonal	51.4
Sm	Hexagonal	49.7
Sm[a]	Orthorhombic	51.7
Lu	Orthorhombic	46.5

[a] After heating at 700° for 2 h.

It has been shown that several carboxylates interfere with the precipitation titration of fluoride with lanthanum nitrate. Those, with chelating properties, of course, dissolve the precipitate of lanthanum trifluoride as well as the electrode membrane, according to the general formula

$$LaF_3(s) + nA^- \rightleftharpoons LaA_n^{(3-n)+} + nF^-$$

whereas the carboxylic acid anions also interfere in yet another way. There are two main ways in which such an interference could be imagined to take place. Carboxylate ions or lanthanum carboxylate complexes could attach themselves to a newly-formed crystallite of lanthanum fluoride in positions normally occupied by the most mobile fluoride ions and thus prevent further growth of the crystal. It is, however, also possible that the carboxylate ions or lanthanum carboxylate complexes are incorporated in the crystal lattice without hindering subsequent crystal growth. This second model is supported by the fact that appreciable amounts of carboxylate ion have been found in the lanthanum fluoride precipitate. Moreover, the tendency to incorporation appears to decrease with increasing number of carbon atoms, probably owing to steric hindrance, and steric effects could also account for the decrease in acetate incorporation with decreasing formula volume of the lanthanide fluorides. The unbranched butyrate ion may, for example, cause $LaF_{3-x}A_x$ to crystallise with a different structure, which could explain the anomalous behaviour of this ion (*cf.* Fig. 1). These phenomena are more easily interpreted in terms of the second model. Moreover, extensive polishing of the electrode surface must be performed after an electrode has been used to follow titrations in the presence of carboxylate buffers, which indicates that the interference is not solely a surface effect. The fact that the electrode does not obey the Nernst law after it has been used to follow titrations of fluoride with lanthanum nitrate in carboxylate or chelating complex media, whereas this effect is not observed after "single point" measurements in the same media, suggests that lanthanum carboxylates or chelates play an important part in the formation of the $LaF_{3-x}A_x$ precipitate. Further support for the second model is provided by the fact that the lanthanide precipitates may be washed extensively without complete loss of carboxylate. Which of the models is correct can probably only be decided by structural analysis. For analytical purposes, however, it is sufficient that carboxylate ions are incorporated in the lanthanum fluoride lattice, whether in the bulk of the crystal or on its surface, causing an unsatisfactory performance of the electrode in such media. Capacitance measurements[12] made on a single crystal of lanthanum fluoride reveal an extremely high capacitance which is correlated with large polarisation effects. If the crystal is soaked in nitric acid, the capacitance is increased and the effect has been interpreted in terms of strong bonds between lanthanum and nitrate oxygen at the surface of the crystal. In the light of the present work, a similar, but probably more pronounced, effect would be expected to occur if the crystal were soaked in carboxylate buffer.

Conclusions

It has been shown that formate, acetate and *n*-butyrate interfere both with the precipitation of lanthanum fluoride and with the working of the lanthanum fluoride membrane electrode in titrations. The interference can be explained by the substitution of mobile fluoride ions by carboxylate oxygen, to form a mixed solid phase, $LaF_{3-x}A_x$. The value of x is lower for propionate and lactate and practically zero for iso-butyrate. Strong complexing agents interfere by preventing the formation of the lanthanum fluoride precipitate. The value of x is low for neodymium fluoride and samarium fluoride, which suggests that these fluorides may be suitable electrode materials. Carboxylate ions do not interfere with the lutetium fluoride precipitate, probably because the lutetium trifluoride has an orthorhombic structure with restricted mobility of the fluoride ions. The solubility product of this fluoride is, moreover, considerably higher than the solubility product of lanthanum fluoride. It is therefore concluded that lanthanide fluorides beyond samarium fluoride are not suitable as electrode materials.

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SUMMARY

By means of potentiometric titration of fluoride with lanthanide nitrates in the presence of carboxylate buffers it has been shown that formate, acetate, propionate and *n*-butyrate (A^-) interfere with the precipitation reaction. Precipitates with the formula $LnF_{3-x}A_x$ (Ln = La, Ce, Pr, Nd, Sm) are formed and the carboxylates cause the lanthanum fluoride membrane electrode to work sluggishly after the titration. Chelating ligands such as lactate, malonate, citrate and acetylacetonate also affect the lanthanum fluoride membrane, and, after titrations in such media, the electrode could be regenerated only by polishing its surface with diamond paste and then immersing it in dilute sodium fluoride saturated with lanthanum fluoride.

RÉSUMÉ

On a constaté, par titrage potentiométrique des fluorures au moyen de nitrate de lanthanide, en présence de tampons carboxyliques, que le formiate, l'acétate, le propionate et le *n*-butyrate gènent considérablement la réaction de précipitation, en modifiant de la membrane de l'electrode. Des ligands tels que lactates, malonates, citrates et acétylacétonates affectent également la membrane de fluorure de lanthane. Après titrage, dans un tel milieu, l'électrode ne peut être régénérée que par polissage de sa surface avec une pâte de diamant, puis par immersion dans une solution diluée de fluorure de sodium saturée de fluorore de lanthane.

ZUSAMMENFASSUNG

Bei der potentiometrischen Titration von Fluorid mit Nitraten der Lanthaniden in Gegenwart von Carboxylat-Puffern werden durch Formiat, Acetat, Propionat und *n*-Butyrat (A^-) ernsthafte Störungen bei der Fällungsreaktion verursacht. Es werden Niederschläge mit der Formel $LnF_{3-x}A_x$ (Ln = La, Ce, Pr, Nd, Sm) gebildet. Die Carboxylate bewirken, dass die Lanthanfluorid-Membranelektrode nach der Titration träge arbeitet. Chelatbildende Liganden wie Lactat, Malonat, Citrat und Acetylacetonat wirken ebenfalls auf die Lanthanfluoridmembran ein. Die Elektrode kann nach Titrationen in derartigen Medien nur dadurch regeneriert werden, dass ihre Oberfläche mit Diamant-Paste poliert und die Elektrode dann in verdünnte Natriumfluorid-Lösung getaucht wird, die an Lanthanfluorid gesättigt ist.

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

PART V. DESTRUCTIVE AND NON-DESTRUCTIVE DETERMINATION OF MANGANESE, INDIUM AND URANIUM

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The classical analytical procedures for the determination of manganese in titanium or titanium dioxide can be divided into four main groups, namely, emission spectrography, titrimetry, colorimetry and polarography. TARASEVICH AND MOSELI[1] determined 0.2–2% manganese in titanium alloys by spectrography. The same technique was used by KARABASH *et al.*[2] who determined 1 p.p.m. of manganese in 0.25-g samples of titanium, adding silver chloride to enhance the intensity of the lines. By volatilization of the matrix as the fluoride, FRATKIN AND SHEBUNIN[3] concentrated the impurities and applied spectrochemical analysis; they determined down to 1 p.p.b. of manganese in titania. The titrimetric methods are based on persulfate oxidation of manganese and subsequent sodium arsenite titration; down to 0.05% of manganese can be determined in this way[4]. Colorimetrically, manganese is determined as permanganate, after periodate oxidation. This was used by THOMPSON[5] and CHERNIKOV AND DOBKINA[6]. The method allows the determination of down to 50 p.p.m. of manganese. Polarography may be used after precipitation of titanium hydroxide with barium carbonate. BROOKSBANK *et al.*[7] determined manganese by means of neutron activation analysis, followed by a separation of the element as manganese sulfide. Down to 10^{-4} μg could be determined at a neutron flux of 10^{12} n cm^{-2} sec^{-1}.

Little attention has been paid to the determination of uranium or indium in titanium or titanium dioxide. The literature contains nothing about the determination of indium, while SANKAR[8] used neutron activation analysis for the determination of uranium in ilmenite, $FeTiO_3$.

In the present work both destructive and non-destructive methods for the determination of manganese, indium and uranium in titanium, titania powder and titanium dioxide crystals, are described. The former show excellent sensitivity in neutron activation analysis, as both cross-section and half-life are highly favourable, and the determination of uranium has a particular interest, since this element gives rise through fission, to an apparent concentration of a number of elements. The estimation of this blank value is thus necessary when accurate determinations of, for example, molybdenum, lanthanum and cerium are performed.

IRRADIATION CONDITIONS AND NUCLEAR DATA

The most important nuclear data for titanium, manganese, indium and uranium are given in Table I. The short half-life of the isotopes ^{56}Mn, ^{116m}In and ^{239}U does not allow lengthy separation procedures. Therefore, the irradiations were carried out in the "Thetis" reactor of the Institute, at a thermal neutron flux of $6 \cdot 10^{10}$ n cm^{-2}sec^{-1}, during 3 h. Table I shows that titanium gives rise to only one high activity, namely ^{51}Ti. This half-life of 5.8 min is however short in comparison to that of ^{56}Mn (2.58 h), ^{116m}In (54 min) and ^{239}U (23.5 min). Table I also indicates the possible formation of the ^{46}Sc, ^{47}Sc and ^{48}Sc isotopes by threshold reactions. The fast neutron flux is about 10^{10} n cm^{-2}sec^{-1} and the cross-sections and saturation factors are also low. Nevertheless, the scandium isotopes decrease the sensitivity of the determinations if they are not separated.

TABLE I

PERTINENT NUCLEAR DATA OF THE ISOTOPES FORMED UPON REACTOR IRRADIATION OF TITANIUM, MANGANESE, INDIUM AND URANIUM

Reaction	*Cross-section (barn)*	*Half-life*	*Most important γ-energies (MeV)*[10,11]
$^{50}Ti(n,\gamma)^{51}Ti$	0.19	5.8 min	0.3200; 0.6084; 0.9285
$^{46}Ti(n,p)^{46}Sc$	$8 \cdot 10^{-3}$	84 d	0.8894; 1.1203
$^{47}Ti(n,p)^{47}Sc$	$15 \cdot 10^{-3}$	3.4 d	0.1600
$^{48}Ti(n,p)^{48}Sc$	$4 \cdot 10^{-3}$	1.83 d	0.9835; 1.0376; 1.3118
$^{55}Mn(n,\gamma)^{56}Mn$	13.3	2.58 h	0.8469; 1.8107; 2.1128
$^{115}In(n,\gamma)^{116m}In$	150	54 min	0.4170; 1.0971; 1.2934
$^{113}In(n,\gamma)^{114m}In$	63	50 d	0.1902
$^{238}U(n,\gamma)^{239}U$			
$\xrightarrow{\beta}$ ^{239}Np	2.7	23.5 min	0.0586; 0.0747

Indium can also be determined by means of the long-lived ^{114m}In ($t_{\frac{1}{2}} = 50$ d) while uranium may be determined by means of the ^{239}Np daughter or delayed neutron counting.

By means of a reactor irradiation, manganese, indium and uranium can be determined non-destructively in a titanium matrix. For this purpose an irradiation position with a favourable ratio of the thermal-to-fast flux was chosen, as this leads to a relatively low activity for the scandium isotopes, allowing a better sensitivity for the impurities. The thermal and fast neutron fluxes were $2 \cdot 10^{10}$ and $9 \cdot 10^{8}$ n cm^{-2} sec^{-1} respectively. For the destructive methods an irradiation at the highest available thermal neutron flux (approximately 10^{11} n cm^{-2} sec^{-1}) was applied.

The self-shielding effect turned out to be negligible both for reactor irradiations of titanium and titania samples[9].

The dominant activities, induced in the titania and the titanium matrix by reactor irradiation are due to ^{56}Mn, ^{24}Na, ^{122}Sb, ^{51}Ti and the scandium isotopes. ^{51}Ti decays very rapidly and does not interfere with the activity measurements. The determinations of manganese, indium and uranium are especially disturbed by the presence of antimony.

EXPERIMENTAL

Instrumental

A γ-spectrometer was used, consisting of an 18-cm^3 Ge(Li) detector and a Tennelec 135M-TC 200 preamplifier–amplifier, Intertechnique CA 13 analog-to-digital converter and BM 96 4K memory unit.

Dissolution of the samples

Titanium metal and sponge were easily dissolved in a small volume of 5 *M* hydrofluoric acid, after which concentrated hydrogen peroxide was cautiously added to convert titanium(III) to titanium(IV). The excess of hydrogen peroxide was destroyed by gently boiling the solution. During this operation care had to be taken not to lose the volatile uranium hexafluoride. Tracer experiments showed that less than 0.3% of the uranium was lost.

Titanium dioxide powder was dissolved by gently boiling with a small volume of concentrated hydrofluoric acid, after which the solution was diluted to 5 *M* hydrofluoric acid. The powder could also be dissolved by careful fusion, in a platinum crucible, with a tenfold excess of potassium hydrogen fluoride. The melt could be dissolved in 3 *M* hydrochloric acid.

Titanium dioxide crystals could also be decomposed by potassium hydrogen fluoride fusion. It appeared experimentally that less than 0.2% of the uranium volatilized in these circumstances.

Separation scheme for titanium metal and titania powder

For both matrices the starting solution consisted of a small volume of 5 *M* hydrofluoric acid. This was percolated through an anion-exchange column Dowex 1-X8, 200–400 mesh (diameter 1 cm; height 10 cm), equilibrated and washed with 5 *M* hydrofluoric acid to elute manganese, indium and sodium.

The measurement of ^{56}Mn was always possible, despite the presence of the ^{24}Na activity and a further separation was unnecessary. Indium, however, could not be detected. To allow a more sensitive analysis, this element was extracted with tri-*n*-butyl phosphate (TBP), 100%, equilibrated with 3 *M* hydrochloric acid. The 5 *M* hydrofluoric acid solution was evaporated and treated with hydrochloric acid to obtain 3 *M* hydrochloric acid, after which the extraction was carried out[12–14].

Subsequent washing of the column with 9 *M* hydrochloric acid eluted titanium, scandium and neptunium, while uranium and antimony remained adsorbed on the resin. Uranium could be separated from the antimony activity by elution with 22 *M* hydrofluoric acid.

Tables II and III show the results of the tracer experiments.

Separation scheme for titania crystals

The main activities obtained from the titania crystals upon reactor irradiation, are ^{51}Ti and the scandium isotopes.

The starting solution consisted of 3 *M* hydrochloric acid solution of the potassium hydrogen fluoride melt. Uranium and indium were extracted from this solution with 100% TBP, equilibrated with 3 *M* hydrochloric acid. A subsequent extraction from 9 *M* hydrochloric acid with 100% TBP equilibrated with 9 *M* hydro-

TABLE II

ELUTION WITH THE VARIOUS ELUANTS

Fraction	*Volume (ml)*	*Element*	*% Recovered*
5 *M* HF	15	Na	>99.6
		Mn	99.2
		In	>99.3
9 *M* HCl	20	Np	>97.5
		Sc	99.9
		Ti	>99.3
22 *M* HF	20	U	>99.1
		Sb	1.5
Resin	7.5	Sb	98.5

TABLE III

EXTRACTIONS WITH TRI-*n*-BUTYL PHOSPHATE (TBP), 100%

Aqueous phase	*Element*	*Number of extractions*	*% in aqueous phase*	*% in TBP*
3 *M* HCl	In	2		>99.8
(+ 2.5% KF)	Mn		99	1
	U		2	98
9 *M* HCl	Sc	2		>99.7
	Mn		99	1

chloric acid, removed scandium from the aqueous solution. Manganese remained in the aqueous phase. The simultaneous determination of indium and uranium in the TBP phase, equilibrated with 3 *M* hydrochloric acid, was always possible since ^{116m}In never gave rise to dominant activities, while even a high activity of ^{239}U never disturbed the measurement of the highly energetic ^{116m}In γ-radiation (see Table I).

The same separation scheme could be applied to the analysis of titania powder, but in this case the high antimony content interfered. Extraction with 100% TBP from a 3 *M* hydrochloric acid solution removed 35% of antimony(V) and 99.2% of antimony(III). As antimony is in the pentavalent state, it is spread over both phases and interferes with the determination of manganese, indium and uranium. The ion-exchange procedure is therefore a better choice for the analysis of titania powder.

Non-destructive analysis

Irradiate 50-mg amounts of the sample for 3 h in an irradiation site with a high ratio of thermal-to-fast flux. Cool for 1 h and measure the sample on a high-resolution Ge(Li) detector. Use the full-energy peaks at 74.7 keV, 846.9 keV and 1293.4 keV for the determinations of uranium, manganese and indium, respectively.

Destructive analysis of titanium metal and titania powder

Dissolve the titanium metal in 3 ml of 5 *M* hydrofluoric acid. Add cautiously concentrated hydrogen peroxide until the solution becomes colourless. Boil gently to destroy the excess of hydrogen peroxide.

Use a teflon reaction vessel and a polythene watercooled condenser for the dissolution of the titania powder in 0.5 ml of 29 *M* hydrofluoric acid. Add 2.5 ml of 0.2 *M* hydrofluoric acid. Percolate the resulting 3 ml of 5 *M* hydrofluoric acid solution of titanium metal or titania powder through a column of Dowex 1-X8, 200–400 mesh (diameter 1 cm; height 10 cm). Wash the column with 12 ml of 5 *M* hydrofluoric acid. Elute a 20-ml fraction of 9 *M* hydrochloric acid and a 20-ml fraction of 22 *M* hydrofluoric acid.

Count the 22 *M* hydrofluoric acid solution for ^{239}U.

Evaporate the 5 *M* hydrofluoric acid eluate, add 3 *M* hydrochloric acid, evaporate again, and dilute to obtain 10 ml of 3 *M* hydrochloric acid. Extract with 10 ml of 100% TBP, equilibrated with 3 *M* hydrochloric acid. Count the organic phase for ^{116m}In, and the aqueous phase for ^{56}Mn.

Destructive analysis of titania crystals

Decompose the crystal by fusion with 500 mg of potassium hydrogen fluoride. Dissolve the residue in 15 ml of 3 *M* hydrochloric acid and extract with 15 ml of 100% TBP, equilibrated with 3 *M* hydrochloric acid. Count the organic phase for ^{116m}In and ^{239}U. Add 30 ml of 12 *M* hydrochloric acid to the aqueous solution and extract twice with 30 ml of 100% TBP equilibrated with 9 *M* hydrochloric acid. Backwash the organic phase once with 30 ml of 9 *M* hydrochloric acid. Count the aqueous phase for ^{56}Mn.

RESULTS AND DISCUSSION

The concentrations were determined by comparison of the photopeak areas in samples and standards. Lower limits were calculated, accepting $4.65\sqrt{N}$ to be the detection limit[15], where N is the number of counts of the background in the energy region of the presumed photopeak.

A number of non-destructive and destructive analyses of titanium metal and sponge, titania powder and titania crystals were carried out. The results of the non-destructive analyses are summarized in Table IV.

The results of the destructive analyses of a titanium sponge and a titania powder sample are summarized in Table V. In the titania crystals none of the three investigated elements could be detected, hence only the lower limits for the determination of manganese, indium and uranium are listed in Table VI.

The lower limits for the destructive determinations are roughly an order of magnitude lower than those obtained non-destructively. For a reactor irradiation at a flux of $5 \cdot 10^{10}$ n cm^{-2} sec^{-1} during 3 h and measurement on an 18-cm^3 Ge(Li) detector, the sensitivities (p.p.b.) for both the destructive and non-destructive method are listed in Table VII. The sensitivity strongly depends on the presence of other impurities. If ^{24}Na forms the preponderant activity, which is very often the case for titania powder, a separation will not enhance the sensitivity for the determination of manganese, since the alkali metals also remain in the aqueous phase upon extraction.

The determination of the uranium concentration is of importance for the

TABLE IV

RESULTS OF NON-DESTRUCTIVE ANALYSES FOR MANGANESE, INDIUM AND URANIUM IN TITANIUM METAL, TITANIUM SPONGE, TITANIA POWDER AND TITANIA CRYSTALS

Matrix	*Element*	*Results (p.p.m.)*						
		1	*2*	*3*	*4*	*5*	$\bar{x}$	σ (%)
Ti-metal	Mn	54.2	44.1	69.4	75.3	63.0	61.2	9
	In	<0.1						
	U	<2						
Ti-sponge 1	Mn	3.4	4.1	4.0	4.5	–	4.0	6
	In	<0.05						
	U	<5						
Titania powder 2	Mn	0.48	0.41	0.34	–	–	0.41	10
	In	<0.05						
	U	<3						
Titania crystal 1	Mn	0.045	0.035	0.058	–	–	0.046	13
	In	<0.02						
	U	<0.5						

TABLE V

RESULTS OF THE DESTRUCTIVE ANALYSES FOR Mn, In AND U IN TITANIUM AND TITANIA POWDER

Matrix	*Element*	*Results (p.p.m.)*				
		1	*2*	*3*	$\bar{x}$	σ (%)
Ti-sponge 2	Mn	8.3	8.8	8.1	8.4	3
	In	<0.03	<0.001			
	U	<3	<0.2			
Titania powder 1	Mn	0.96	0.88	0.96	0.93	3
	In	<0.005				
	U	7.9	6.7	7.1	7.2	5

TABLE VI

RESULTS OF THE DESTRUCTIVE ANALYSIS FOR Mn, In AND U IN TITANIA CRYSTAL

Element	*Concentration (p.p.m.)*
Mn	<0.006
In	<0.0002
U	<0.05

evaluation of the positive errors in the analytical results for other elements, whose concentrations are determined by means of radioactive isotopes that have a high fission yield from ^{235}U.

^{99}Mo, ^{122}Sb, ^{140}La, ^{141}Ce and ^{152}Eu have percentage fission yields from ^{235}U, of 6.1, 0.013, 6.3, 6 and 0.3 respectively[16]. Taking these fission yields into account, one calculates an apparent concentration of 0.87 p.p.m. molybdenum, 0.0001 p.p.m. antimony, 0.019 p.p.m. lanthanum and 0.54 p.p.m. cerium per p.p.m. of uranium.

TABLE VII

COMPARISON OF THE SENSITIVITY FOR THE ANALYSIS OF U, Mn AND In BY DESTRUCTIVE AND NON-DESTRUCTIVE METHODS

Method	*Matrix*	*Concentration of present impurities (p.p.m.)*			*Sensitivity (p.p.m.) for*		
		Sb	*Mn*	*Na*	*Mn*	*In*	*U*
Non-destructive	Crystal	$< 10^{-3}$	0.5	0.5	0.05	0.002	0.5
	Titania powder Titanium metal	100	5–50	100	0.5	0.01	5
Anion exchange and extraction	Titania powder Titanium metal	100	5–50	100	0.2	0.001	0.2
Liquid–liquid extraction	Crystal	$< 10^{-3}$	0.5	0.5	0.005	0.0002	0.05

In one of the analysed titania powder samples, uranium was detected. Table V shows that titania powder 1 contains 7.2 p.p.m. of uranium. Hence, the positive error introduced for molybdenum is 5.8 p.p.m. In a former article[9] the lower limit for the molybdenum analysis was set equal to 5 p.p.m., which is lower than our calculated interference. DAMS AND HOSTE[17] showed experimentally that the positive error for molybdenum introduced by fission of ^{235}U is 0.58 ± 0.03 p.p.m. per p.p.m. of uranium. Using this experimental value, one obtains an interference of 4.2 p.p.m. of molybdenum in the titania powder 1 sample. This interference cannot be detected as the lower limit is 5 p.p.m.

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SUMMARY

Manganese, indium and uranium in titanium, titania powder and titania crystals can be determined non-destructively or destructively, by means of solvent extraction with tri-*n*-butyl phosphate. Destructively, the sensitivity for the determinations is enhanced by a factor of 20.

RÉSUMÉ

Le manganèse, l'indium et l'uranium peuvent être dosés dans le titane, la poudre ou les cristaux d'oxyde de titane par activation neutronique, avec extraction au tributylphosphate, soit par voie destructive soit par voie non destructive. Par voie destructive la sensibilité des dosages est 20 fois plus grande.

ZUSAMMENFASSUNG

Mangan, Indium and Uran in Titan, Titandioxid-Pulver und Titandioxid-Kristallen können zerstörungsfrei oder durch Extraktion mit Tri-n-butylphosphat auf nassem Wege bestimmt werden. Bei der zweiten Methode wird die Empfindlichkeit für die Bestimmungen um den Faktor 20 gesteigert.

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THE POSSIBILITY OF ABSOLUTE ATOMIC ABSORPTION AND ATOMIC EMISSION FLAME SPECTROMETRIC ANALYSIS

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Any quantitative analytical procedure may be formulated quite generally as

$$X = \mathrm{f}\,(C) \tag{1}$$

where C is the concentration or the amount of the compound to be determined, and X is the measured signal, that may represent almost any physical quantity, but very often is simply a scale reading. In some cases (*e.g.* the measurement of spot areas in quantitative thin-layer chromatography), the correlation between X and C can only be established empirically from the signals measured for reference samples of known composition. In some other cases, a theoretical expression is known for the function f (C) that is reliable enough to allow a direct calculation of the concentration from a single measurement (in absolute units) of the physical quantity represented by X. Such methods of quantitative analysis are referred to as *absolute* methods of analysis and well-known examples are gravimetric and titrimetric analysis.

For the great majority of quantitative methods of analysis, including virtually all spectrometric methods, the theoretical expression for f (C) involves characteristic parameters that are only approximately known or subject to erratic changes with the conditions used in the analysis. Quantitative analysis is still possible when, at regular intervals, analytical curves are established for f (C) by means of references of known composition. Because the signal X can then be measured on the relative scale fixed by the reference samples, such methods are known as *relative* methods of analysis.

This pragmatic approach to quantitative analysis does not diminish the value of even an approximate theoretical expression for eqn. (1), because such an expression permits an evaluation of the factors affecting the determination and the optimization of the analytical procedure. This important contribution of theory to practical analysis justifies the continuing efforts to improve the expression for f (C) and to enlarge the knowledge of the characteristic parameters appearing in the equations. Every step forward provokes the question whether a hitherto relative method of analysis may be converted into an absolute one. Apart from practical consequences this would form an ultimate proof that the theoretical expression proposed for f (C) is correct and complete.

For atomic spectrometric methods of analysis few attempts have been made at an absolute application of eqn. (1). Some years ago one of the authors discussed the possibility of absolute *emission* analysis with the d.c. carbon arc[1] and concluded that the theoretical equation for f (C) in this case was sound, but that the practical applicability seemed remote.

RANN[2] has proposed an experimental arrangement for a possible absolute atomic *absorption* analysis with flames, although its practical applicability may be questioned[3]. However, additional fundamental data have recently become available for analytical flames, that allow a further exploration of the possibility of absolute flame spectrometric analysis either by absorption or by emission of atomic radiation.

THEORY

The theoretical expression for eqn. (1) in the case of flame spectrometry will not be derived from basic principles, but the relevant steps will be indicated and the reader is referred to previous literature[2-8] and to textbooks on atomic radiation[9,10].

The phase transition in a flame

Before emission or absorption of atomic radiation in a flame can be observed a phase transition is required to convert the dissolved sample molecules into free atoms. For this purpose a continuous flow of solution droplets is aspirated into the flame. The solvent evaporates completely and contributes to the flame volume that is occupied mainly by the burning flame gases, rapidly expanding at the high flame temperature. The remaining salt particles evaporate more slowly and decompose partly into the free atoms required for atomic spectrometric analysis.

Consequently[4,5]

$$N_{\mathrm{at}} = \frac{298}{T} \, \frac{\beta \, \varepsilon \, V_{\mathrm{liq}} \, 10^{-3}}{(24 \, V_{\mathrm{liq}}/M_{\mathrm{s}} + V_{\mathrm{gas}} \, n_{\mathrm{T}}/n_{298})} \, \frac{6.02 \cdot 10^{17} \, C}{M_{\mathrm{a}}} \tag{2}$$

where N_{at} is the number of free atoms of the element per cm^3 of flame gases,
C is the solution concentration of the element in p.p.m.,
M_{s} is the relative molecular mass of the solvent,
M_{a} is the relative atomic mass of the element,
V_{gas} is the total flow rate of flame gases at room temperature in l/min,
n_{T}/n_{298} converts this to the molar composition in the flame,
V_{liq} is the flow rate of solution actually reaching the flame in g/min (or ml/min for aqueous solutions),
ε is the fraction of salt particles evaporated to sample molecules,
β is the fraction of sample molecules dissociated into free, neutral atoms, and $298/T$ allows for the expansion of flame gases and solvent vapour from room temperature to flame temperature, T.

Excitation in a flame

The monochromator of the flame spectrometer is assumed to select radiation of a single atomic transition and consequently the emission or absorption of radiation is determined by the concentration of free atoms of an element in a single, specified energy level

$$N = (g/B) \, N_{\mathrm{at}} \exp(-E/kT) \tag{3}$$

Here it is assumed that the flame is in thermal equilibrium, g and E are the statistical weight and the excitation energy of the level *from which the transition starts*, k is Boltzmann's constant and B is the partition function of the atom at flame temperature, T.

Emission of radiation

For a *laminar* flame with a uniform temperature and atomic concentration along the optical axis, the intensity, I, of radiation emitted in a certain transition, free from self-absorption, is given[8] by:

$$I = (A_t/4\pi)\, h\nu\, L\, N \tag{4}$$

where A_t is the transition probability, h is Planck's constant, ν is the frequency of the radiation, and L is the path length in the flame. For *turbulent* flames the atomic concentration N varies across the flame and the poorly defined path length L must be replaced by an effective value[6].

Measurement of intensity

The deflection of a current meter or a recorder pen is proportional to the radiant power incident upon the detector, which in turn is proportional to the emission intensity (in erg sec^{-1} cm^{-2} sr^{-1}), thus

$$u = K\, I \tag{5}$$

The proportionality constant is determined by the properties of the monochromator (slit dimensions, aperture, reflection losses), of the detector (sensitivity), and of the amplifier (gain). Although the optimization of this factor may yield a substantial improvement of analytical results, it should properly be discussed in connection to the noise generated in the spectrometer, as has been done by Winefordner and Vickers[4].

For the present discussion it is sufficient to note that the value of K can be readily calibrated with a standard source of radiation, such as a tungsten ribbon lamp of known radiance[6].

Absorption of radiation

The apparently simple Beer–Lambert law for the absorption of radiation takes a complicated form in atomic absorption spectrometry because the atomic absorption coefficient may change appreciably over the effective spectral bandwidth that is determined by the intensity profile of the source of radiation. The complete integral equation has been given by Rann[2], but in the present discussion an approximate expression will be used, that has been derived previously for a line source of radiation[7]

$$A = -\log \frac{I_t}{I_0} = 0.434 \sqrt{\frac{\pi M_a}{2\,RT}}\; \frac{\lambda^3 g_u A_t LN\ \delta(a,v)}{8\,\pi^2 g} \tag{6}$$

Here A is the absorbance, I_t and I_0 are the transmitted and the incident total source intensitities, R is the gas constant and λ is the wavelength of the transition *starting* from a level with statistical weight g and *ending* at an upper level with statistical weight g_u. Again, the path length L is well defined for uniform, laminar flames, but should be replaced by an effective value for non-uniform, turbulent flames. The critical quantity in eqn. (6) is the function $\delta(a, v)$, which formally accounts for the relative profiles of the source line and the absorption line in the flame; this will be discussed in the next section.

Final equations

When the above equations are combined, numerical factors are collected and some terms are rearranged, the following explicit expressions are derived for eqn. (1)

in the case of atomic flame spectrometry.

From eqns. (2), (3), (4) and (5) for the absolute emission intensity

$$I = \frac{u}{K} = 1.43 \cdot 10^{16}\, LC \left(\frac{A_{\mathrm{t}}\, g\, h\, \nu}{B\, M_{\mathrm{a}}}\right)\left(\frac{\exp(-E/kT)}{T}\right)\left(\frac{V_{\mathrm{liq}}}{24\, V_{\mathrm{liq}}/M_{\mathrm{s}} + V_{\mathrm{gas}} n_{\mathrm{T}}/n_{298}}\right) \varepsilon\beta \qquad (7)$$

From eqns. (2), (3), (5) and (6) for the absorbance

$$A = -\log \frac{u_{\mathrm{t}}}{u_0} =$$

$$= 1.24 \cdot 10^{15}\, LC \left(\frac{\lambda^3 g_{\mathrm{u}} A_{\mathrm{t}}}{B\sqrt{RM_{\mathrm{a}}}}\right)\left(\frac{\exp(-E/kT)}{T^{\frac{3}{2}}}\right)\left(\frac{V_{\mathrm{liq}}}{24 V_{\mathrm{liq}}/M_{\mathrm{s}} + V_{\mathrm{gas}} n_{\mathrm{T}}/n_{298}}\right) \varepsilon\beta\delta(a,v) \qquad (8)$$

It is recalled that C is expressed in p.p.m., V_{gas} in l/min, V_{liq} in g/min, and the remaining quantities in cgs-units.

It should be emphasized that the equations are not restricted to flames, but are quite generally applicable to all sources of excitation that are in thermal equilibrium and are operated under forced convection, such as gas-stabilized arcs[11–14] and high-frequency plasmas[14–16] (the introduction of solid samples requires a slight modification). The equations also allow a mutual comparison of such sources, but, unfortunately, for most sources the necessary data are lacking. Therefore, the present discussion will be restricted to flames. Before the possibility of absolute flame spectrometric analysis is considered, the equations will be discussed in general terms to evaluate the significance of various parameters in flame spectrometry.

FACTORS AFFECTING THE SIGNALS IN FLAME SPECTROMETRY

The right-hand sides of eqns. (7) and (8) are written as the product of five terms that will be considered successively. The first term expresses the fact that the emission intensity and the absorbance are proportional to the solution concentration, C, of the element concerned. Indeed, this is true for the somewhat ideal, though not unrealistic conditions assumed presently. In practice, however, analytical curves may bend for a variety of reasons: self-absorption in emission analysis[8], broad hollow-cathode lines[17] or source background radiation[18] in absorption analysis, non-linear aspiration, ionization or dissociation equilibria in both[19]. The first term also states that the signal is proportional to the (effective) path length in the flame, which explains the popularity of slot burners, both in atomic absorption and atomic emission flame spectrometry[20].

The second term in the equation includes physical constants characteristic of the element that is determined (B, M_{a}) and of the transition selected (A_{t}, ν, λ). All other factors being equal, the transition with the highest probability, A_{t}, yields the largest signals. This is generally true for atomic absorption spectrometry (where actually the product $A_{\mathrm{t}}\lambda^3$ should be considered), but for atomic emission spectrometry a gain in transition probability may be offset by a reduction of the Boltzmann factor in the third term of eqn. (7). For example, in the case of manganese the triplet at 2800 Å is preferred in absorption, because its transition probability is twenty times larger than that for the triplet at 4030 Å (Tables II and III). At 2500°K, however, the ratio of the Boltzmann factors is 500 in favour of the triplet at 4030 Å, so this transition is preferred in flame emission spectrometry.

The third term in eqns. (7) and (8) accounts for the *explicit* influence of the flame temperature, T. Obviously, the excitation potential, E, of the *starting* level of the transition must be chosen as small as possible. For absorption spectrometry this is the *lower* level of the transition and consequently E can be very small or zero (resonance transitions). In emission spectrometry this is of course not possible and then the resonance transition with the largest wavelength (smallest E) is usually the most sensitive one, as was demonstrated for manganese.

In flame emission spectrometry the temperature should be as high as possible (compare the results in Table II). It is true that ionization may deplete the number of free atoms, especially for alkali and alkaline earth metals, but generally this can be suppressed sufficiently by the addition of excess cesium or potassium[20,21]. For resonance atomic absorption, however, where $\exp(-E/kT) = 1$, the denominator, $T\sqrt{T}$, seems to imply that the absorbance increases with lower temperature. This is indeed true, but only if the *implicit* influence of the flame temperature through other variables, notably ε and β, can be ignored. *The general rule for atomic absorption spectrometry is, that the flame temperature must be high enough to ensure complete evaporation and dissociation of sample molecules, but a further increase of the flame temperature is actually unfavourable.* Indeed, for such readily atomized elements as Mg, Cu, Cd, Ag, etc., low-temperature, air-supported flames yield better sensitivity than high-temperature, nitrous oxide-supported flames (Table III).

Very often, however, evaporation or dissociation of sample molecules is incomplete and then the *implicit* influence of the flame temperature markedly exceeds the *explicit* influence through the factor $T\sqrt{T}$[22]. High-temperature flames are clearly required to atomize "refractory" elements[5] and to minimize chemical interferences[23,24].

The fourth term is equal for both eqns. (7) and (8) and characteristic for the burner–nebulizer combination used. The flow rate of the flame gases, V_{gas}, should be as low as possible, but several factors restrict the lower limit that can be reached in conventional burner systems. With pneumatic aspiration the pressure (and thus the flow rate) of the aspirating gas must be large enough to nebulize a sufficient amount of solution into the flame. Together with the desired fuel-to-oxidant ratio, this puts a lower limit to V_{gas}. For other nebulizing devices (ultrasonic nebulizers), the gas flow is ultimately restricted by the balance between the burning velocity of the flame and the linear gas flow required to prevent back-flash. For an acetylene–air flame (burning velocity 3 m/sec[10]) on a burner with preferably a long slot ($L = 10$ cm) and minimum slotwidth of 0.5 mm (to prevent clogging), this results in a glas flow not less than 10 l/min.

The flow rate of solution droplets *into the flame*, V_{liq}, appears in the numerator as well as in the denominator of the equations. Consequently, the emission intensity and the absorbance first increase linearly with the solution flow rate, but gradually the increase is reduced and a limiting value of $M_s/24$ is approached. Physically this means, that at extremely large solution flow rates the flame volume is equal to the volume of evaporated solvent. Obviously, this can not even be approximated in practice.

For aqueous solutions and a gas flow of 10 l/min, this can be summarized as follows. For solution flow rates up to 1 ml/min, the signals increase linearly with flow rate to one tenth of their limiting value. If the solution flow rate is raised to 5 ml/min, the signals still increase substantially to about one third of their limiting value. However, even if a further increase of the solution flow rate were possible without changing the flame conditions, this could only raise the signals threefold. *Consequently, an* *effective solution flow rate of about 5 ml/min represents a practical upper limit in conventional flame spectrometers.*

A solution flow rate of 5 ml/min can be realised with total-consumption burners, but the evaporation of sample particles is far from complete ($\varepsilon < 1$). A substantial improvement is observed with organic solvents[25,26], for which sample evaporation is enhanced and also the molecular mass, M_s, is larger. On the other hand, the diameter of the flame on a total-consumption burner is rather small (1 cm).

For slot-burners the optical path length can be as large as 10 cm, but the solution flow rate of chamber-type aspirators with pneumatic or ultrasonic nebulizers is only about 0.5 ml/min[15,27]. From eqns. (7) and (8) it might be expected that for this type of aspirator an increase of the solution flow rate would produce a proportional increase of the signals. In practice, however, it is found that the droplet size increases with solution flow rate[27] and this tends to reduce sample evaporation, which is virtually complete at small flow rates of 0.5 ml/min[5]. Increased droplet size also enhances the interferences resulting from incomplete sample evaporation.

The quantities discussed so far are either characteristic for the spectral transition selected (excitation potential E, probability A_t, wavelength λ), or characteristic for the flame chosen (temperature T, conversion factor n_T/n_{298}), or determined by the burner (flow rates V_{gas} and V_{liq}). By contrast, the quantities in the final term of eqns. (7) and (8) depend more or less critically upon all parameters in flame spectrometric analysis, *i.e.* the element to be determined, the sample offered for analysis, the burner used, and the flame selected. In addition to this, the function $\delta(a,v)$ depends upon the source of radiation used. These quantities are the most difficult ones to discuss and form the major obstacle to possible absolute quantitative flame spectrometric analysis.

The droplet generator described by HIEFTJE AND MALMSTADT[28] offers interesting possibilities for studying evaporation processes in the flame, but at present, very little is known about the sample evaporation efficiency, ε, that was briefly mentioned above. In the present equations it is assumed that the *solvent* is completely evaporated. This will probably be true for chamber-type aspirators with their small solution flow rate and small droplet size. Light scattering measurements indicate that for total-consumption burners solvent evaporation proceeds also rapidly and is practically complete at the regions normally considered in flame spectrometry[29]. On the other hand, incomplete *sample* evaporation is generally believed to be a major cause of chemical interferences[27,30], especially in turbulent flames where sample evaporation is kinetically controlled rather than thermally controlled[25]. The minimization of interferences in high-temperature laminar flames has been attributed to the nearly complete sample evaporation in these flames[23,31].

In principle, the degree of atomization, β, may be calculated theoretically from rather simple equations[19,22], but this requires accurate knowledge of the flame composition and the dissociation energies. Generally, this information is not available, although a few promising results have been reported[32]. Experimental measurement of degrees of atomization, based upon eqn. (8) or its equivalent for a continuum source of radiation, have been reported for several premixed, laminar flames[5,32,33]. Although the results provide valuable information about the degree of atomization of various elements in different flames, their applicability in analytical practice should not be overrated. The data actually represent the product $\varepsilon\beta$ in eqns. (7) and

(8) and refer to "pure" solutions where a single compound is aspirated at rather low concentrations (thus, $\varepsilon \approx 1$).

Consequently, the results can only be used in the absence of chemical interferences from other sample constituents. Also, degrees of atomization appear to depend markedly upon both the element and the flame, and the data reported so far cannot be used to predict values for other elements or for other flame compositions.

The final quantity in eqn. (8), which does not appear in eqn. (7), is the function $\delta(a,v)$ that accounts for the relative profiles of the absorption line in the flame and the emission line of the hollow-cathode lamp. If the width of the hollow-cathode source line is negligible compared to the width of the absorption line, $v=0$ and eqn. (8) is exact. If, moreover, the profile of the absorption line is determined by Doppler-broadening only, a is also zero, and $\delta(0,0)=1$[9]. However, in analytical flames at atmospheric pressure collisional broadening is usually important and this results in $a>0$ and $\delta(a,0)<1$. For any value of a the corresponding value of $\delta(a,0)$ can be found in the literature[9,34], but unfortunately, very little information is available about the a-parameter for transitions and flames of analytical interest. The results reported[35] indicate that a varies between 0.5 and 1.0 for most lines and, therefore, $\delta(a,0)$ ranges from 0.8 to 0.4.

However, complications arise. The width of the hollow-cathode emission line may not be negligible compared to the width of the absorption line[36,37]. In that case, $\delta(a,v)$ in eqn. (6) should be replaced by an integral that can only be computed numerically if the complete profile functions of the source line and the absorption line are known[2]. However, even if such data were available, the result might still be incorrect if the transition under consideration shows hyperfine structure from multiple isotopes or nuclear magnetic moments. The general conclusion is that the value to be substituted for $\delta(a,v)$ in eqn. (8) is smaller than unity and usually also smaller than the range given for $\delta(a,0)$ above. Indeed, from a comparison of the absorptions measured with a continuum source and a hollow-cathode lamp, respectively, a few "effective" values for $\delta(a,v)$ that indicate a range between 0.1 and 0.7, have been reported[7,38].

The limited applicability of reported degrees of atomization and the uncertainty of the value to be substituted for $\delta(a,v)$ form the major obstacles to absolute flame spectrometric analysis. This will be illustrated in the next section.

AN ATTEMPT AT ABSOLUTE FLAME SPECTROMETRIC ANALYSIS

The application of eqns. (7) and (8) to absolute analysis must necessarily be restricted to those flames and elements for which all variables in the equations are known. Accordingly, premixed laminar flames were chosen, for which temperatures and degrees of atomization (actually $\varepsilon\beta$) have been reported previously[5]. Values for the pertinent flame parameters are presented in Table I.

In the usual single-beam flame spectrometric arrangement, the chopper was placed either between the hollow-cathode lamp and the flame for absorption measurements or between the flame and the monochromator for emission measurements. Emission intensities were converted to absolute values by calibrating the spectrometer with a standard tungsten ribbon lamp, calibrated against a black body, placed at the position of the flame with the same setting of the spectrometer.

Dilute solutions of a single compound were aspirated into the flame to ensure

TABLE I

FLAME PARAMETERS[5]

Flame	*L (cm)*	*T (°K)*	V_{liq} *(g/min)*	V_{gas} *(l/min)*	n_T/n_{289}
C_2H_2–N_2O	5.1	2950	0.39	11.14	1.64
H_2–N_2O	5.1	2900	0.39	20.7	1.00
C_2H_2–air	10.2	2450	0.33	10.4	1.03
H_2–air	10.2	2000	0.33	20.0	0.91

the absence of chemical interferences. The burner height was optimized for each element and analytical curves were prepared ranging over at least one decade. In the emission mode linear analytical curves confirmed the absence of self-absorption. In the absorption mode commercial hollow-cathode lamps were run at the lowest possible current to minimize the width of the source line. The observation that the analytical curves were linear up to high absorbance values ($A > 1$) indicated that the source line width is indeed reasonably smaller than the absorption line width in the flame[17]. The analytical curves yielded experimental values for the emission intensity and the absorbance corresponding to a 1-p.p.m. solution of the element. It may be pointed out that these are actually *sensitivity* values derived from the slopes of the analytical curves, *i.e.* the change of the intensity or the absorbance for a 1-p.p.m change in the concentration. Theoretical values for the slopes were calculated from eqns. (7) and (8) and the results were compared.

Table II shows the results for the emission intensity of eight spectral lines in three different flames. The hydrogen–air flame was not considered, because the suspected lack of thermal equilibrium in this flame[5] makes eqn. (3) inapplicable. The line Al 3944 could only be observed in the nitrous oxide–acetylene flame, whereas strong self-absorption prevented a reliable measurement of Na 5890 in this flame. As is clear from the last column in the Table the difference between the experimental and the theoretical values never exceeds a factor of two and 12 out of 21 values agree within 30%. This is about as good as may be expected from the accuracy of the data for the degrees of atomization and the flame temperatures[5] and the accuracy of absolute intensity measurements. It should be appreciated that the calculated intensities are extremely sensitive to deviations of the assumed temperatures[5,10,23,39,40] from their true values during the experimental observations.

Table III presents the results for the absorbance of five spectral lines measured with hollow-cathode lamps in four premixed, laminar flames. Again, the experimental value of the absorbance corresponding to a 1-p.p.m. solution is readily derived from the analytical curve. In the theoretical calculation, however, the relative profiles of the source line and the absorption line present an additional problem. The column headed $A^0{}_{th}$ presents absorbance values calculated from eqn. (8) on the assumption that $\delta(a,v) = 1$; this corresponds to a negligible width of the source line and a purely Doppler-broadened absorption line. As expected the absorbance calculated in this way exceeds the experimental values, typically by a factor of two to three. This indicates an "effective" value of $\delta(a,v)$ between 0.3 and 0.5.

A substantial improvement is obtained, if literature data for the a-parameter are used to account for the collisional broadening of the absorption line. Unfortunately, no a-parameters have been measured yet for the C_2H_2–N_2O, the H_2–N_2O and the

H_2–air flame. However, the values measured by McGEE AND WINEFORDNER[35] for turbulent C_2H_2–O_2, H_2–O_2 and H_2–Ar-entrained air flames can be used as a first approximation. It should be pointed out, that the absorbance values in the column headed A_{th} ($= A^0_{th}\ \delta(a,0)$) still assume a negligible source line width. Yet, the final column of the Table shows that the theoretical values calculated in this way agree satisfactorily with the experimental data. Because no information is available on collisional broadening of manganese and tin lines, such calculations cannot be carried out for the final two transitions in Table III. However, the Table as a whole suggests as a rule-of-thumb that agreement within a factor of two can be obtained for all transitions in flames at atmospheric pressure, if a is taken to be unity, or $\delta(a,0) \approx 0.4$.

Now, what conclusions can be drawn from this? It is clear that absolute flame spectrometry does not offer new opportunities for practical analysis. A theoretical calculation of concentrations from absorbances or intensities (measured in absolute units) with eqns. (7) and (8) is limited to specific flames and spectral transitions and, in general, can only claim an accuracy of a factor of two. Obviously, the analyst may just as well estimate the concentration of his sample solution by comparison with a simple standard, or even simpler, by comparison with a table of sensitivity values prepared previously or reported in the literature[41].

It should also be pointed out that in the present study the flames were carefully adjusted to the same fuel-to-oxidant ratio as used in measuring the temperature and the degrees of atomization[5]. For some elements (Cu, Mn) the absorbance and the emission intensity are fairly insensitive to changes of the flame composition. The emission intensity of some other transitions, however, depends critically upon the flow rate of the fuel gas and the height of observation in the flame (*e.g.* Ca 4226, Ba 5535 and Al 3944). Thus, it may be argued that the agreement between experimental and theoretical values shown in Tables II and III merely demonstrates the internal consistency of the present measurements and the previous determination of temperature and degrees of atomization.

However, this conclusion would be too pessimistic. The continuum-source absorption used in measuring the degrees of atomization[5] differs from the line-source absorption and emission intensity measured presently. Also, a different burner was used for the air-supported flames, resulting in a change of the variables V_{llq} and L. Finally, the values used for the flame temperatures and the degrees of atomization are supported by other data[10,23,32,33,39,40]. Consequently, the observed agreement between experimentally measured absorbances or intensities and theoretically predicted values justifies the conclusion that eqns. (7) and (8) form a correct description of these quantities. The expressions can therefore be used with confidence in further studies of flames and similar sources of excitation. Obvious applications are the mutual comparison of various flames and burners, as has been mentioned above, and the expansion of our knowledge of fundamental data. Thus, absolute thermal emission intensities can provide values for the product $\varepsilon\beta$, whereupon line-source absorption measurements yield an estimate of the collisional broadening of spectral lines.

However, the possibility of a theoretical verification of atomic emission and atomic absorption signals can also be of practical value to the analyst who wishes to check the analytical performance of his particular burner–flame combination. The signals (or rather sensitivities or slopes of analytical curves) measured for reference

TABLE II

ABSOLUTE ATOMIC EMISSION FLAME SPECTROMETRY

Element	*λ (Å)*	A_t^5 *(10^8 sec^{-1})*	*Flame*	β^5	I_{th}	I_{exp}	I_{exp}/I_{th}
					(erg cm^{-2} sec^{-1} sr^{-1} p.p.m.$^{-1}$)		
Al	3944	0.523	C_2H_2–N_2O	0.13	0.958	1.08	1.13
Ba	5535	1.05	C_2H_2–N_2O	0.17	90.4	56.2	0.62
			H_2–N_2O	0.0046	1.89	1.03	0.55
			C_2H_2–air	0.0018	0.61	0.63	1.03
Ca	4226	1.93	C_2H_2–N_2O	0.52	176	155	0.88
			H_2–N_2O	0.036	8.99	8.82	0.98
			C_2H_2–air	0.07	7.81	4.7	0.60
Cr	4254	0.23	C_2H_2–N_2O	0.63	8.27	6.98	0.85
			H_2–N_2O	0.042	0.41	0.34	0.83
			C_2H_2–air	0.071	0.33	0.39	1.18
Cu	3247	0.95	C_2H_2–N_2O	0.66	1.82	3.39	1.85
			H_2–N_2O	0.92	1.77	1.78	1.00
			C_2H_2–air	0.88	0.38	0.19	0.50
Fe	3720	0.14	C_2H_2–N_2O	0.83	0.58	1.00	1.72
			H_2–N_2O	0.91	0.46	0.69	1.50
			C_2H_2–air	0.84	0.15	0.11	0.73
Mn	4031	0.176	C_2H_2–N_2O	0.77	4.60	6.40	1.39
			H_2–N_2O	0.54	2.37	1.21	0.51
			C_2H_2–air	0.62	1.09	1.9	1.74
Na	5890	0.64	H_2–N_2O	0.90	1710	2250	1.32
			C_2H_2–air	1.00	1570	1330	0.85

TABLE III

ABSOLUTE ATOMIC ABSORPTION FLAME SPECTROMETRY

Element	*λ (Å)*	$A_t^{5,44}$ *(10^8 sec^{-1})*	*Flame*	β^5	a^{35}	*Absorbance for 1 p.p.m.*			
						A^0_{th} $\lvert\delta = 1\rvert$	A_{th} $\lvert\delta(a,o)\rvert$	A_{exp}	A_{exp}/A_{th}
Ag	3281	1.57	C_2H_2–N_2O	0.57	0.95	0.0546	0.024	0.021	0.88
			H_2–N_2O	0.72	0.64	0.0628	0.035	0.029	0.83
			C_2H_2–air	0.70	1.0	0.257	0.11	0.112	1.0
			H_2–air	0.85	0.84	0.252	0.12	0.096	0.8
Cu	3247	0.95	C_2H_2–N_2O	0.66	0.56	0.0476	0.028	0.0135	0.5
			H_2–N_2O	0.92	1.0	0.0604	0.025	0.0175	0.7
			C_2H_2–air	0.88	0.46	0.245	0.16	0.082	0.5
			H_2–air	0.96	0.7	0.218	0.115	0.073	0.6
Mg	2852	3.03	C_2H_2–N_2O	0.88	0.32	0.338	0.25	0.183	0.73
			H_2–N_2O	0.97	0.30	0.339	0.25	0.203	0.81
			C_2H_2–air	1.00	—	1.469	—	0.770	—
			H_2–air	0.87	0.46	1.034	0.67	0.770	1.15
Mn	2795	3.65	C_2H_2–N_2O	0.77		0.099		0.026	
			H_2–N_2O	0.54		0.063		0.028	
			C_2H_2–air	0.62		0.304		0.106	
			H_2–air	0.75		0.299		0.092	
Sn	2863	0.54	C_2H_2–N_2O	0.82		0.0077		0.00094	
			H_2–N_2O	0.059		0.00051		0.00015	
			C_2H_2–air	0.043		0.0018		0.00081	
			H_2–air	0.38		0.016		0.0054	

elements, such as Ag, Cu, Mg, Mn and Na, can be compared with theoretically expected values.

It should also be possible to compare such signals with results reported in the literature, where the expressions could be used to correct for minor differences between burner parameters, such as L, V_{liq} and V_{gas}. Unfortunately, there appears to be a strong tendency to prefer the presentation of limits of detection over the quotation of sensitivities[15,16,20,24,39,42]. As the limit of detection is based upon the signal-to-noise ratio[4], low limits of detection often result from low noise levels that cannot be expected from moderately priced commercial instruments. By contrast, sensitivity values should be repeatable with any instrument and are open to theoretical verification. The exaggerated controversy between atomic absorption and atomic emission protagonists[31,42,43] could also be raised to a more sophisticated level, if sensitivities were presented in addition to limits of detection. Sensitivities would also permit a more objective appraisal of new types of burners and flames and novel sources of excitation.

SUMMARY

Complete expressions are given relating the solution concentration of an element with the absolute intensity of a spectral transition emitted in a flame and with the absorbance measured with a line-source of radiation. The variables appearing in the equations are discussed for their significance in analytical flame spectrometry. It is shown that theoretically calculated emission intensities and absorbances agree within a factor of two with experimentally measured values. Although this agreement is insufficient for practical absolute flame spectrometric analysis, it is concluded that the expressions can be used with confidence in further theoretical studies. It is argued that sensitivities form a better criterion for the characterization of flames and burners than limits of detection.

RÉSUMÉ

Les auteurs examinent la possibilité d'analyse spectrométrique absolue par absorption atomique et émission atomique de flamme. Des expressions complètes sont données tenant compte de la concentration d'un élément en solution, de l'intensité et de l'absorption mesurées. On constate que les intensités d'émission et les absorptions calculées théoriquement concordent, avec un facteur de deux, avec les valeurs mesurées expérimentalement. Bien que ce soit insuffisant pour des analyses spectrométriques de flamme, absolues, ces expressions peuvent cependant être utilisées pour des études théoriques ultérieures.

ZUSAMMENFASSUNG

Es werden quantitative Beziehungen hergestellt zwischen der Lösungskonzentration eines Elements und der absoluten Intensität eines Spektralüberganges, der in einer Flamme stattfindet, sowie der Extinktion, die bei Verwendung eines Linienstrahlers gemessen wird. Die variablen Grössen in den Gleichungen werden diskutiert bezüglich ihrer Bedeutung für die analytische Flammenspektrometrie. Es wird gezeigt, dass die theoretisch berechneten Emissionsintensitäten und Extinktionen innerhalb eines Faktors von zwei mit den experimentell gemessenen Werten übereinstimmen. Obgleich diese Übereinstimmung für eine praktische Absolut-Flammenspektralanalyse unzureichend ist, können die Beziehungen für weitere theoretische Untersuchungen benutzt werden. Es wird erörtert, dass die Empfindlichkeiten ein besseres Kriterium für die Charakterisierung von Flammen und Brennern darstellen als die Nachweisgrenzen.

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DETERMINATION OF SELENIUM IN SULFUR BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Relatively little attention has been given to the atomic absorption spectrophotometry of selenium. ALLAN[1] was the first to report the atomic absorption of selenium. SPRAGUE *et al.*[2] determined selenium in copper and copper alloys. RANN AND HAMBLY[3] and DAGNALL *et al.*[4] described the use of a selenium electrodeless discharge tube as a radiation source. In all these studies an air–acetylene flame was used. Recently, CHAKRABARTI[5] mentioned that an air–acetylene flame is more sensitive than an air–hydrogen flame for all the selenium lines, including the most sensitive 196.0-nm line, although this line is more strongly absorbed by the gases of the air–acetylene flame than by those of the air–hydrogen flame.

The present paper describes the use of an air–hydrogen flame for the atomic absorption spectrophotometric determination of selenium in sulfur. The usual slot burner for air–acetylene flames was not suitable for this determination, because of clogging of the slot by the high concentration of materials in the sample solutions. Clogging was completely avoided by the use of a total-consumption burner with an air–hydrogen flame.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash AA-1 atomic absorption spectrophotometer, equipped with a scanning wavelength-selector, a total-consumption air–hydrogen nebulizer burner, and a selenium hollow-cathode lamp (Westinghouse Co. Ltd.) were used.

In order to reduce the absorption losses caused by air, mirrors and lenses, the optical-pass system was changed from the original quintuple-pass to a triple-pass and, moreover, all mirrors and lenses were replaced by those made of "Suprasil" which is more transparent to radiation in the vacuum ultraviolet region than commercial quartz.

A hydrogen discharge lamp was used as a radiation source for the measurement of the background absorption in the ultraviolet region.

The spectrophotometer has a reciprocal dispersion of 1.6 nm/mm with a grating of 1180 lines/mm blazed for 300.0 nm. An HTV-R106 photomultiplier (Hamamatsu Television Co. Ltd.) was employed as a detector.

Reagents

Standard solution of selenium. A stock solution containing 1000 p.p.m. of selenium was prepared by dissolving 5.0 g of metallic selenium (99.999%) in 20 ml of concentrated nitric acid and diluting the resultant solution to 500 ml with distilled water. Various other concentrations were made by diluting the stock solution.

Other reagents such as those used for interference studies were prepared from analytical-grade chemicals.

RESULTS AND DISCUSSION

Selection of analytical line

The 196.0-nm line was chosen for the atomic absorption measurement of selenium, because it is the most sensitive. The intensity of this line, however, is weak compared with other lines (204.0, 206.3, 207.5 and 216.4 nm) and, therefore, the applied voltage for the photomultiplier as well as the slit width had to be increased when the absorption was measured at this wavelength.

Lamp current

The hollow-cathode lamp was operated at 14 mA. The absorbance of selenium was constant at a lamp current from 10 to 18 mA and increased slightly as the current decreased below 10 mA.

Slit width

The widths of the entrance and exit slits of the spectrophotometer can be changed independently of each other at 100, 300 and 500 μ. Experiments with various combinations of the entrance and exit slits indicated that the slit width was not critical for the measurements of the absorbance of selenium at 196.0 nm. This reflects the absence of undesirable attendant emission lines. The entrance and exit slits were therefore both maintained at 300 μ.

Flame composition and burner height

The ratios of hydrogen pressure to air pressure were varied from 0.3 to 1.2 and the absorbances were measured for 25 p.p.m. of selenium in aqueous solution in various parts of the flame to find the optimum flame composition and burner height. The results are shown in Fig. 1; the burner height was taken as the distance between the lowest lightbeam of the three beams and the burner tip. Figure 1 indicates that the absorption caused by selenium atoms is stronger in fuel-rich flames than in fuel-lean flames and depends strongly on the burner height. The optimum conditions for selenium were as follows: hydrogen pressure, 0.9 kg cm^{-2}, air pressure, 1.0 kg cm^{-2}, burner height, 35 mm below the light beam.

Sample feed rate

The effect of the sample feed rate on the absorbance of selenium (25 p.p.m.) was examined in the flame of the optimal composition. The feed rate was varied by changing the air pressure, the pressure ratio of hydrogen to air being kept constant at 9:10. As the feed rate was increased from 2 to 6 ml min^{-1}, the absorbance increased, but further increase in the feed rate up to 7 ml min^{-1} caused only a negligible variation in absorbance. The sample feed rate for an air pressure of 1.0 kg cm^{-2}, was used in all later work.

Calibration curve

Under the optimal conditions outlined above, a straight calibration graph was found over the range 0–50 p.p.m. of selenium. The sensitivity for selenium was 0.4 p.p.m. for 1% absorbance.

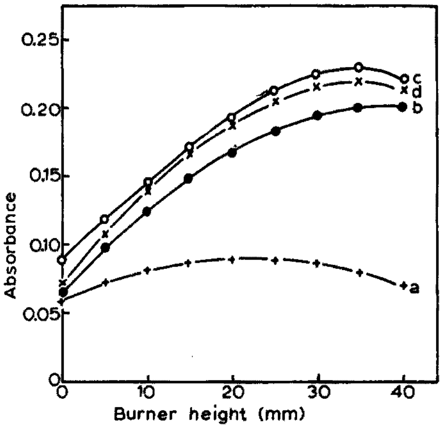


Fig. 1. Absorbances of selenium in an air–hydrogen flame of various compositions and at various burner heights. Air pressure: 1.0 kg cm^{-2}. Concentration of selenium: 25 p.p.m. Hydrogen pressure: (a) 0.3, (b) 0.6, (c) 0.9, (d) 1.2 kg cm^{-2}.

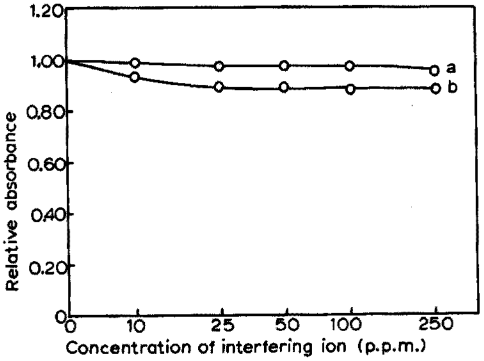


Fig. 2. Effects of lithium and sodium on absorbance of 25 p.p.m. of selenium. (a) Sodium, (b) lithium.

TABLE I

EFFECTS OF DIVERSE ELEMENTS ON ATOMIC ABSORPTION OF SELENIUM AT 196.0 nm WITH AN AIR–HYDROGEN FLAME

Concentration of elements added, 500 p.p.m.; selenium added, 50.0 p.p.m.)

Element	*Se found (p.p.m.)*	*Recovery of Se (%)*	*Element*	*Se found (p.p.m.)*	*Recovery of Se (%)*	*Element*	*Se found (p.p.m.)*	*Recovery of Se (%)*
Al[a]	48.5	97.0	Hg[a]	49.0	98.0	P[d]	51.0	102.0
As[b]	50.0	100.0	K[a]	49.2	98.4	Pb[c]	22.5	45.0
Ba[a]	38.0	76.0	La[a]	48.5	97.0	Sb[a]	49.0	98.0
Bi[c]	51.0	102.0	Li[a]	43.9	87.8	Sr[c]	43.1	86.2
Ca[c]	49.0	98.0	Mg[e]	50.2	100.4	Te[b]	48.8	97.6
Cd[e]	49.8	99.6	Mn[c]	51.0	102.0	V[d]	48.8	97.6
Co[e]	50.2	100.4	Mo[d]	50.2	100.4	W[b]	49.4	98.8
Cr[c]	49.2	98.4	Na[a]	47.0	94.0	Zn[a]	50.5	101.0
Cu[c]	49.0	98.0	Ni[e]	52.0	104.0	Zr[c]	47.8	95.6
Fe[a]	49.2	98.4						

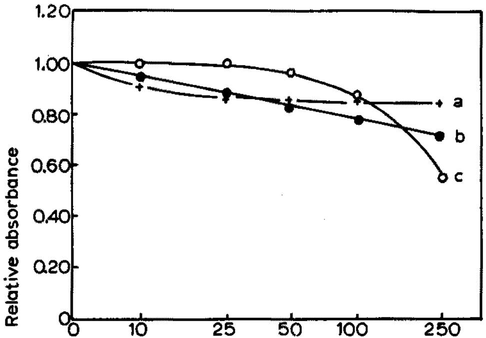
Added as chloride.
Added as sodium arsenite, tellurite or tungstate, respectively.
Added as nitrate.
Added as ammonium molybdate, phosphate or vanadate, respectively.
Added as sulfate.

Effect of other elements

The effect of various other elements on the atomic absorption of selenium was first studied at constant concentration levels: aqueous solutions containing 50 p.p.m. of selenium and 500 p.p.m. of other elements. The results are shown in Table I. Most elements, except for barium, lead, lithium, sodium and strontium, gave no interference, the deviation of the absorbance of selenium being less than 5%. The effects of the interfering ions were studied in more detail.

Lithium and sodium as chloride showed a depressing effect on the absorbance of selenium, whereas potassium chloride had no effect. As shown in Fig. 2, the absorbance of selenium gradually decreased with an increase of the concentrations of lithium and sodium. This decrease cannot be explained satisfactorily.

Figure 3 shows the effects of barium, lead and strontium ions on the absorbance of selenium. These cations had a depressing effect, the extent of which depended on the nature of the cations. These interferences are probably chemical in nature, since these cations form only slightly soluble selenites[6]; selenite is assumed to be the predominant form of selenium in the solutions tested. The thermal decomposition of these metal selenites may be difficult in the flame.



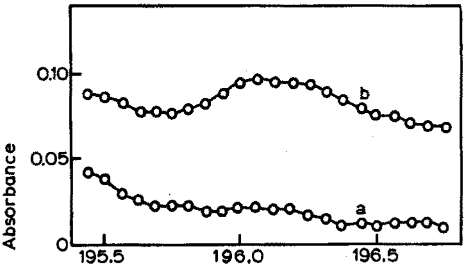


Fig. 3. Effects of barium, lead and strontium on absorbance of 25 p.p.m. of selenium. (a) Strontium, (b) barium, (c) lead.

Fig. 4. Background absorption caused by sulfuric acid in an air–hydrogen flame. Concentration of sulfuric acid: (a) 0.5, (b) 5 *N*.

Effect of acids

Hydrochloric, nitric, phosphoric and perchloric acids had no effect on the absorbance for 25 p.p.m. of selenium in the concentration range 0–2.0 *N*. Sulfuric acid, however, caused a gradual increase in the absorbance of selenium, as the acid concentration increased over the range 0–1.0 *N*.

In order to obtain more detailed information on this effect, the background absorption in the vicinity of the 196.0-nm selenium line was measured with the relevant solutions with a hydrogen discharge lamp as a light source. A transmittance–wavelength curve was first recorded with the solution of sulfuric acid sprayed into the flame. The curve thus obtained was converted to an absorbance–wavelength curve by calculation after correction for the background obtained with water alone sprayed into the flame. Curves a and b in Fig. 4 represent the results for 0.5 and 5 *N* sulfuric acid solutions, respectively. No detectable amount of impurity of selenium was found in the sulfuric acid employed, as will be shown later, and, therefore, this Figure shows the dependence of the background absorption on the concentration of sulfuric acid, although there was no linear relationship between the absorbance and the concentration of sulfuric acid at the wavelengths examined. This background absorption may be ascribed mainly to molecular absorption by sulfur dioxide which is known to give an absorption band between 180 and 230 nm[7]. The lack of a linear relationship between absorbance and concentration suggests additional effects such as light scattering, variation of refractive index within the flame caused by vaporization of concentrated solutions, etc.

DETERMINATION OF SELENIUM IN SULFUR

Based on the above observations, the following procedure for the determination of selenium in sulfur was developed.

Procedure

Weigh out a 5-g sample of powdered sulfur into a covered vessel, add about 50 ml of concentrated nitric acid and about 10 ml of bromine, and warm gently, removing the heat if the action becomes violent. After dissolution is complete, heat the solution to fumes of sulfur trioxide. Cool the solution. Transfer the cooled solution to a 100-ml volumetric flask and cautiously dilute to volume with distilled water. Spray the solution into the flame and measure the absorbance at 196.0 nm under the conditions discussed above. The preparation of sample solutions required about 1 h.

Recovery tests in the decomposition process

Two 2-g samples were taken. To one of the samples was added 5 ml of a standard selenium solution (500 p.p.m.) and then the above treatment with concentrated nitric acid and bromine was carried out. The other sample was treated with concentrated nitric acid and bromine, and then mixed with 5 ml of the standard selenium solution. In both cases the resultant solutions were made up to 50 ml and the atomic absorption measurement was made on each solution.

The experiment on the sample of powdered sulfur was repeated and gave a recovery of 100.1% of the added selenium, indicating that there was no loss of selenium by spray during the decomposition process.

Results for determination

Selenium in reagent-grade sulfur supplied from various sources was determined by the standard addition method. In the decomposition of the samples, sulfuric acid is produced and this interferes with the determination as described above. In the present work, the necessary correction was made by measuring the absorbance at 196.0 nm with the selenium hollow-cathode lamp on a solution of sulfuric acid alone, the concentration of which was nearly equal to that in the sample solution. The absence of selenium impurities in the sulfuric acid employed as a blank was checked by the colorimetric method based on 3,3'-diaminobenzidine[8], the sensitivity of which is approximately ten times better than that of the proposed atomic absorption method. The results of the determinations are shown in Table II.

The results were compared with those obtained by colorimetry. DANZUKA AND UENO[9] have determined traces of selenium(IV) in sulfuric acid by the colorimetric 3,3′-diaminobenzidine method and suggested the possibility of applying the method to the determination of selenium in sulfur. However, part of the selenium was found to be oxidized to selenate during the oxidative decomposition of the sample with concentrated nitric acid and bromine, and selenate does not react with the reagent. Therefore, the selenate thus produced had to be reduced to selenite before color development. For this reduction treatment with hydrochloric acid[10] seemed to be effective. On the basis of the above considerations, the sample solution for the colorimetric determination was prepared as follows. An accurately weighed 2-g sample was treated with concentrated nitric acid and bromine as described above. After removal of excess of nitric acid and bromine by heating, 50 ml of hydrochloric acid (6 *N*) was added to the solution and the mixture was refluxed for *ca.* 1 h. The solution was cooled and made up to 100 ml with distilled water. Portions (3 ml) of this sample solution were used for the colorimetric determination of selenium.

TABLE II

DETERMINATION OF SELENIUM IN SULFUR

Sample no.	*Selenium (%)*	
	Atomic absorption method	*Colorimetric method*
1	0.028_2	0.026_5
2	0.025_6	0.023_9
3	0.027_7	0.025_8
4	0.030_5	0.028_7
5	0.016_9	0.015_4

TABLE III

COMPARISON OF PRECISION OF ATOMIC ABSORPTION METHOD WITH THAT OF COLORIMETRIC METHOD

	No. of run	*Se found (%)*	*Relative standard deviation (%)*
Atomic absorption method	10	0.024_8	2.5
Colorimetric method	8	0.022_9	4.8

Table II shows that the values obtained by the atomic absorption method are slightly higher than those obtained by the colorimetric method. This small difference might be ascribable to incomplete reduction of selenate in the latter method, because selenate gives the same results as selenite in the atomic absorption method while this is not the case in the colorimetric method.

The atomic absorption method is superior to the colorimetric method not only in simplicity and rapidity but also in precision (Table III).

SUMMARY

Selenium in sulfur can be determined rapidly by atomic absorption spectrophotometry. The sample is decomposed with concentrated nitric acid and bromine.

The resultant solution is sprayed into an air–hydrogen flame and the absorbance is measured at 196.0 nm. Sulfur gives a small background absorption to interfere with the atomic absorption measurement of selenium and proper corrections must be made for accurate results. The results were compared with those obtained by the colorimetric 3,3′-diaminobenzidine method.

RÉSUMÉ

Le sélénium dans le soufre peut être dosé rapidement par spectrophotométrie par absorption atomique. L'échantillon est décomposé à l'aide d'acide nitrique concentré et de brome. La solution obtenue est vaporisée dans une flamme air–hydrogène; l'absorption est mesurée à 196.0 nm. Le soufre donne un faible bruit de fond pouvant gêner la mesure d'absorption atomique du sélénium. Il est nécessaire de faire les corrections appropriées pour obtenir une bonne précision. Les résultats ont été comparés avec ceux obtenus par colorimétrie au moyen de diamino-3,3′-benzidine.

ZUSAMMENFASSUNG

Selen in Schwefel kann auf schnelle Weise durch Atom-Absorptionsspektrophotometrie bestimmt werden. Die Probe wird mit konzentrierter Salpetersäure und Brom zersetzt. Die erhaltene Lösung wird in eine Luft–Wasserstoff-Flamme gesprüht und die Extinktion bei 196.0 nm gemessen. Schwefel ergibt eine kleine Untergrundabsorption, die die Atomabsorptionsmessung von Selen stört; daher sind für genaue Ergebnisse geeignete Korrekturen notwendig. Die Ergebnisse werden mit jenen verglichen, die kolorimetrisch nach dem 3,3′-Diaminobenzidin-Verfahren erhalten werden.

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METHODE CHIMIQUE DE DOSAGE DE FRACTIONS DE p.p.m. DE CHLORE DANS LES CALOPORTEURS ORGANIQUES A USAGE NUCLEAIRE

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Les caloporteurs organiques sont utilisés dans divers types de réacteurs nucléaires[1,2]. Le chlore qu'ils contiennent est une des causes principales de corrosion des circuits métalliques et des tubes de force. Cet élément n'était pas mentionné dans les premières spécifications imposées en 1963 par Atomics International pour ces fluides organiques[3], des teneurs inférieures à 5 p.p.m. étant considérées comme satisfaisantes, il l'est dans des spécifications ultérieures où les valeurs maxima sont alors ramenées à 1–2 p.p.m.[4]. Des études récentes[5] sur la corrosion des tubes de force en Zircaloy démontrent la nécessité de ne tolérer qu'une teneur encore inférieure, de l'ordre de 0.2 p.p.m. On tend donc à éliminer le plus possible le chlore; des purificateurs en continu sont actuellement installés sur les circuits. Il est donc nécessaire d'effectuer un contrôle analytique précis de l'élément chlore au niveau de 0.1 p.p.m., non seulement dans les caloporteurs vierges, mais également dans les fluides qui, pyrolysés et radiolysés, contiennent d'importantes quantités de produits lourds (high-boiling liquids).

Des techniques existantes, l'analyse par activation[6] est la seule, qui, à notre connaissance, puisse répondre à cette exigence. En effet, les méthodes chimiques classiques se basant sur la fusion alcaline, la réaction avec le sodium-diphényl[4], la combustion à la bombe[7] ou au chalumeau oxhydrique[7,8], les méthodes physiques telle que la fluorescence X[9], ont des limites de sensibilité insuffisantes bien que déjà assez basses dans certains cas. Afin de pouvoir disposer d'une alternative à l'analyse par activation qui requiert l'emploi d'un réacteur nucléaire, notre but, après la mise au point du dosage du bore[10] et du phosphore[11], a été de développer une méthode chimique simple, rapide et suffisamment sensible.

Parmi les réfrigérants organiques primaires les plus employés, notre étude a porté plus particulièrement sur l'OM-2, l'OMD, l'HB-40, dénominations commerciales de différents mélanges de di- et terphényles.

En ce qui concerne les fluides secondaires, nous nous sommes limités au Thermip-P2 et au Solvesso 200, fractions de distillation comprises entre 230 et 280° de résidus provenant du procédé catalytique de "Reforming".

La composition et quelques propriétés physiques importantes de ces produits sont rassemblées dans le Tableau I.

TABLEAU I

COMPOSITION ET QUELQUES PROPRIÉTÉS PHYSIQUES DE DIVERS CALOPORTEURS ORGANIQUES À USAGE NUCLÉAIRE

Dénominations	*Compositions*	*Temp. de fusion (°)*	*Temp. d'ébullition (°)*	*Temp. d'inflammation (°)*	*Temp. d'autoinflammation (°)*	*Densité ($g\ cm^{-3}$)*	*Viscosité cinématique $\cdot 10^{-2}$ ($cm^2\ s^{-1}$)*	*Pression de vapeur (atm)*
OM-2	Ø-2: ≦ 1% o-Ø-3: 15–25% m-Ø-3: 70–80% p-Ø-3: ≦ 5% Phénanthrène: ≦ 1%	60–65	355 ± 15	> 150	> 500	1.02 (à 100°)	≦ 3 (à 120°)	~ 3 (à 420°)
OMD	Ø-2: 25–27% o-Ø-3: 50–55% m-Ø-3: 17–19% p-Ø-3: ≦ 1% Phénanthrène: ≦ 3%	< 20	295 ± 15	> 130	> 500	1.07 (à 25°)	≦ 50 (à 25°)	~ 8 (à 420°)
HB-40 usagé	Mélange hydrogéné à 40% de o-Ø-3: 7% m-Ø-3: 50% p-Ø-3: 23% "Lourds": 20%	< 0	350 ± 5	174	374	1.001 (à 25°)	~ 50 (à 25°)	—
Thermip-P2	α + β méthylnaphtalène: 69% naphtalène: 7.5% somme de: 23.5% naphtalène bisubstitué ethylnaphtalène diphényle	entre −5 et −15	de 230 à 255	≧ 100	485	0.993 (à 15°)	≦ 3 (à 20°)	~ 7 (à 350°)
Solvesso 200	naphtalène: 7% α + β méthylnaphtalène: 38% autres alkylnaphtalènes: 29% divers composés aromatiques: C_6–C_{10}: 13% "Lourds": 13%	entre −18 et −28	de 230 à 280	≧ 100	485	0.99 (à 15°)	≦ 4 (à 20°)	~ 7 (à 350°)

DESCRIPTION DE LA MÉTHODE

Principe

Les substances organiques sont volatilisées dans un courant d'argon et ensuite brûlées par l'oxygène dans un chalumeau type WICKBOLD modifié[12]. L'eau et l'acide chlorhydrique formés, sont, après refroidissement, recueillis dans une tour d'absorption et dosés dans la solution finale par potentiométrie à point nul[8,13,14].

Description du chalumeau

La Figure 1 donne un schéma de l'appareil utilisé[15]. Il est composé:

(A) d'un tube en quartz où la matière organique est vaporisée à l'aide d'une flamme à gaz, dans un courant d'argon. La prise d'essai est placée dans une nacelle d'une capacité de 25–30 ml. Le débit du gaz est réglé entre 80 et 100 l h^{-1}. La substance à analyser est ainsi amenée au gicleur 2.

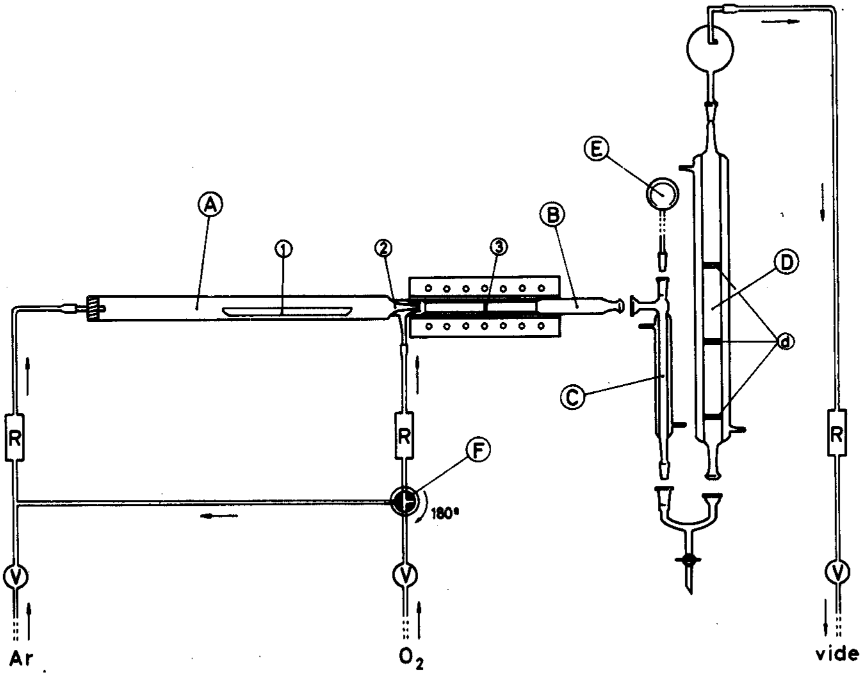

Fig. 1. Schéma du chalumeau: (A) chambre de vaporisation, (B) chambre de combustion, (C) réfrigérant, (D) tour d'absorption avec 3 frittes (d), (E) manomètre, (F) robinet à trois voies, (R) débitmètre, (V) vanne de réglage du débit, (1) nacelle porte échantillon, (2) gicleur, (3) disque troué en Al_2O_3.

(B) d'une chambre à combustion en quartz, chauffée à 900–1000° par un four électrique. Les vapeurs organiques y sont brûlées par un courant d'oxygène dont le débit horaire est compris entre 200 et 300 l. Pour obtenir une combustion complète, il est nécessaire de placer à 10 cm du gicleur un disque 3 en Al_2O_3 ou ZrO_2, perforé de trous de 2 mm de diamètre. La version originale du chalumeau prévoit, à cet effet, un tamis de quartz. Mais, celui-ci se déforme très rapidement lorsqu'on minéralise à la

vitesse de 1 g min^{-1}. Une spirale de platine fait de même. Le disque doit être fixé de manière lâche et il est préférable de renforcer la partie du tube le contenant. A cette vitesse, la chambre de combustion a une vie limitée à 500 g de substance à minéraliser; il est ensuite nécessaire de remplacer 3 à 4 cm de tube au voisinage du disque. En réduisant la vitesse de combustion, c'est-à-dire, en augmentant proportionnellement le temps d'analyse, la vie du chalumeau est prolongée de manière appréciable.

(C) d'un réfrigérant: également en quartz.

(D) d'une colonne d'absorption en verre Pyrex contenant trois disques d, en verre fritté (G1) afin d'améliorer le contact entre le gaz de combustion et le liquide d'absorption. De 10 à 15 ml d'eau bidistillée suffisent à retenir le chlore aux concentrations rencontrées dans les produits examinés. Le remplissage et la vidange de la colonne s'effectuent en appliquant une pression à son sommet au moyen des gaz disponibles sur l'appareil. Le robinet permettant cette opération n'apparait pas sur le schéma.

(E) d'un manomètre. En régime, la pression dans l'appareil est maintenue au moyen d'une trompe à eau, de 20 à 30 mm Hg en dessous de la pression atmosphérique. Une dépression supérieure déformerait la chambre de combustion.

(F) d'un robinet à trois voies permettant d'introduire un mélange d'argon et d'oxygène dans le tube A, lorsqu'il s'avère nécessaire de compléter la combustion d'éventuels résidus charbonneux restés dans la nacelle 1 à la fin de la vaporisation dans le courant d'argon.

(G) d'un système d'introduction des gaz. Les débits d'argon et d'oxygène purs sont contrôlés au moyen des robinets V et des rotamètres R. Ces gaz, de qualité PP, proviennent de bouteilles commerciales munies de détendeurs, sans purification ultérieure. Le blanc, dont la valeur varie d'environ 1–1.6 μg de Cl pour des temps de combustion de 10–60 min, est surtout dû, pense-t-on, aux manipulations subies par la solution avant le titrage. Pour des raisons pratiques nous avons choisi des temps de combustion de l'ordre de 30 min. Il est probable qu'en prolongeant davantage la minéralisation, la limite de sensibilité de la méthode proposée puisse être améliorée.

Titrage par potentiométrie à point nul

La technique est basée sur le fait que la différence de potentiel entre deux électrodes identiques plongées dans le même électrolyte est nulle. Dans notre cas, une première électrode Ag–AgCl est immergée dans un électrolyte à concentration connue en Cl$^-$, la seconde est en contact avec la solution inconnue. Si les quantités de Cl$^-$ présentes dans les deux solutions sont égales, la différence de potentiel entre les deux électrodes sera nulle.

Si au contraire, elles ne sont pas identiques, il s'établira entre les deux électrodes, une différence de potentiel mesurable à l'aide d'un microvoltmètre. En la ramenant à zéro, soit par addition de Cl$^-$ soit par dilution, il est aisé de calculer la concentration en Cl$^-$ de la solution inconnue. La technique simple et très sensible permet de titrer jusqu'à 0.5 μg de Cl$^-$ dans un volume de 50 ml.

L'appareillage est constitué:

(a) d'un récipient de titrage en verre Pyrex thermostatisé, contenant les deux électrodes Ag–AgCl (voir Fig. 2). L'électrolyte de référence et la solution inconnue sont agitées à l'aide d'un même agitateur magnétique.

(b) d'un microvoltmètre Keithley—type 150B microvolt Ammeter—qui a la possibilité d'éliminer, par l'intermédiaire d'un compensateur de zéro, les petites

différences de potentiel qui existeraient éventuellement entre les deux électrodes Ag–AgCl plongées dans une même solution de chlorures.

(c) de deux burettes automatiques Metrohm—type Multidosimat E 415—qui permettent l'addition à la solution inconnue, soit d'un électrolyte à titre connu en Cl^-, soit de diluant. Nous donnons quelques détails sur la préparation des électrodes et du compartiment de référence afin d'éviter les diverses difficultés rencontrées en utilisant les modes opératoires déjà publiés[8].

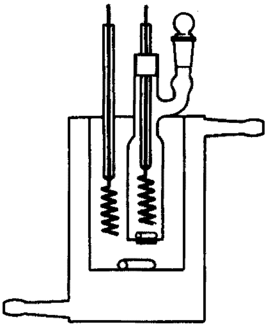

Fig. 2. Schéma du récipient de titrage.

Préparation des électrodes Ag–AgCl. On utilise un fil d'argent de 1 mm de diamètre et 23 cm de longueur. Une des extrémités est en spirale, 6 spires de 7 mm de diamètre extérieur sur une hauteur de 2 cm. Le morceau rectiligne restant, est enfilé dans un tube de verre dont l'ouverture est colmatée à l'aide de résine époxy. Cette opération a pour but de rendre le fil plus rigide et d'éviter que l'argent métallique ne vienne en contact avec l'électrolyte. Les électrodes (voir Fig. 2) sont ensuite dégraissées à l'éther éthylique. On chlorure directement le fil d'argent, naturellement oxydé, par électrolyse dans une solution d'acide chlorhydrique 0.1 *N*, pendant 1 h à 3 mA, en utilisant comme cathode un tamis circulaire de platine de 3 cm de diamètre et de 4 cm de hauteur.

Les électrodes sont ensuite lavées successivement à l'eau bidistillée et avec la solution de référence (voir *Réactifs*). Elles sont finalement immergées dans cette même solution pendant 24 h au moins. La différence de potentiel entre les deux électrodes, préparées de cette manière, est toujours inférieure à 0.2 mV lorsqu'elles sont plongées dans la solution de référence. Elle reste constante pendant plusieurs mois. Par la suite, la couche noire de chlorure d'argent perd son homogénéité et la différence de potentiel augmente progressivement. Bien qu'il soit possible d'opérer avec une différence de potentiel de l'ordre du millivolt aisément compensée par l'instrument, il est alors conseillé de remplacer les électrodes vu la simplicité de leur préparation.

Description du compartiment de référence. Le compartiment de référence est très nettement visible dans la Fig. 2. Une des électrodes est plongée dans la solution de référence (voir *Réactifs*) contenue dans le petit récipient de verre Pyrex d'une capacité d'environ 10 ml et agitée à l'aide d'un agitateur magnétique. Le contact électrique avec la solution inconnue est assuré par l'intermédiaire d'un disque en verre poreux (G3) de 1 cm de diamètre soudé sur le fond du compartiment de référence. La résistance mesurée entre les deux électrodes de l'ensemble de la cellule de titrage est de l'ordre de 300 ohms.

Réactifs

(a) Electrolyte de référence: solution aqueuse à 1 p.p.m. de Cl^-, contenant 100 ml d'H_2SO_4 (1+4) par litre.

(b) Solution titrante: solution aqueuse à 10 p.p.m. de Cl^-, contenant 100 ml d'H_2SO_4 (1+4) par litre.

(c) Diluant: 100 ml d'H_2SO_4 (1+4) sont dilués à un litre par de l'eau.

(d) Acide sulfurique: H_2SO_4 (1+4).

(e) Eau: déminéralisée et bidistillée dans le quartz. Il est souhaitable d'utiliser pour la préparation des réactifs, de l'eau et de l'acide sulfurique (1+4) provenant d'une même réserve afin d'éviter les éventuelles variations de teneurs en Cl^- entre différents lots.

(f) Solution de base à 100 p.p.m. Cl^-: elle est obtenue en dissolvant dans l'eau la quantité équivalente de KCl. Tous les réactifs décrits ci-dessus sont préparés à partir de cette solution.

Mode opératoire

L'échantillon (jusqu'à 20 g pour des teneurs en Cl inférieures à 0.5 p.p.m.) est placé dans la nacelle en quartz 1 et introduit dans le tube *A* du chalumeau. Le débit d'argon est réglé entre 80 et 100 l h^{-1}, celui d'oxygène entre 200 et 300 l h^{-1}. La température du four électrique doit atteindre 900–1000°. L'appareil est balayé pendant 1–2 min pour en chasser l'air. 10–15 ml d'eau déminéralisée et bidistillée dans le quartz sont versés au sommet de la tour *D* et chassés par pression en dessous du premier disque poreux *d*. Le manomètre *E* est branché au sommet du réfrigérant *C* et une dépression de 10 à 20 mm Hg en dessous de la pression atmosphérique est appliquée dans l'appareil par l'intermédiaire d'une trompe à eau. L'échantillon est alors chauffé progressivement à l'aide d'une lampe à gaz placée à l'extérieur du tube *A* jusqu'à ce que les vapeurs organiques s'enflamment dans la chambre à combustion *B*. A ce moment, le four électrique est éteint. Avec un peu de pratique, il est possible de brûler 1 g de substance par minute sans former de dépôts charbonneux dans le distillat. La combustion de l'OM-2 est aisée, tandis que l'OMD et l'HB-40 requièrent un chauffage initial plus modéré. La vaporisation du Thermip-P2, plus volatil, doit être contrôlée pendant toute l'opération de combustion. De toute façon, de petites quantités de matières charbonneuses, n'interfèrent pas de manière appréciable sur la titration par potentiométrie à point nul. La nacelle 1 et le tube *A* doivent être parfaitement chauffés jusqu'à volatilisation totale de l'échantillon. Le résidu que peuvent laisser les réfrigérants organiques pyrolysés et radiolysés est détruit aisément par un mélange d'argon et d'oxygène introduit grâce au robinet à trois voies *F*.

La combustion terminée, la trompe à eau est arrêtée et le courant gazeux est envoyé au sommet de la colonne *D*. Le robinet placé en bas de la tour permet de recueillir la solution d'absorption dans un ballon jaugé de 50 ml. Les eaux de lavage de la colonne et du réfrigérant sont jointes au ballon. 5 ml d'H_2SO_4 (1+4) sont ajoutés à la solution qui est ensuite thermostatisée à 25°, portée au volume et agitée.

De l'électrolyte de référence est ajouté dans la cellule de titration. L'éventuelle différence de potentiel est éliminée à l'aide du suppresseur de zéro du microvoltmètre. Après rinçage, la solution contenue dans le ballon de 50 ml est transvasée dans le vase de titration. La différence de potentiel est ramenée à zéro par addition, soit de la solution titrée à 10 p.p.m. en Cl^-, soit du diluant selon que la concentration en chlore de la solution inconnue est inférieure ou supérieure à celle de l'électrolyte de référence à 1 p.p.m. en Cl^-. Le titrage est terminé lorsque la valeur du potentiel reste nulle au moins 15 sec.

La teneur en chlore de l'échantillon se calcule au moyen d'une des formules suivantes:

$$\text{p.p.m. Cl} = \frac{9\,(V_B - V_R)}{P} \tag{1}$$

$$\text{p.p.m. Cl} = \frac{9\,V_B + V_D}{P} \tag{2}$$

où V_B = volume de solution titrante à 10 p.p.m., employé pour l'essai à blanc, V_R = volume de la solution titrante à 10 p.p.m., utilisé pour l'échantillon, V_D = volume de diluant pour l'échantillon, P = poids en gramme de substances à analyser.

La relation (1) est utilisée lorsqu'on titre avec la solution à 10 p.p.m. en Cl^-, l'éqn. (2) est appliquée lorsqu'on doit employer du diluant. Dans ce cas, il n'est pas souhaitable de titrer des concentrations supérieures à 2 p.p.m. dans la solution inconnue (100 μg Cl^- dans 50 ml).

Il est évident que l'éqn. (1) n'est valable que dans notre cas particulier où l'électrolyte de référence contient 1 p.p.m. de Cl^- et le titrage s'effectue à l'aide d'une solution contenant 10 p.p.m. de Cl^-. Elle découle du bilan total des ions Cl au potentiel zéro:

$$(V_O + V_R)\cdot 1 = V_R \cdot 10 + V_O \cdot (C_X + C_B) \tag{3}$$

où V_O = volume initial de la solution (50 ml dans notre cas), V_R = volume de la solution titrante à 10 p.p.m., utilisé pour l'échantillon, C_X = concentration en p.p.m. de la solution à titrer, C_B = concentration en p.p.m. de l'essai à blanc.

Un calcul similaire pour l'essai à blanc conduit à la relation:

$$(V_O + V_B)\cdot 1 = 10\ V_B + V_O C_B \tag{4}$$

où V_B = volume de la solution titrante à 10 p.p.m., employé pour l'essai à blanc.

Des éqns. (3) et (4), on peut calculer $V_O C_X$ qui représente les microgrammes de chlore provenant de l'échantillon dans le volume V_O:

$$V_O C_X = 9(V_B - V_R) \tag{5}$$

en divisant par le poids de substance mise en jeu, on retrouve la relation (1).

Un raisonnement analogue permet de remonter à l'éqn. (2).

Pour réaliser un titrage correct, il s'avère indispensable de porter une attention particulière aux facteurs suivants:

(a) La force ionique de la solution inconnue, obtenue par addition d'acide sulfurique doit être rigoureusement identique à celle de l'électrolyte de référence. Une variation de 1% de la concentration en H_2SO_4 peut provoquer une différence de potentiel d'environ 0.2 mV.

(b) Le potentiel d'une électrode étant fonction de la température, il est nécessaire que toutes les solutions utilisées dans la cellule aient la même température.

(c) Le niveau de l'électrolyte de référence doit être légèrement supérieur (environ 1 cm) à celui de la solution à titrer, afin de réduire les phénomènes de diffusion.

TABLEAU II

RÉSULTATS OBTENUS ET COMPARAISON AVEC D'AUTRES TECHNIQUES

Dénominations	*Valeur théorique*	*Analyse par activation*[6]		*Fluorescence X*[9]		*Chalumeau oxhydrique*[7]		*Méthode proposée*	
	(p.p.m.-Cl)	*(p.p.m.-Cl)*	*(n)*[a]	*(p.p.m.-Cl)*	*(n)*	*(p.p.m.-Cl)*	*(n)*	*(p.p.m.-Cl)*	*(n)*
OM-2 avec addition de Cl[b]	20.2	22.3	5	24.0	5	21.0	5	20.1	8
OM-2 avec addition de Cl[b]	5.3	5.8	4	5.4	5	5.3	5	5.2	8
OM-2 usagé à ~ 35% H.B.	—	0.8	5	< 2[c]	—	1.2	5	1.02	8
OMD	—	0.52	4	—	—	—	—	0.53	8
OMD	—	0.36	2	—	—	—	—	0.38	3
HB-40	—	0.98	2	—	—	—	—	1.02	2
HB-40	—	0.86	2	—	—	—	—	0.82	2
Thermip purifié	< 0.2	0.13	4	—	—	—	—	0.14	10
OMD + Thermip	—	0.98	2	—	—	—	—	1.00	8
OMD + Thermip	—	1.88	2	—	—	—	—	1.92	2
Solvesso	—	0.50	2	—	—	—	—	0.48	2

[a] *n* représente le nombre de mesures.

[b] Echantillons de référence préparés à l'occasion d'une campagne d'analyses circulaires[15].

[c] Limite de sensibilité de la technique.

(d) L'eau et l'acide sulfurique doivent être les plus purs possible pour permettre d'atteindre le maximum de sensibilité de la méthode.

(e) Les contaminations en Cl sont aisées lorsqu'on travaille à des niveaux de concentrations aussi faibles. Pour obtenir de bons résultats, l'opérateur doit posséder l'esprit et l'expérience d'un laboratoire de traces. Normalement on peut titrer des solutions contenant 0.1 p.p.m. de Cl avec un coefficient de variation de 2%.

DISCUSSION DES RÉSULTATS

Le Tableau II rassemble les résultats obtenus avec différents caloporteurs organiques, par comparaison avec d'autres techniques analytiques. La concordance est excellente. Pour les teneurs inférieures à 1 p.p.m., seule l'analyse par activation possède une limite de sensibilité suffisante.

Le Tableau III donne la reproductibilité de la méthode proposée. Même pour des teneurs aussi faibles que 0.14 p.p.m., voisines de la limite de sensibilité, le coefficient de variation est encore très acceptable.

TABLEAU III

REPRODUCTIBILITÉ DE LA MÉTHODE

Dénominations	*Nombre de mesures, n*	$\bar{X}$ *(p.p.m.-Cl)*	σ *(p.p.m.-Cl)*[a]	$\sigma(\%)$[b]
Thermip	10	0.14	0.017	12.1
OMD	8	0.53	0.067	12.6
OM-2 usagé (35% H.B.)	8	1.02	0.10	9.8
OM-2 avec addition de Cl	8	5.2	0.10	1.9
OM-2 avec addition de Cl	8	20.1	0.30	1.5

[a] Ecart type $(\sigma) = \sqrt{\frac{\Sigma(X-\bar{X})^2}{n-1}}$

où X = valeur d'une mesure et $\bar{X}$ = valeur moyenne de n mesures.

[b] Coefficient de variation $(\sigma\%) = (\sigma \cdot 100)/\bar{X}$.

La valeur du blanc calculée sur 16 mesures effectuées au cours de plusieurs jours et avec une durée de combustion de 30 min, est de 1.2 μg de chlore. Son écart type est de 0.26 μg. Comme les substances analysées permettent la minéralisation de 20 à 25 g d'échantillon pendant ce laps de temps, la limite de sensibilité de la méthode proposée est de l'ordre de 0.1 p.p.m., si on la calcule à l'aide de la formule[16]:

$$\text{limite de sensibilité} = \bar{X}_{\text{blanc}} + 3\sqrt{2}\cdot\sigma_{\text{blanc}}$$

Elle est comprise entre 0.03 et 0.04 p.p.m., si l'on estime comme le triple de l'écart type de la valeur du blanc.

Cette limite étant suffisante, il n'a pas été jugé opportun de purifier les gaz utilisés pour la combustion, bien que le volume total d'oxygène et d'argon mis en jeu pendant 30 min soit de l'ordre de 150 à 300 l. La méthode possède l'avantage d'effectuer le titrage final du chlore directement sur la solution d'absorption, ce qui évite les dangers de contamination, toujours aisés au niveau des traces, des que les manipulations se multiplient. D'autre part, compte-tenu des simplifications apportées à la préparation des électrodes, le dosage du chlore par potentiométrie à point nul permet la détermination des chlorures dans l'eau à la cadence d'une analyse à la minute. Le chlore éventuellement combiné sous forme de $FeCl_3$ dans le caloporteur est également dosé[8]. Les interférences sont analogues à celles de la potentiométrie classique. Le fluor peut être toléré jusqu'à 50 μg[8]. Le brome qui, provoquant une instabilité du point nul, rend la technique inapplicable[14] est, dans les matériaux qui nous intéressent, normalement absent ou en quantité insuffisante pour perturber le dosage du chlore. Les oxydes d'azote doivent être également absents, d'où l'emploi d'argon comme gaz de transport au lieu d'azote qui provoque la formation de nitrites et nitrates dans la solution finale, à des concentrations de l'ordre de 10 à 20 μg par millilitre.

Il faut noter que le dosage des chlorures dans la solution inconnue pourrait s'exécuter par mesure de la différence de potentiel entre les électrodes par comparaison avec une courbe d'étalonnage expérimentale tracée dans les mêmes conditions opératoires en faisant varier la teneur en Cl^-. Dans ce cas, il est impératif que les solutions aient la même force ionique et que les mesures soient toujours effectuées à la même température. Les dosages réalisés sur les échantillons examinés ont donné des résultats concordants avec ceux de la potentiométrie à point nul. Le gain de temps que l'on obtient en éliminant le titrage est évidemment négligeable puisqu'il est de l'ordre de une à deux minutes.

La méthode proposée est simple, relativement rapide, et, à la portée d'un laboratoire classique d'analyse chimique. Sans vouloir substituer l'analyse par activation, elle en constitue une alternative valable.

Nous tenons à remercier MM. H. LAURENT et J. L. COLLIN de leurs conseils, MM. F. GIRARDI et G. VOS qui ont bien voulu exécuter les analyses de comparaison par activation et fluorescence X, ainsi que le laboratoire de chimie analytique de la société Bayer, Leverkusen, qui a construit le chalumeau.

RÉSUMÉ

La méthode proposée est basée sur la combustion de la substance organique par un excès d'oxygène dans un chalumeau en quartz et le titrage des chlorures dans la solution finale par potentiométrie à point nul. Sa limite de sensibilité est de 0.1 p.p.m. en utilisant 20 grammes d'échantillon. Son coefficient de variation est de 12% pour des teneurs de l'ordre de 0.14 p.p.m. La méthode est rapide, un dosage s'effectuant en 30 min environ.

SUMMARY

A method for the determination of traces of chlorine in organic coolants is described. The proposed method is based on the combustion of the organic matter in a quartz burner with a flow of oxygen, and final determination of chloride by a null-point potentiometric titration. With a 20-g sample a detection limit of 0.1 p.p.m. is achieved. At the 0.14-p.p.m. level the coefficient of variation is about 12%. The method requires 30 min for one determination.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren Chlor in organischen

Kühlmitteln beschrieben. Das vorgeschlagene Verfahren beruht auf der Verbrennung der organischen Substanz in einem Quarzbrenner unter Sauerstoff-Zufuhr und Titration des Chlorids in der schliesslich erhaltenen Lösung durch Nullpunktspotentiometrie. Bei einer 20-g Probe wird eine Nachweisgrenze von 0.1 p.p.m. erreicht. Bei Gehalten von etwa 0.14 p.p.m. beträgt der Variationskoeffizient ungefähr 12%. Für eine Bestimmung werden etwa 30 Minuten benötigt.

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ON THE FISSION TRACK METHOD FOR THE DETERMINATION OF THE URANIUM CONTENT OF WHOLE ROCK SAMPLES

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PRICE AND WALKER[1] were the first to point out that a count of induced track density following neutron irradiation provides an extremely sensitive method of measuring trace amounts of uranium in mineral grains. FLEISCHER *et al.*[2] applied the technique to study the uranium distribution of mineral separates of the Vaca Muerta meteorite. However, this method cannot be easily adapted to determine the aggregate uranium content of whole rock samples because the precise etching conditions are known for only a few of the large number of rock-forming minerals[3-5].

FLEISCHER *et al.*[2] and FISHER AND BOSTROM[6] overcame the difficulty by developing the induced tracks on mica and "Lexan", respectively, which were fixed close to the samples before neutron irradiation. However, the errors involved in deducing the uranium content of overall samples by counting the induced track density arising from a few planes of minerals are likely to be high, because of the heterogeneous distribution of uranium in individual minerals and the wide variation of uranium content in different rock-forming minerals[7].

In this laboratory an attempt has been made to determine the uranium content of whole rock samples by the fission track method in conjunction with the method of standard addition which is described in this paper.

EXPERIMENTAL

Special apparatus and reagents

The etching set-up is shown in Fig. 1.

"Lexan" plastic (Overseas Market Development, General Electric Co., Mass., U.S.A.) was used.

The standard uranium solution contained 1 μg uranium per ml.

A binocular research microscope (with 400 × and 1000 × magnification) was used.

All the reagents used were of recognised analytical grade.

Procedure

The powdered rock sample (1 g) was treated with a mixture of 5 ml of 40% hydrofluoric acid and 5 ml of concentrated nitric acid and evaporated to dryness. The treatment was repeated twice and the final residue was taken up in 1% (v/v) nitric acid and made up to 25 ml. A reagent blank was run simultaneously with the sample.

Three 5-ml aliquots of the above solution were transferred to 10-ml standard flasks containing 1.0, 2.0 and 3.0 μg of uranium and then made up to the mark with de-ionized water. Aliquots of 25 μl from each of the 10-ml volumetric flasks and also from the original sample solution were transferred to separate 1.5-cm^2 clean, dry pieces of "Lexan" and then dried under an infrared lamp. The rinse solution of each aliquot was transferred to the "Lexan" only after the main solution had almost completely dried, thus confining the sample spread to the same small area. The dried residue was covered by another clean, dry piece of "Lexan" and the sandwich was held together by stretched "Parafilm".

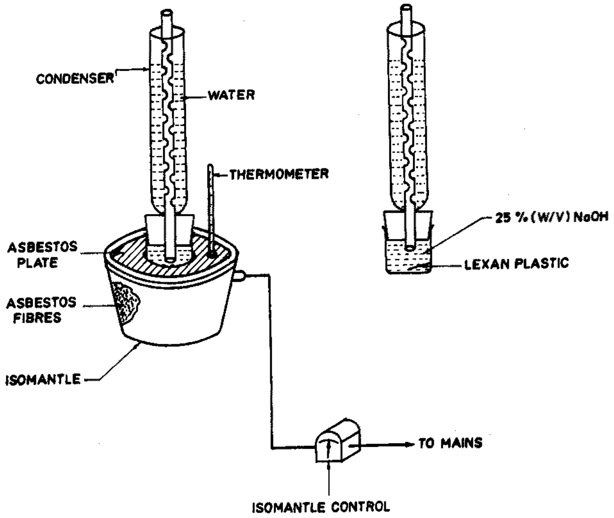

Fig. 1. Etching apparatus.

The samples were irradiated along with the blank in one of the self-serve positions of CIRUS (thermal flux $2 \cdot 10^{12}$ n cm^{-2} sec^{-1}) for a period of 40 min. After irradiation, the two "Lexans" were separated from the "Parafilm" and both the pieces were etched in the etching bath shown in Fig. 1 (etching conditions: 3 g of sodium hydroxide in 12 ml of water for 2 min after the solution starts boiling; bath temperature, *ca.* 200°).

The densities of the uranium fission-induced tracks on the "Lexan" were counted under the binocular microscope.

RESULTS AND DISCUSSIONS

During preliminary investigations carried out to optimise the experimental conditions, 1 μg of pure uranium (as uranyl nitrate) was irradiated after depositing and drying on the "Lexan". Examination of the tracks on the etched "Lexan" showed non-uniform "sun-bursts" indicating agglomeration of uranium atoms on the plastic during evaporation (Fig. 2). Deposition of the sample solution on a filter paper disc as in Weisz's ring-oven technique[8] was also tried to see if a uniform spread of uranium could be obtained. After deposition and drying, the filter paper was sand-

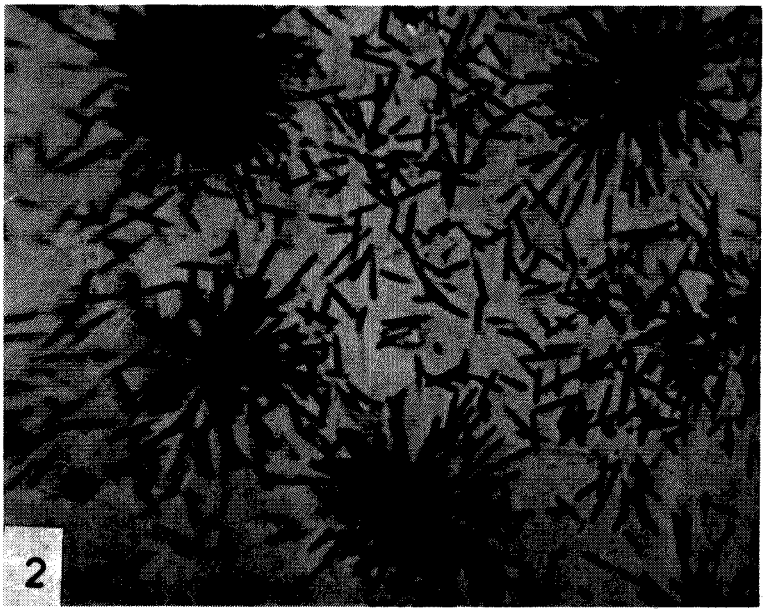

Fig. 2. "Sun-bursts" obtained after deposition of pure uranium solution on "Lexan". Field view is *ca.* $2 \cdot 10^4\,\mu m^2$.

wiched between two pieces of "Lexan" and then irradiated. Though "sun-bursts" could be avoided, this method gave a radial gradient in track density, which varied by a factor of four from centre to periphery presumably because of the selective leaching and migration of uranium by the nitric acid. Moreover, these tracks on "Lexan" were faint so that the counting became difficult.

During these runs a small aliquot of sample solution that was deposited and dried was also irradiated. On etching, a fairly uniform distribution of tracks on the plastic was observed, indicating that in contrast to the case of pure uranium solution, the presence of other cations prevents the clustering of uranium ions during the evaporation; the method of standard addition was therefore adopted. Figure 3a shows the typical tracks on "Lexan" plastic obtained for the sample while Figs. 3b and 3c are for samples to which 2.5 and 5.0 ng of uranium had been added. Besides eliminating the clustering of uranium atoms, the method of standard addition also eliminates the various sources of errors arising from factors like deposit thickness, variation in neutron flux, etc. Under the experimental conditions, the approximate thickness of the sample deposit was calculated to be of the order of 1–2 μm as against the fission track range of 36 μm in "Lexan"[9]. For each deposition, the track densities in both the "Lexan" pieces sandwiching the sample were measured; the variations in the track densities found for these two pieces were within the statistical limits of counting.

The observed track densities for the two rock standards G-2 and BCR-1 are given in Table I. The standard deviation in the track density indicated in the last column of Table I is the observed variation when 50–100 fields of view (100 μm × 100 μm) were counted covering a total of $\geqslant$ 1000 tracks.

Table II shows a comparison of the sensitivity and accuracy of the present method with those of other nuclear techniques previously employed in the determination of uranium in rock samples. The absolute sensitivity for Methods 2 and 3 is defined as that weight of uranium which gives an activity of 100 dpm of the product nuclide at the end of irradiation. In the case of the present method, this term may be

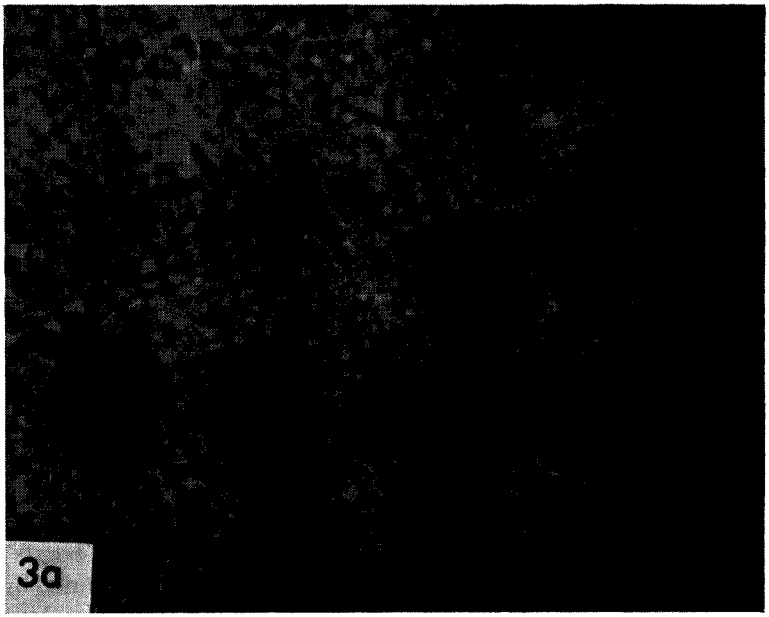

Fig. 3a. Track density from 25 μl of BCR-1 sample solution.

Fig. 3b. Track density from 25 μl of BCR-1 sample solution plus 2.5 ng of uranium.

3c

Fig. 3c. Track density from 25 μl of BCR-1 sample solution plus 5 ng of uranium. In all the above photographs the field of view is *ca.* $2 \cdot 10^4$ μm^2.

TABLE I

TRACK DENSITY AS A FUNCTION OF URANIUM CONCENTRATION

Sample	*Amount of uranium (in ng) added to 25 μl of sample solution*	*Track density*[a] *(units of 10^4 cm^{-2})*
BCR-1	0	18[b] ± 2[c]
	2.5	40 ± 2
	5.0	66 ± 5
	7.5	86 ± 5
G-2	0	22[b] ± 2
	2.5	47 ± 3
	5.0	68 ± 3
	7.5	92 ± 5

[a] Track density values have been corrected for a reagent blank of $0.2 \cdot 10^4$ tracks cm^{-2}.

[b] Values of 9 and 11 were used (see procedure) for calculating the uranium content of samples by the least squares method.

[c] The variations represent the standard deviation in the track density for a single field of view.

defined as that amount of uranium which gives a track density of 10^3 cm^{-2} on irradiation for an nvt value of 10^{17}. Up to this value of total flux, no perceivable radiation damage is caused in the "Lexan" plastic. However, the practical sensitivity of this method becomes restricted by the uranium content of the reagents employed in dissolving the sample. As is evident from Table II, the values obtained by the present method calculated by least squares analysis of the mean values of track density obtained in the experiment[12], agree well with the values of MORGAN AND HEIER[11] who used a neutron activation technique of comparable sensitivity.

TABLE II

COMPARISON OF THE SENSITIVITY AND ACCURACY OF THE FISSION TRACK METHOD WITH OTHER NUCLEAR TECHNIQUES

Method	*Neutron flux ($n\ cm^{-2}\ sec^{-1}$)*	*Period of irradiation*	*Absolute sensitivity (μg uranium)*	*Sample*	*Uranium (p.p.m.)*
γ-ray spectrometry	—	—	~ 25	G-2 BCR-1	1.32–2.1[a] 1.2 –2.14[a]
Neutron activation analysis					
(i) via ^{239}U or ^{239}Np	$1 \cdot 10^{12}$	To saturation	$\sim 2 \cdot 10^{-4}$	G-2 BCR-1	2.16 ± 0.08[b] 1.81 ± 0.14[b]
(ii) via fission product (*e.g.* ^{140}Ba)	$1 \cdot 10^{12}$	To saturation	$\sim 2 \cdot 10^{-2}$	—	—
Delayed fission neutron method	$1 \cdot 10^{12}$	To saturation	$\sim 1 \cdot 10^{-2}$	G-2	2.07 ± 0.03[a] 1.64[a]
				BCR-1	1.80 ± 0.05[a] 1.42[a]
Induced fission track method	$1 \cdot 10^{12}$	One day	$\sim 1 \cdot 10^{-5}$	G-2 (6/26)[d]	2.01 ± 0.12[c]
				BCR-1 (49/15)[d]	1.64 ± 0.09[c]

[a] FLANAGAN[10].
[b] MORGAN AND HEIER[11].
[c] Present work.
[d] Split/position as described by USGS.

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SUMMARY

The induced fission track technique in conjunction with internal standard addition has been used for the determination of uranium in geological samples. Convenient aliquots of the sample solution spiked with known amounts of uranium, deposited and dried on "Lexan", were irradiated in CIRUS (thermal flux $2 \cdot 10^{12}$ n cm^{-2} sec^{-1}; irradiation time 40 min). These irradiated "Lexan" pieces were etched with 25% (w/v) sodium hydroxide for 2 min at 200° to reveal the tracks. From a count of track densities in the "Lexan", the uranium contents of the two USGS rock standards G-2 and BCR-1 were determined to be 2.01 and 1.64 p.p.m. of uranium, respectively; these results are in good agreement with the literature values.

RÉSUMÉ

Une technique par fission induite est décrite pour le dosage de l'uranium dans des échantillons géologiques, avec addition d'un étalon interne. La solution à analyser est déposée et séchée sur "Lexan", puis irradiée à un flux thermique de 2×10^{12} n cm^{-2} sec^{-1} pendant 40 minutes. On a trouvé pour deux roches étalons G-2 et BCR-1 des teneurs en uranium de 2.01 et 1.64 p.p.m. respectivement, correspondant bien aux valeurs données dans la littérature.

ZUSAMMENFASSUNG

Die Methode der induzierten Kernspaltungsspuren wurde in Verbindung mit der Zugabe eines inneren Standards für die Bestimmung von Uran in geologischen Proben benutzt. Geeignete Anteile der Probenlösung wurden mit bekannten Uranmengen versetzt und nach Abscheidung und Trocknung auf "Lexan" im CIRUS bestrahlt (thermischer Flux $2 \cdot 10^{12}$ n cm^{-2} sec^{-1}; Bestrahlungsdauer 40 min). Die bestrahlten "Lexan"-Stücke wurden mit 25%iger (Gew./Vol.) Natronlauge 2 min lang bei 200° geätzt, um die Kernspaltungsspuren sichtbar zu machen. Durch Auszählen dieser Spuren im "Lexan" wurden die Urangehalte der beiden USGS-Standard-Gesteine G-2 und BCR-1 zu 2.01 bzw. 1.64 p.p.m. Uran bestimmt; diese Ergebnisse stimmen mit den Literaturwerten gut überein.

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THE THERMAL PROPERTIES OF SOME METAL PYRIDINECARBOXYLATES

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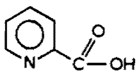
The 2-, 3-, and 4-pyridinecarboxylic acids,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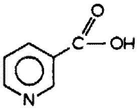
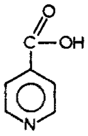
acid (picolinic acid)


3-pyridinecarboxylic
acid (nicotinic acid)


4-pyridinecarboxylic
acid (isonicotinic acid)

readily form metal complexes with divalent transition metal ions in solution. These compounds have been isolated, and in the case of 2-pyridinecarboxylic acid (picolinic acid) complexes, have been studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques[1-5]. Although most of the work has been concerned with picolinic acid, one study[6] has reported the thermal stability of the complexes of 3-pyridinecarboxylic acid (nicotinic acid) and 4-pyridinecarboxylic acid (isonicotinic acid) as well.

There are a number of discrepancies concerning the thermal properties of the metal complexes of these three acids in the literature, especially with the results obtained by KANEDA AND HARA[6]. Accordingly, the manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II) complexes of 2-, 3-, and 4-pyridinecarboxylic acids were prepared and their thermal properties determined by TGA, DTA, differential scanning calorimetry (DSC) and high temperature (HTRS) and dynamic reflectance spectroscopy (DRS).

EXPERIMENTAL

Instruments employed

The TGA curves were obtained by use of a DuPont Model 950 thermobalance with dynamic air or nitrogen furnace atmospheres. The sample sizes were 10–12 mg; a furnace heating rate of 10° per min was employed.

A Du Pont Model 920 Thermograph was used to obtain the DTA curves. The samples were studied in both dynamic air and nitrogen furnace atmospheres at a heating rate of 10° per min. Sample sizes were 5–10 mg.

The Perkin-Elmer Model DSC-1B differential scanning calorimeter was used

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TABLE I

PROCEDURAL DECOMPOSITION TEMPERATURES FROM TGA AND DTA CURVES OF METAL 2-PYRIDINECARBOXYLATES

Metal		*TGA*					*DTA*				
		H_2O I	*H_2O II*	*Decomp I*	*Decomp II*	*Decomp III*	*H_2O I*	*H_2O II*	*Peak I*	*Peak II*	*Peak III*
Mn(II)	Air			265[a] 245–275[c]	400 275–475	492 475–550					
	N_2								265[b] 235–280		445 430–460
Fe(II)	Air	140 120–180		440 325–465							
	N_2						140 100–170		445 390–460		
Co(II)	Air	95 70–115	137 115–150	410 325–445							
	N_2						125 110–135	145 135–155	418 340–455		
Ni(II)	Air	95 75–110	165 110–200	405 325–460							
	N_2						95 70–125	170 125–220	410 345–440		
Cu(II)	Air	82 55–95		270 255–295	325 295–335						
	N_2						105 95–120		315 300–320		
Zn(II)	Air	93 60–125		390 320–435	470 435–515						
	N_2						110 100–125		405 360–445		

[a] Maximum rate.
[b] Peak minimum.
[c] Temperatures at beginning and end of reaction.

to obtain the calorimetric data. A dynamic nitrogen furnace atmosphere was employed at a heating rate of 10° per min. Sample sizes were 5–10 mg. Duplicate, and in many cases, triplicate, runs were made on each sample. The curve peaks were integrated by a planimeter technique. The calibration standard was high-purity indium metal, 6.75 cal per g.

The reflectance studies were carried out with the heated sample holder previously described by WENDLANDT[7–9] and a Beckman Model DK-2A spectroreflectometer. White glass-fiber cloth covered with a thin cover glass was used as the reflectance standard. A heating rate of 10° per min was employed for the DRS mode.

Preparation of compounds

The 2-, 3-, and 4-pyridinecarboxylic acids (Eastman Organic Chemicals, Rochester, N. Y.) were used without further purification. The other chemicals employed were all of reagent-grade quality.

The general procedure for the preparation of the complexes consisted of adding a 1 *M* solution of the divalent metal chloride to a 1 *M* solution of the acid, maintained at a pH of 4, until an acid:metal concentration of 3:1 was attained. The resulting mixture was heated to boiling and mechanically stirred for about 1 h. The metal complex precipitate, if present, was filtered off, washed with a 1:1 water–ethanol mixture, and then with 95% ethanol and dried *in vacuo* for 48 h at room temperature. If precipitation from the solution was not spontaneous, 95% ethanol was added until a precipitate was obtained.

The complexes were analyzed for water and metal contents by TGA.

RESULTS

Owing to the large number of TGA, DTA, and reflectance curves obtained, only representative curves are shown in Figs. 1–5. The thermal decomposition data are summarized in Tables I–III. Each compound will be discussed briefly. The temperatures referred to are the procedural decomposition temperatures at the heating rate indicated.

Manganese(II) 2-pyridinecarboxylate

This compound is precipitated as the anhydrous complex, $Mn(2PC)_2$. It dissociates in three steps to give the oxide, Mn_3O_4, beginning at 550° (found 25.5%, theor. 25.49%). Constant weight could not be obtained for the metal oxide in a nitrogen atmosphere. The DTA curve contained two endothermic peaks, the latter of which was not very well defined. The HTRS (high temperature reflectance spectroscopy) curve had a reflectance maximum of 500 nm which shifted to a higher wavelength as the compound was heated to 200°. With DRS, the curve obtained at 500 nm began to decrease slowly when heated with a rather large decrease indicated between 180° and 225°.

Manganese(II) 3-pyridinecarboxylate

Unlike the 2-pyridinecarboxylate complex, this compound precipitates as the dihydrate, $Mn(3PC)_2 \cdot 2H_2O$. The water of hydration is evolved by a one-step process (10.7% found, 10.75% theor.) while the anhydrous $Mn(3PC)_2$ is stable up to 330°

TABLE II

PROCEDURAL DECOMPOSITION TEMPERATURES FROM TGA AND DTA CURVES OF METAL 3-PYRIDINECARBOXYLATES

Metal		*TGA*				*DTA*			
		H_2O I	*H_2O II*	*Decomp I*	*Decomp II*	*H_2O I*	*H_2O II*	*Peak I*	*Peak II*
Mn(II)	Air	150 135–180		425 330–445					
	N_2					140 130–160		440 405–475	
Fe(II)	Air	60 35–80	132 80–165	415 342–475					
	N_2					112 110–125	130 125–140	420 380–455	
Co(II)	Air	145 105–175		412 385–430					
	N_2					135 130–155		410 380–455	
Ni(II)	Air	142 75–165		402 300–420					
	N_2					145 80–165		415 380–440	
Cu(II)	Air	50 35–70	102 70–130	288 275–290	415 290–475				
	N_2					65 55–75	105 85–120	275 270–280	
Zn(II)	Air	115 75–130		415 350–460					
	N_2					80 70–85	100 95–115	425 325–440	

where it undergoes almost explosive decomposition to give the metal oxide, Mn_3O_4 (23.3% found, 22.75% theor.). The DTA curve has an endothermic peak for the dehydration reaction and a smaller endothermic peak for the decomposition of the complex. The HTRS curve has a maximum at 425 nm with a shoulder peak at 400 nm. This maximum shifts slowly to higher wavelengths as the compound is heated. A pronounced change in the DRS curve takes place above 150°; however, the curve continued to decrease gradually all the way to 250°.

Manganese(II) 4-pyridinecarboxylate

This compound precipitates from solution as the tetrahydrate, $Mn(4PC)_2 \cdot 4H_2O$. According to the TGA curve, the water of hydration is evolved by a one-step process (19.2% found, 19.41% theor.). The anhydrous complex decomposes very rapidly to give the oxide, Mn_3O_4 (21.1% found, 20.54% theor.). The DTA curve shows the one-step dehydration reaction as a single endothermic peak followed by another endothermic peak for the decomposition of the anhydrous compound. Only a shoulder

TABLE III

PROCEDURAL DECOMPOSITION TEMPERATURES FROM TGA AND DTA CURVES OF METAL 4-PYRIDINECARBOXYLATES

Metal		*TGA*				*DTA*			
		H_2O I	*H_2O II*	*Decomp I*	*Decomp II*	*H_2O I*	*H_2O II*	*Peak I*	*Peak II*
Mn(II)	Air	120 93–150		405 325–418					
	N_2					120 110–130		420 395–440	
Fe(II)	Air	125 105–140		310 270–320	410 365–415				
	N_2					130 95–140		310 290–330	425 380–445
Co(II)	Air	100 85–115	135 115–155	390 350–415					
	N_2					100 75–120	170 150–180	420 360–450	
Ni(II)	Air	160 120–200		368 275–380					
	N_2					140 120–200		330 310–335	375 335–420
Cu(II)	Air	135 80–165		280 250–290	330 290–360				
	N_2					130 125–150		270 265–275	280 275–295
Zn(II)	Air	113 85–135		443 330–463					
	N_2					105 90–130		440 390–470	

peak at 410 nm is indicated in the HTRS curve and this moves to a higher wavelength as the compound is heated to 250°. This change is shown more dramatically in the DRS curve where the reflectance of the compound decreases sharply above 125°. A more gradual change in reflectance then takes place up to 250°.

Iron(II) 2-pyridinecarboxylate

According to the TGA curve, $Fe(2PC)_2 \cdot 4H_2O$ loses its water of hydration in one step (19.3% found, 19.36% theor.) followed by decomposition of the anhydrous complex to give the oxide, Fe_2O_3 (21.9% found, 21.46% theor.). The DTA curve contained a single endothermic peak for the dehydration reaction; however, the peak contained two shoulders indicating that the reaction may consist of two steps but they were not very well resolved. A shift in the HTRS curve maximum took place from 670 to 725 nm in the temperature range 125–175°.

Iron(II) 3-pyridinecarboxylate

This compound precipitates from solution as $Fe(3PC)_2 \cdot 3.5H_2O$. The water is lost in two steps, the first of which involves 0.5 mole of water followed by the other 3 moles per mole of complex (for 0.5 mole H_2O: 2.6% found, 2.48% theor.; for 3 moles H_2O: 17.3% found, 17.36% theor.). This was followed by the decomposition of anhydrous $Fe(3PC)_2$ to give the oxide, Fe_2O_3 (22.1% found, 21.99% theor.). The DTA curve also shows that the water is evolved in two steps. The behavior of the HTRS curves was similar to that of $Fe(2PC)_2 \cdot 4H_2O$.

Iron(II) 4-pyridinecarboxylate

This compound precipitates as $Fe(4PC)_2 \cdot 2.5H_2O$, the water of which is evolved in a single step (12.9% found, 13.05% theor.). The anhydrous compound, $Fe(4PC)_2$, explodes on heating at practically every heating rate down to 2.5° per min, giving the oxide as the residue. The DTA curve gives endothermic peaks for the dehydration and decomposition reactions. The reflectance behavior was similar to that found for $Fe(2PC)_2 \cdot 4H_2O$.

Cobalt(II) 2-pyridinecarboxylate

The tetrahydrate, $Co(2PC)_2 \cdot 4H_2O$, dehydrates in two steps. The first two moles of water are evolved over the range 70–115° while the remaining two are evolved up to 150°. This is in good agreement with the work of THOMAS[5] who reported 75–150° while LUMME[4] gave the dehydration range as 80–217°. The water evolved was 9.7 and 19.1% found (9.60 and 19.20% theor.) for the loss of two and four moles of water, respectively. The anhydrous complex was stable up to 325° where it began to decompose to the oxide, Co_3O_4 (21.7% found, 21.39% theor.). The DTA curve showed two endothermic peaks for the dehydration reaction followed by another endothermic peak caused by the decomposition reaction. The HTRS curve contained two peak maxima at 400 nm and 625 nm, respectively. The latter maximum shifted to 675 nm between 100° and 125° and to 690 nm above 125°. Two rather indistinct reflectance decreases were observed in the DRS curve between 75° and 135°.

Cobalt(II) 3-pyridinecarboxylate

Like the 2-pyridinecarboxylate complex, four moles of water were found for this compound, $Co(3PC)_2 \cdot 4H_2O$. However, the TGA curve indicated that all four moles of water are evolved in a single step (19.8% found, 19.20% theor.). The residue of the decomposition reaction is Co_3O_4 (21.2% found, 21.39% theor.). The DTA curve indicated only a single endothermic peak for the dehydration reaction and another such peak for the decomposition reaction.

Cobalt(II) 4-pyridinecarboxylate

The complex precipitates from solution as the pentahydrate, $Co(4PC)_2 \cdot 5H_2O$. Two moles of water are evolved in the first step (9.4% found, 9.16% theor.) while the remaining three moles are evolved in the second step (23.9% found, 22.90% theor.). Anhydrous $Co(4PC)_2$ decomposes in one step giving Co_3O_4 as the residue (20.2% found, 20.41% theor.). The DTA curve contained two endothermic peaks for the dehydration reaction and a single endothermic peak for the decomposition reaction.

Nickel(II) 2-pyridinecarboxylate

This compound precipitates from solution as the tetrahydrate, $Ni(2PC)_2 \cdot 4H_2O$.

The water of hydration is evolved in two steps (Fig. 1), each involving two moles of water (9.6% found, 9.61% theor. for the first two moles of water, and 19.3% found, 19.22% theor. for the loss of four moles of water). Anhydrous $Ni(2PC)_2$ dissociates to the oxide, NiO, in a single step (20.1% found, 19.92% theor.). Two endothermic peaks are present in the DTA curve (Fig. 2) corresponding to the loss of the four moles of water. The third endothermic peak is due to the decomposition of the anhydrous complex.

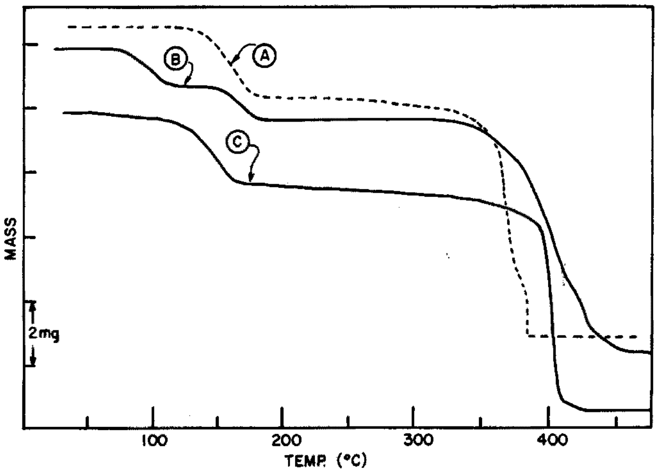


Fig. 1. Mass-loss curves of nickel(II) pyridinecarboxylates; air atmosphere; 10° per min; 10-mg sample. (A) Nickel(II) 4-pyridinecarboxylate 4-hydrate, (B) nickel(II) 2-pyridinecarboxylate 4-hydrate, (C) nickel(II) 3-pyridinecarboxylate 4-hydrate.

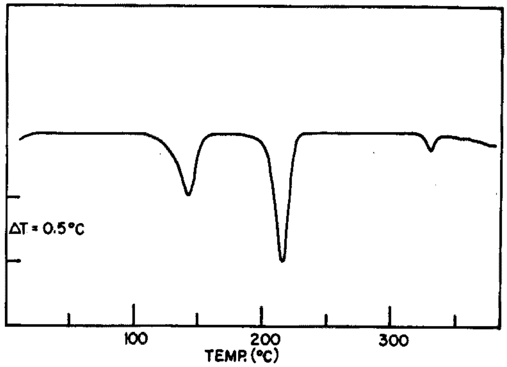


Fig. 2. DTA curve of nickel(II) 2-pyridinecarboxylate; N_2 atmosphere; 10° per min; 10-mg sample.

Nickel(II) 3-pyridinecarboxylate

As in the case of the 2-pyridinecarboxylate, this compound precipitates as the tetrahydrate, $Ni(3PC)_2 \cdot 4H_2O$. All four moles of water evolved in a single step on the TGA (Fig. 1 curve, (B)) (19.0% found, 19.22% theor.). The anhydrous complex decomposes in a single step to give the oxide, NiO (20.1% found, 19.92% theor.). The DTA curve contains two endothermic peaks; one for the dehydration reaction, the other for the decomposition of the anhydrous compound.

Nickel(II) 4-pyridinecarboxylate

Like the 3-pyridinecarboxylate complex, the tetrahydrate, $Ni(4PC)_2 \cdot 4H_2O$, loses its water of hydration in a single step (19.1% found, 19.22% theor.) (Fig. 1) Decomposition of the anhydrous complex, $Ni(4PC)_2$, is quite rapid to give the oxide, NiO (20.0% found, 19.92% theor.). The DTA curve contained three endothermic peaks, one for the dehydration reaction, the other two for the decomposition reaction.

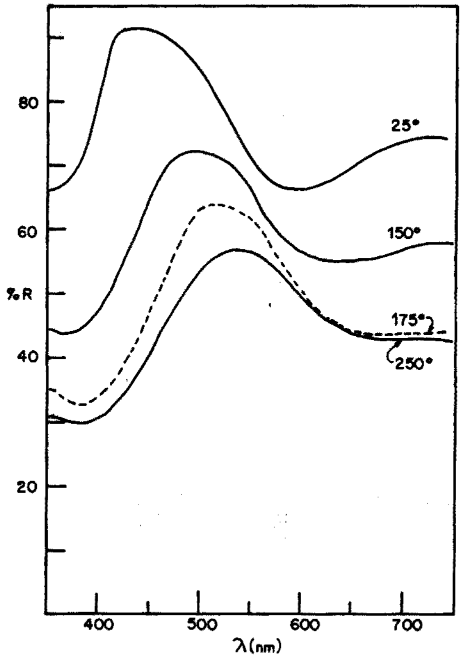


Fig. 3. High temperature reflectance curves of nickel(II) 4-pyridinecarboxylate.

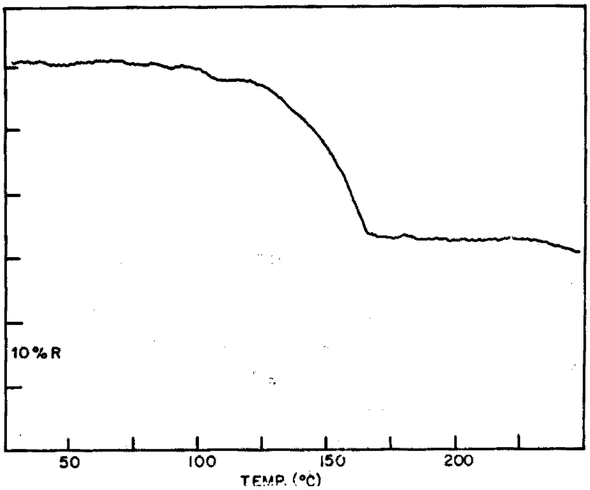


Fig. 4. DRS curve of nickel(II) 4-pyridinecarboxylate; 10° per min; 650 nm.

The HTRS curve (Fig. 3) has a single reflectance maximum at 425 nm which shifts to a higher wavelength as the temperature increases. At 170°, the peak maximum is 515 nm. The DRS curve (Fig. 4) indicates a one-step reaction, beginning at about 75°.

Copper(II) 2-pyridinecarboxylate

This compound, which is precipitated as the monohydrate, $Cu(2PC)_2 \cdot H_2O$, loses the water in a single step (5.6% found, 5.53% theor.) to give the anhydrous compound, $Cu(2PC)_2$. The latter dissociates almost explosively at 255° to give the oxide, CuO (24.1% found, 24.42% theor.). The DTA curve, as expected, contained only two endothermic peaks, one for the dehydration, the other for the decomposition reaction. The HTRS curves of this compound at various temperatures are shown in Fig. 5. One rather sharp reflectance maximum, at 430 nm, is present in all of the curves. The maximum decreases with increasing temperature and according to the DRS curve, increases to the original reflectance value on cooling. Thus, the $Cu(2PC)_2 \cdot H_2O$ complex exhibits thermochromic behavior. The other copper(II) compounds are also thermochromic, the only metal ion to exhibit this behavior.

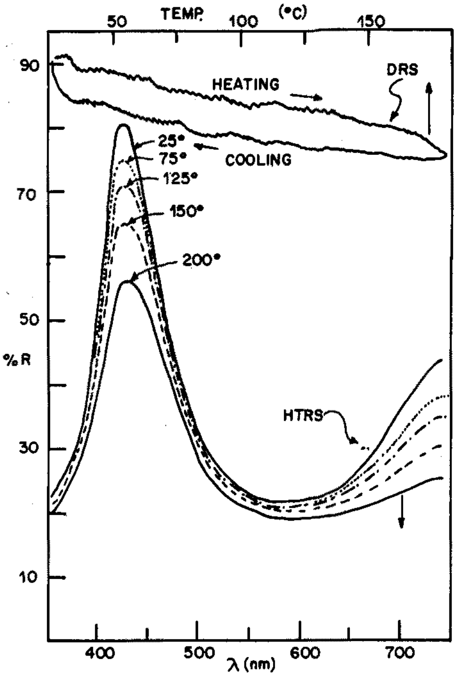


Fig. 5. High temperature reflectance curves and DRS curves of copper(II) 2-pyridinecarboxylate.

Copper(II) 3-pyridinecarboxylate

Like the preceding complex, the monohydrate, $Cu(3PC)_2 \cdot H_2O$, is precipitated from solution. This hydrate-bound water is evolved in two steps in the TGA curve; the first step corresponds to a loss of 2.8% and the second to a total mass-loss of 5.5%. The theoretical values are 2.76% for the loss of 0.5 mole of water and 5.53% for the evolution of one mole of water. The anhydrous complex, $Cu(3PC)_2$, decomposes at a very rapid rate to give the oxide, CuO (24.7% found, 24.42% theor.). The DTA curve confirms the above reactions in that there are two endothermic peaks for the loss of water and a single very narrow peak for the decomposition reaction.

Copper(II) 4-pyridinecarboxylate

Unlike the above complexes, the tetrahydrate is precipitated from solution as $Cu(4PC)_2 \cdot 4H_2O$. All four moles of water are evolved in one step (18.6% found, 19.01% theor.), giving the anhydrous compound, $Cu(4PC)_2$, which dissociates in two steps to give the oxide, CuO (20.8% found, 20.99% theor.). The DTA curve contained one endothermic peak for the dehydration and two for the decomposition reaction.

Zinc(II) 2-pyridinecarboxylate

The tetrahydrate, $Zn(2PC)_2 \cdot 4H_2O$, dehydrates in a single step (18.8% found, 18.88% theor.) to give the anhydrous compound, $Zn(2PC)_2$. The latter decomposes in two steps to give the oxide, ZnO (21.5% found, 21.32% theor.). The DTA curve contained one endothermic peak for the dehydration reaction and two not very well resolved peaks for the decomposition reaction.

Zinc(II) 3-pyridinecarboxylate

Unlike the above complex, this compound precipitates from solution as the trihydrate, $Zn(3PC)_2 \cdot 3H_2O$. The three moles of water are evolved in a single step (15.8% found, 14.86% theor.) giving the anhydrous compound, $Zn(3PC)_2$. The

TABLE IV

HEATS OF DEHYDRATION OF METAL PYRIDINECARBOXYLATES

Metal complex	*Dehydration reaction*	*Temp. range (°)*	ΔH *(cal/mole)*
2-Pyridinecarboxylates			
Fe(II)	4 → 0	85–140	32,000 ± 950
Co(II)	4 → 0	61–140	53,000 ± 1600
Ni(II)	4 → 2	61–114	23,000 ± 700
	2 → 0	140–188	27,000 ± 800
Cu(II)	1 → 0	71–88	4,600 ± 150
Zn(II)	4 → 0	61–127	50,000 ± 1500
3-Pyridinecarboxylates			
Mn(II)	2 → 0	128–162	23,000 ± 700
Fe(II)	3.5 → 3	45–89	5,100 ± 15
	3 → 0	95–140	27,500 ± 800
Co(II)	4 → 0	111–167	53,000 ± 1600
Ni(II)	4 → 0	103–171	48,000 ± 1450
Cu(II)	1 → 0.5	59–76	3,800 ± 100
	0.5 → 0	82–122	6,500 ± 200
Zn(II)	3 → 0	63–96	50,000 ± 1500
4-Pyridinecarboxylates			
Mn(II)	4 → 0	84–135	54,000 ± 1600
Fe(II)	2.5 → 0	81–144	23,000 ± 700
Co(II)	5 → 0	66–149	71,000 ± 200
Ni(II)	4 → 0	123–177	54,000 ± 160
Cu(II)	4 → 0	103–149	47,000 ± 1400
Zn(II)	4 → 0	84–112	28,000 ± 800

anhydrous complex dissociates in a single step, giving the oxide, ZnO (22.7% found, 22.38% theor.). There are two endothermic peaks present in the DTA curve caused by the dehydration reaction and a single endothermic peak caused by the decomposition reaction.

Zinc(II) 4-pyridinecarboxylate

This compound precipitates from solution as the tetrahydrate, $Zn(4PC)_2 \cdot 4H_2O$. All of the water of hydration is evolved in a single step in the TGA curve (18.9% found, 18.88% theor.), giving the anhydrous complex, $Zn(4PC)_2$. The latter dissociates in a single step to give the oxide, ZnO (21.1% found, 21.32% theor.). The DTA curve contains one endothermic peak from the dehydration reaction and another endothermic peak from the decomposition reaction.

Heats of dehydration

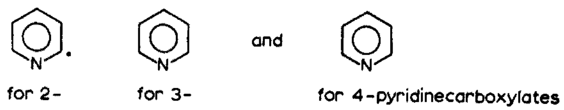
The heats of dehydration of the metal complexes are given in Table IV. For the tetrahydrates, the ΔH values ranged from 2800 ± 80 to 5400 ± 160 cal per mole with the majority of the values in the 4000–5000 cal per mole range. In general, the ligand has little effect on the dehydration reaction although there are some exceptions to this rule. The ΔH values were lowest for the monohydrate in terms of cal per mole of water evolved.

DISCUSSION

The thermal stability of the metal complexes is dependent on both the metal ion and the ligand. For the 2- and 3-pyridinecarboxylates, the order of decreasing stability was: $Mn > Zn = Fe > Co > Ni > Cu$; the order was similar for the 4-pyridinecarboxylates except that the zinc complex was more stable than that for manganese. With changing ligand, the order of decreasing stability for all of the metal ions, except zinc, 2-pyridinecarboxylates > 3-pyridinecarboxylates > 4-pyridinecarboxylates. In the case of zinc, the 4- is more stable than the 3-pyridinecarboxylate.

The higher thermal stability of the 2-pyridinecarboxylates is probably due to the ability of this ligand to form chelate bonds through the pyridine nitrogen and carboxylic oxygen to give two five-membered rings. The 3- and 4-pyridinecarboxylates cannot form such a chelate ring owing to steric factors caused by the position of the carboxyl group. Hence, their metal chelates possess a lower thermal stability.

With regard to the mechanism of the thermal dissociation processes of these compounds, it is interesting to note that KANEDA AND HARA[6] found exothermic peaks in the nitrogen atmosphere DTA curves for the cobalt(II), nickel(II), and zinc(II) 2-pyridinecarboxylates and nickel(II) 3-pyridinecarboxylates. The results of this investigation do not confirm these observations. In a nitrogen atmosphere, only endothermic peaks were found in the DTA curves. However, in an air atmosphere, there was occasionally a violent, exothermic decomposition reaction. The DTA curves in air usually contained an endothermic followed by an exothermic peak for the decomposition reaction. The first stage of the dissociation is therefore endothermic followed by the exothermic oxidation of the reaction products (or intermediates). According to KANEDA AND HARA[6], the first step in the decomposition of the anhydrous compounds is the release of the free-radical,



and one mole of carbon dioxide. These radicals then form pyridine and/or bipyridyls.

In general, the results described here agree with those previously reported[3–5] for the degree of hydration of the compounds. There were, however, a number of differences between this work and that of KANEDA AND HARA[6], especially for the manganese, cobalt, and nickel 3-pyridinecarboxylates. The thermal, as well as the magnetic susceptibility and infrared data[3,4,10,11], support an octahedral structure for the iron(II), cobalt(II) and nickel(II) 2-pyridinecarboxylates, while those for copper(II) and zinc(II) have a *trans*-planar configuration. For manganese(II) 2-pyridinecarboxylate, PARIS AND THOMAS[3] found that the dihydrate was octahedral while the anhydrous compound had the *trans*-planar configuration. The data available on the 3- and 4-pyridinecarboxylates does not permit any conclusions concerning this situation.

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SUMMARY

The thermal properties of the divalent metal complexes of 2-, 3-, and 4-pyridinecarboxylic acids were determined by TGA, DTA, DSC, high temperature reflectance spectroscopy, and dynamic reflectance spectroscopy. The complexes generally precipitate from solution as the hydrate containing 1–5 moles of water per mole of complex. The decomposition sequence is first the loss of hydrate water followed by the total disruption of the anhydrous complex to yield the metal oxide as the residue. Each dissociation reaction is discussed in terms of the above thermoanalytical techniques.

RÉSUMÉ

On a déterminé les propriétés thermiques de complexes de métaux divalents des acides 2-, 3- et 4-pyridinecarboxyliques par diverses méthodes spectroscopiques. Les complexes précipitent généralement sous forme d'hydrates, renfermant 1 à 5 molécules d'eau par molécule de complexe. Le premier stade de décomposition consiste en la perte de l'eau de cristallisation; il est suivi d'une décomposition totale du complexe anhydre, conduisant à l'oxyde métallique comme résidu.

ZUSAMMENFASSUNG

Die thermischen Eigenschaften der Komplexe von zweiwertigen Metallen mit 2-, 3- und 4-Pyridincarbonsäuren wurden ermittelt mit Hilfe von TGA, DTA, DSC, Hochtemperatur-Reflexionsspektroskopie und dynamischer Reflexionsspektroskopie. Die Komplexe fallen im allgemeinen aus Lösungen als Hydrate aus mit 1–5 Mol Wasser pro Mol Komplex. Die Zersetzung beginnt mit der Abgabe von Hydrat-Wasser, danach wird der wasserfreie Komplex vollständig zerstört und ergibt Metalloxid als Rückstand. Jede Zersetzungsreaktion wird entsprechend den angewandten thermoanalytischen Verfahren diskutiert.

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POLAROGRAPHIC ANALYSIS OF SOLUTIONS CONTAINING ADSORBABLE COMPLEXES

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In solutions containing complex-forming molecules or ions adsorbable at the electrode surface, the metal cations can accumulate at the electrode–solution interface by entering into complexes with the adsorbed ligands. Several authors have studied such cases[1–4] and some have applied the phenomenon for increasing the sensitivity of electroanalytical determinations[5–9]. The effect of adsorption of the oxidized form of an electroactive species on its electrolytic reduction and therefore also the potential increase of sensitivity of the determination depends upon the particular method of electrolysis used.

RIPAN AND DIMA[10] have shown that in aqueous solutions of divalent cations of Cd, Ni, Cu, Co, Ru, Fe and Mn in presence of thiocyanate ion and hexamethylenetetramine, slightly soluble addition compounds are formed, the solubility of which increases in the given series. WEISS[7,11] has found that in solutions containing thiocyanate ions and hexamethylenetetramine as masking agents, the above cations can be determined by oscillographic polarography at applied alternating current, with a sensitivity more than one order better than the usual. WEISS ascribed the higher sensitivity to the accumulation of the complex cations at the electrode by adsorption. A similar increase of sensitivity in the oscillopolarographic determination of cations has been observed by KALVODA AND JUAN AI-CHUA[8] with solutions of sulphuric acid containing thiocyanate ions and thiourea.

In the present paper, the behaviours of some addition complexes of cations with thiocyanate and hexamethylenetetramine (urotropine) or thiourea are compared for various methods of polarization of the dropping mercury electrode.

EXPERIMENTAL

Electrocapillary measurements were carried out with a capillary electrometer as described by GOUY. Polarographic curves were recorded with a P 101 polarograph (Yanagimoto, Kyoto) which contains the circuits for both a.c. and d.c. polarography. The recording of the *i–t* curves was photographic by means of a string galvanometer, as described by SMOLER[12]. For the study of the single-sweep curves a cathode-ray polarograph Type P 01 (Academy of Sciences, U.S.S.R.) was used. For a.c. oscillographic polarography, a Polaroscope P 576 (Křižík, Prague) which shows on the screen

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the dependence $dE/dt = f(E)$, was used. This apparatus was combined with an arrangement for polarization with single a.c. cycles[13]. The chronopotentiometric studies were made with an apparatus described by STURROCK[14] for derivative cyclic constant current voltammetry. Dropping mercury electrodes (D.M.E.) were applied throughout the work.

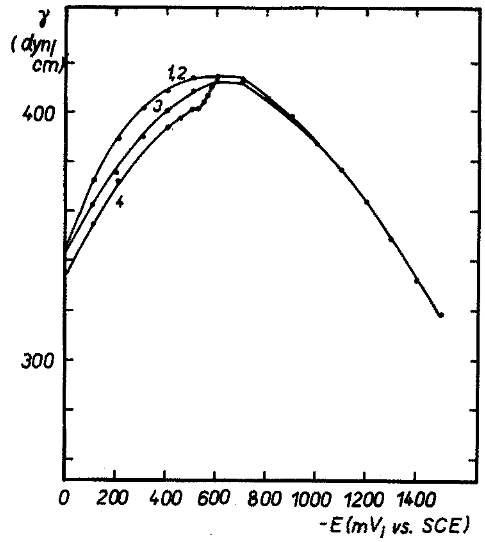
In most of the experiments a saturated calomel electrode was used as reference electrode; for a.c. oscillopolarography the mercury pool served as reference electrode.

All solutions were prepared from analytical-grade chemicals. Atmospheric oxygen was removed from the electrolytic cells by a stream of pure nitrogen.

RESULTS AND DISCUSSION

The adsorption of the ions on mercury in complexing solutions is demonstrated on electrocapillary curves. Figure 1 shows such curves for increasing concentrations of cadmium ions in solutions containing 0.5 *M* ammonium nitrate, 0.25 *M* urotropine and 0.1 *M* ammonium thiocyanate. In this medium, cadmium forms a slightly soluble addition complex of the composition[10] $[Cd\ C_6H_{12}N_4(H_2O)_2](SCN)_2$; in such a form a cation can become adsorbed on a positively charged electrode. At concentrations of cadmium(II) of about $5 \cdot 10^{-3}$ *M*, the growth of small crystals can be observed with a magnifying glass on the walls of the vessel and with a microscope on the surface of the D.M.E.

Figure 2 shows a d.c. polarographic curve of 10^{-3} *M* cadmium(II) in the above solution. In comparison with the curve of cadmium(II) in ammonium nitrate alone, hardly any shift of the half-wave potential is noticeable, and only a small maximum



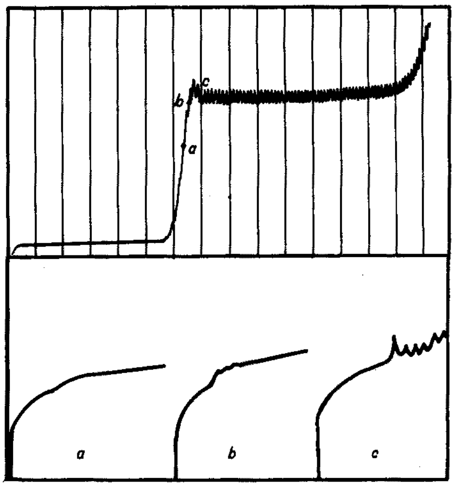


Fig. 1. Electrocapillary curves. (1) 0.5 *M* NH_4NO_3–0.25 *M* urotropine–0.1 *M* NH_4 SCN, (2) as (1) $+5 \cdot 10^{-4}$ *M* $CdSO_4$; (3) as (1) + $1.5 \cdot 10^{-3}$ *M* $CdSO_4$; (4) as (1) + $3 \cdot 10^{-3}$ *M* $CdSO_4$.

Fig. 2. D.c. polarographic curve of 10^{-3} *M* $CdSO_4$ in 0.5 *M* NH_4NO_3–0.25 *M* urotropine–0.1 *M* NH_4 SCN from 0 V (S.C.E.), 100 mV/absc. (a), (b), (c): *i–t* curves recorded at ascending part of the polarographic curve at the denoted potentials.

appears on the wave. The diffusion-controlled *i–t* curve recorded at the potential of the foot of the wave proved that the reduction of the complex proceeds reversibly. However, around the half-wave potential an inflexion appears on the *i–t* curve (Fig. 2a) which becomes more prominent at more negative potentials (Fig. 2b) until, in the potential range of the maximum, the instantaneous current begins to oscillate after a certain period of the drop-life (Fig. 2c). These irregularities on the *i–t* curves are accompanied by an upward streaming of the solution around the mercury drop, as observed with a microscope after suspending fine charcoal particles in the solution. At the limiting current of the d.c. polarographic wave, the current is again purely diffusion-controlled. The reason for the occurrence of the streaming maximum can be seen on the electrocapillary curve: the reduction of cadmium(II) from the adsorbed complex is accompanied by a change in the surface tension of mercury which is sufficiently strong to bring about a motion of the mercury surface and of the surrounding solution, as described by BARKER AND BOLZAN[5] for the case of reduction of a specifically adsorbed depolarizer.

Characteristic features pointing to the adsorption of the oxidized form of the depolarizer are shown by cations in the urotropine or thiourea complexing solutions when studied by a.c. polarography. The a.c. reduction peaks are directly proportional to concentration only at concentrations lower than 10^{-4} *M*; the whole dependence has the form of a Langmuir isotherm (Fig. 3). In the linear part of the dependence, the peaks are 2–3 times higher than those recorded in solutions of non-complexing electrolytes (Fig. 4). The sensitivity increase in a.c. polarography due to adsorption has been discussed by BARKER AND BOLZAN[5]. When compared with the a.c. curve of the supporting solution alone, the curve of the solution with depolarizer shows a depression of the base current where the adsorption occurs, *i.e.* at potentials more positive than the reduction peak. This depression increases with increasing depolarizer concentration, also in the form of an adsorption isotherm.

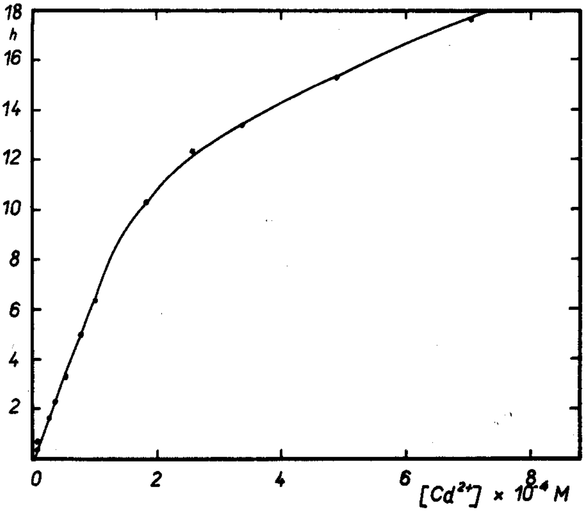
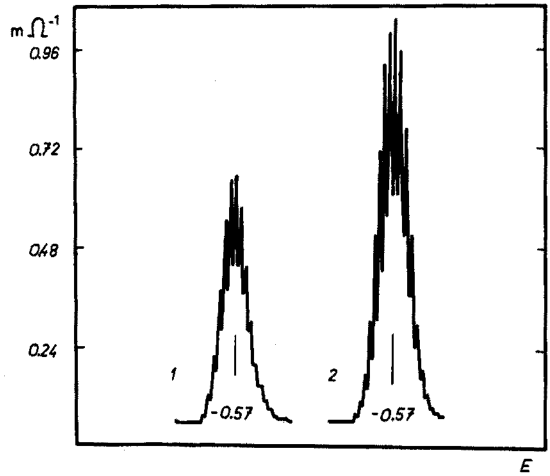


Fig. 3. Concentration dependence of the a.c. polarographic peak of cadmium(II) in 0.5 *M* NH_4NO_3–0.25 *M* urotropine–0.1 *M* NH_4SCN.

At the potentials of the a.c. peaks in complexing solutions at concentrations of depolarizer higher than about $5 \cdot 10^{-4}$ *M*, a streaming motion around the D.M.E. can be observed which ceases when the peak falls. The intensity of streaming increases in the sequence of cations Pb < Ni < Cd, in accordance with decreasing solubility of the complexes formed. The streaming motion was observed also when the hanging mercury drop electrode was used; in this case, in order to obtain reproducible effects, the drop had to be renewed after each experiment. Since the increase of sensitivity occurs at low depolarizer concentrations when no streaming can be observed, it appears, in accordance with the conclusion of BARKER AND BOLZAN[5], that the streaming is not the primary cause of the higher current peaks.



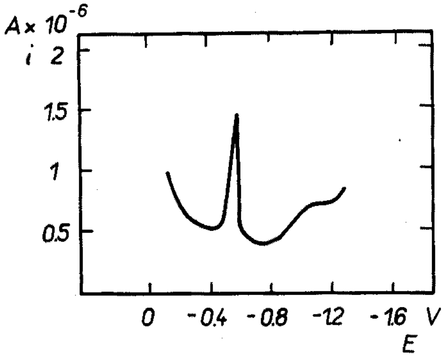


Fig. 4. The height increase of the a.c. peak of a specifically adsorbed depolarizer. (1) 10^{-4} *M* $CdSO_4$ in 0.1 *M* H_2SO_4, (2) 10^{-4} *M* $CdSO_4$ in 0.1 *M* H_2SO_4–0.1 *M* NH_4SCN–0.01 *M* thiourea.

Fig. 5. Single-sweep *i–E* curve of $6 \cdot 10^{-6}$ *M* $CdSO_4$ in 0.1 *M* NH_4NO_3–0.25 *M* urotropine–0.2 *M* NH_4SCN; $v = 0.5$ V/sec.

The special advantage of the high sensitivity of determinations of adsorbable complexes becomes apparent in methods where the electrode potential undergoes a rapid continuous change. Figure 5 shows a single-sweep oscillographic polarogram of $6 \cdot 10^{-6}$ *M* cadmium(II) in the urotropine–thiocyanate complexing solution. The high, narrow, symmetrical shape of the reduction peak already indicates that the depolarizer has been reduced in the adsorbed state[15,16]. The same conclusion follows from the dependence of the peak height on the rate of change of potential v (Fig. 6); whereas the diffusion-controlled peaks increase linearly with the square root of v, the peaks which are due to capacity changes are directly proportional to the first power of v; the present case, although the current is faradaic, is very near to the latter type. This offers the possibility of determining traces of depolarizers which undergo the electrode reaction in the adsorbed state in excess of an electroactive species transported to the electrode by diffusion, merely by increasing sufficiently the rate of change of potential. While at a high rate of potential change, the diffusion-controlled peaks are overlapped by the high base (essentially condenser) current, the peaks which are due to adsorbed depolarizers remain unaffected.

In oscillographic polarography at controlled alternating current with the usual a.c. frequency of 50 c sec^{-1}, the rate of change of potential v is higher than 200 V/sec, *i.e.* much in favour of a distinct development of the peak caused by the electrolytic reaction of an adsorbed depolarizer. This is why with solutions forming adsorption complexes, the sensitivity of oscillopolarographic determinations is considerably increased (Fig. 7).

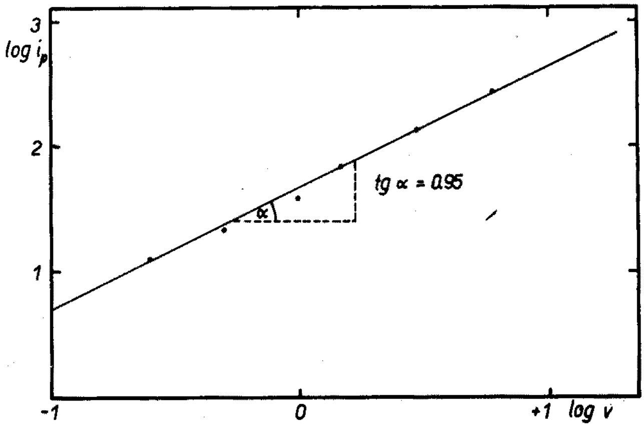


Fig. 6. Dependence of the single-sweep peak current from Fig. 5 on the rate of change of potential $v = dE/dt$.

Fig. 7. $dE/dt = f(E)$ curve of 10^{-5} *M* $CdSO_4$ in 0.5 *M* NH_4NO_3–0.25 *M* urotropine–0.1 *M* NH_4SCN.

Table I shows a comparison of the sensitivity of oscillopolarographic determinations by means of $dE/dt = f(E)$ curves, of several ions in various base electrolytes. Solution A consisting of 0.1 *M* sulphuric acid, 0.1 *M* ammonium thiocyanate and 0.01 *M* thiourea, and solution B consisting of 0.5 *M* ammonium nitrate, 0.25 *M* uro-

TABLE I

COMPARISON OF OSCILLOPOLAROGRAPHIC SENSITIVITIES FOR VARIOUS CATIONS WITH AND WITHOUT FORMATION OF ADSORPTION COMPLEXES

Ion	*Base solution*	*Minimum concentration yielding a measurable incision*	*Sensitivity increase*
Pb^{2+}	1 *M* KOH	$5 \cdot 10^{-5}$ *M*	
	A	$4 \cdot 10^{-5}$ *M*	—
	B	$4 \cdot 10^{-5}$ *M*	—
Cd^{2+}	1 *M* H_2SO_4	$1 \cdot 10^{-4}$ *M*	
	1 *M* NH_4NO_3	$1 \cdot 10^{-4}$ *M*	
	A	$3 \cdot 10^{-6}$ *M*	33 ×
	B	$3 \cdot 10^{-6}$ *M*	33 ×
Cu^{2+}	1 *M* NH_4NO_3	$1 \cdot 10^{-4}$ *M*	
	A	$1.5 \cdot 10^{-6}$ *M*	66 ×
	B	$1.5 \cdot 10^{-6}$ *M*	66 ×
Ni^{2+}	1 *M* $NH_4Cl + NH_4OH$	$1 \cdot 10^{-4}$ *M*	
	A	$3 \cdot 10^{-6}$ *M*	33 ×
Tl^{+}	1 *M* KOH	$1 \cdot 10^{-4}$ *M*	
	A	$2 \cdot 10^{-5}$ *M*	5 ×
	B	$1 \cdot 10^{-5}$ *M*	10 ×

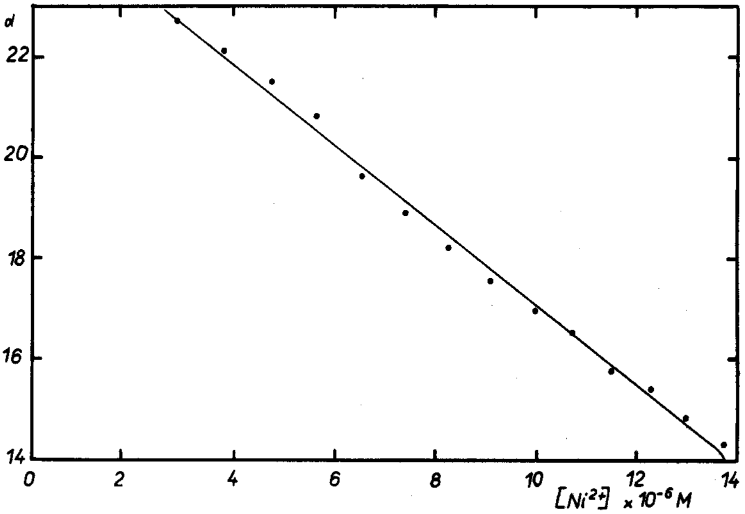


Fig. 8. Concentration dependence of the depth of incision in the dE/dt=f(E) curve of $NiSO_4$ solution in 0.1 *M* NH_4SCN–0.5 *M* NH_4NO_3–0.25 *M* urotropine.

tropine and 0.1 *M* ammonium thiocyanate are compared with solutions where no adsorption complexes are formed.

Figure 8 shows the concentration dependence of the depth of the incision in the dE/dt = f(E) curve for the case of nickel(II) in the urotropine–thiocyanate solution. As Table I shows, the sensitivity increase caused by formation of adsorptive complexes is greater than one order of magnitude, as reported by WEISS[7,11].

A further increase in the sensitivity of determination can be attained by polarizing the dropping electrode by a single cycle of alternating current at a definite moment of the drop-time[8]. In this way, during the period before the polarization cycle is applied, sufficient time is given for the full establishment of the adsorption equilibrium (Figs. 9, 10). By polarizing the electrode in the course of the quiescent period from a d.c. source at a certain constant potential, the amount of the adsorbed complex can be affected. The effect of the potential of the d.c. polarization on the depth of the incision is shown in Fig. 11. From this, it follows that in each case, the potential corresponding to maximum adsorption should be chosen for the d.c. polarization. In this way cadmium(II), copper(II) and nickel(II) can be determined even at concentrations of $5 \cdot 10^{-7}$ *M* (Fig. 9).

Fig. 9. d*E*/d*t* = f(*E*) curves for $1.5 \cdot 10^{-6}$ *M* Ni(II) in 0.5 *M* NH_4NO_3–0.25 *M* urotropine–0.1 *M* NH_4SCN. Electrode polarized by several cycles of a.c.; during the quiescent period of 2.5 sec polarized at −0.4 V (the deepest incision corresponds to the first cycle).

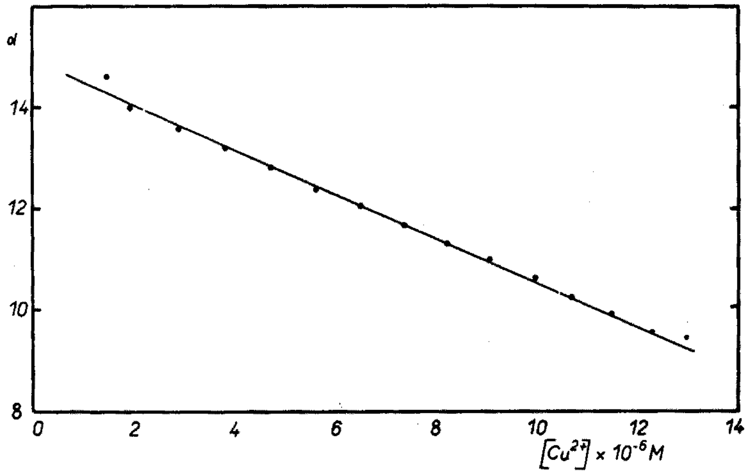


Fig. 10. Concentration dependence of the depth of incision in the d*E*/d*t* = f(*E*) curve of CuSO solution in 0.1 *M* NH_4SCN–0.5 *M* NH_4NO_3–0.25 *M* urotropine; single polarization cycle.

Results analogous to the a.c. oscillopolarography were obtained by the technique of derivative chronopotentiometry[14]. Here, the electrode is polarized by a pulse of constant current within a controlled range of potentials (between −0.2 and −1.35 V *vs.* S.C.E.). Cd(II) in the urotropine–thiocyanate solution yielded an incision in the dE/dt=f(E) curve (Fig. 12) at $E = -0.63$ V, as in oscillopolarography, but the incision became evident at the unusually low concentration of $7 \cdot 10^{-8}$ M; in 0.5 M ammonium nitrate solution, the cadmium incision appeared only at concentrations higher than $5 \cdot 10^{-6}$ M. The transition times calculated from the dE/dt=f(E) curves by means of the formula derived by PETERS AND BURDEN[17] were considerably higher than would be expected for diffusion-controlled processes. For the concentration $7.9 \cdot 10^{-8}$ M cadmium(II), at a current density of $5.56 \cdot 10^{-3}$ A cm^{-2}, the transition time measured was $1.5 \cdot 10^{-4}$ sec. The chronopotentiometric constant $i_0\tau^{\frac{1}{2}}/c$ shows a dependence on τ in the sense that it increases with decreasing τ, which is a possible indication of adsorption of the depolarizer[18]. The same conclusion follows from the dependence of the chronopotentiometric constant on the concentration of depolarizer. The value around 0.5 mA sec$^{\frac{1}{2}}$ cm^{-2} mM^{-1} of this constant, characteristic for dif-

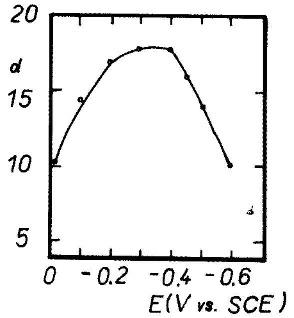


Fig. 11. Dependence of the depth of incision in the single-cycle dE/dt = f(E) curve of $5 \cdot 10^{-6}$ M CdSO$_4$ in the urotropine complexing solution on the potential of d.c. prepolarization.

Fig. 12. Incision in the dE/dt = f(E) curve obtained by the derivative cyclic constant-current chronopotentiometric method in $1 \cdot 10^{-6}$ M CdSO$_4$ in the urotropine complexing solution.

TABLE II

CHRONOPOTENTIOMETRIC CONSTANTS FOR VARIOUS CONCENTRATIONS OF IONS

Ion	*Solution*	*Concentration range ($M\ l^{-1}$)*	*Chronopotentiometric constant ($mA\ sec^{\frac{1}{2}}\ cm^{-2}\ mM^{-1}$)*
Cd^{2+}	Urotropine + thiocyanate	10^{-7}–10^{-6}	13.34
		$7.9 \cdot 10^{-6}$–10^{-5}	3.03
		$7.4 \cdot 10^{-5}$–$1.4 \cdot 10^{-4}$	0.593
		$1.4 \cdot 10^{-4}$–$3.0 \cdot 10^{-4}$	0.488
Cd^{2+}	NH_4NO_3	10^{-5}–10^{-4}	0.44
Cu^{2+}	Urotropine + thiocyanate	$2.0 \cdot 10^{-6}$–$7.5 \cdot 10^{-6}$	8.3

fusion-controlled electrode processes, appears in the solutions yielding adsorbable complexes only at concentrations higher than 10^{-4} *M*; at lower concentrations this value increases up to about 20 times (Table II).

SUMMARY

The electrolytic reduction of some adsorbable addition complexes was followed by d.c. and a.c. polarography, single-sweep and a.c. oscillographic polarography and chronopotentiometry. The adsorption of the depolarizer leads to an increase in the sensitivity of the analytical determination with different methods to different extents; the highest increase, almost 100-fold, was found with the controlled-current methods.

RÉSUMÉ

On a examiné la réduction électrolytique de certains complexes adsorbables, par polarographie, polarographie à balayage simple et oscillographique et chronopotentiométrie. L'adsorption du dépolarisant conduit à une augmentation de la sensibilité qui varie suivant la méthode. Les plus fortes augmentations (presque 100 fois) ont été observées avec les méthodes à courant contrôlé.

ZUSAMMENFASSUNG

Die elektrolytische Reduktion einiger adsorbierbarer Additionskomplexe wurde untersucht durch Gleichstrom- und Wechselstrompolarographie, "single sweep"- und Wechselstrom-Oscillopolarographie und Chronopotentiometrie. Die Adsorption des Depolarisators führt, je nach Methode in unterschiedlichem Ausmass, zu einer Steigerung der Empfindlichkeit der analytischen Bestimmung; die höchste Steigerung, beinahe 100-fach, wurde bei den stromkontrollierten Methoden festgestellt.

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DETERMINATION OF PHOSPHORUS IN NIOBIUM, ZIRCONIUM, TITANIUM AND TUNGSTEN

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Phosphorus has been determined by the molybdenum blue procedure directly, or with prior extraction of the yellow molybdo-phosphoric acid with isobutyl alcohol in titanium[1] and zirconium[2,3]. In niobium[4] it has been determined using a preliminary extraction with isobutyl methyl ketone.

The yellow arsenomolybdate complex is also extracted by isobutyl alcohol and so arsenic must be separated by volatilization as the bromide. To avoid this separation, PAKALNS[5] has recommended isobutyl acetate as an extractant to overcome arsenic interference. ELWELL AND WOOD[6] have determined phosphorus in titanium, zirconium and tungsten by forming the yellow phosphovanadomolybdate in dilute acid solutions containing tartrate and subsequently extracting the coloured solution into isoamyl alcohol.

Trace amounts of titanium and niobium interfere with phosphorus determinations in zirconium solutions containing no complexing agents[2,3]. The addition of complexing agents such as fluoride[5] and tartrate[6] allows phosphorus to be determined in zirconium solutions containing titanium, but niobium interferes seriously[5]. Tartrate does not complex niobium completely, and low results are produced when extraction is carried out with isobutyl methyl ketone[6].

This paper describes the determination of phosphorus in niobium, zirconium, titanium and tungsten by forming the yellow phosphovanadomolybdate in solutions containing fluoride, and subsequent extraction of the yellow complex into isobutyl methyl ketone. Fluoride also forms strong complexes with manganese, tin, silicon and other metals which interfere with the determination of phosphorus by previous methods. The new procedure allows phosphorus to be determined in various niobium, zirconium, titanium and tungsten alloys.

EXPERIMENTAL

Apparatus

A Unicam SP 600 spectrophotometer with 2-cm cells.

Reagents

Standard phosphorus solution. Prepare a stock solution containing 0.1 mg P/ml by dissolving 0.4393 g of potassium dihydrogen phosphate in 1 l of water. Prepare a working solution (0.04 mg P/ml) by diluting 100 ml of stock solution to 250 ml.

Ammonium molybdate solution (15%). Prepare from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and store in a polythene bottle.

Ammonium vanadate solution (0.25%). Dissolve 2.5 g of ammonium metavanadate in 500 ml of water by heating. Cool and dilute to 1 l.

Recommended procedure

Transfer 0.5 g of the sample to a 250-ml Teflon beaker and add 13 ml of 9 *M* sulphuric acid, 5 ml of 15 *M* nitric acid and 2 ml of 40% hydrofluoric acid (add 5 ml of hydrofluoric acid if niobium is present). After dissolution, evaporate until fumes of sulphur trioxide appear, and then cool. Add 35 ml of water, 3 ml of 40% hydrofluoric acid, and bring to the boil. Add 1.5 ml of 1% potassium permanganate solution, boil for 2 min, then add 0.75 ml of 5% sodium nitrite solution and boil until free of nitrous oxide fumes. Cool, add 10 ml of ammonium vanadate solution and 65 ml of ammonium molybdate solution, and then allow to stand for 15 min. Add 30 ml of water, transfer the solution to a 250-ml separating funnel and dilute to 150 ml with water.

Add 40 ml of isobutyl methyl ketone (IBMK) and shake for 30 sec. Allow the two layers to separate and discard the aqueous layer. Filter the ketone layer through a double-layer rapid filter paper into a small dry beaker. Measure the absorbance immediately in 2-cm cells at a wavelength of 425 nm for 50–400 μg of phosphorus, and in 4-cm cells at 400 nm for 0–50 μg of phosphorus, using water as reference solution. Subtract the blank value.

To prepare a blank and a standard curve in the range 0–400 μg of phosphorus, add 13 ml of 9 *M* sulphuric acid to aliquots of the standard phosphorus solutions and evaporate to fumes. Cool and continue as in the recommended procedure.

In the case of tungsten metal incorporate 0.5 g of pure tungsten metal in the preparation of blank and the standard curve.

DISCUSSION

Sensitivity and stability of the method

The absorbance of the phosphovanadomolybdate can be measured in the region between 400 and 480 nm. The absorbance of the complex and blanks increases with decreasing wavelength. The 2-cm cells and wavelength of 425 nm were selected to determine phosphorus between 0.01 and 0.08% in a 0.5-g sample. Below 0.01% phosphorus must be determined by using 4-cm cells and a wavelength of 400 nm, where the sensitivity is twice that obtained at 425 nm. The molar absorptivity of the complex in IBMK is 1740 and 3100 at 425 and 400 nm, respectively. Beer's law is obeyed to at least 38 μg P/ml.

The colour of the complex in the organic phase is stable for at least 1 h, when measured against the reagent blank. The absorbance of the phosphovanadomolybdate does not change in the investigated temperature range 19–25°.

Dissolution of sample

Samples were dissolved in Teflon beakers already containing the correct amount of sulphuric acid necessary for the colour development of the phosphovanadomolybdate. Samples may also be dissolved in platinum dishes, but then the sample, after fuming with sulphuric acid, must be transferred to a Teflon beaker with 35 ml of water for washing. Hydrofluoric acid is used to volatilize silicon, to dissolve niobium, zirconium, titanium and tungsten, and to prevent the precipitation of tungsten, tin and other oxides during the initial dissolution step. Tungsten oxide precipitates on fuming with sulphuric acid, is not dissolved completely on addition of 3 ml of 40% hydrofluoric acid, and interferes slightly with the phosphorus determination.

Choice of acidity and effect of varying reagent concentrations

The amount of sulphuric acid was varied to determine the effect of sulphuric acid concentration on the absorbance. Constant absorbances were obtained when 3.5–7.5 ml of 18 *M* sulphuric acid was used in the sample dissolution procedure, and the total volume for colour development was 115 ml.

An amount of 3 ml of 40% hydrofluoric acid was required to complex titanium, niobium and tungsten completely, thus releasing phosphorus to form the yellow phosphovanadomolybdate. Although only 2 ml of 40% hydrofluoric acid was required to complex zirconium when 50 ml of 15% ammonium molybdate solution was used, this method was designed to cover phosphorus determination in all four metals or their mixtures. Also, 3 ml of 40% hydrofluoric acid was required to minimise interference by chromium.

The amount of ammonium molybdate was increased to 65 ml to compensate for the added fluoride. It was necessary to add 17 ml of 15% ammonium molybdate for each ml of 40% hydrofluoric acid, otherwise the maximum colour development of phosphovanadomolybdate was not obtained. The concentration of ammonium vanadate was left unchanged[6] because addition of larger amounts of reagent did not affect the results.

Reagent blanks and standard curve

The absorbance of the reagent blank was low (0.020 and 0.105 abs. units against water at 425 and 400 nm respectively) and depended on the phosphorus content of the ammonium molybdate reagent.

It was established that niobium, zirconium and titanium had no effect on the absorbance and therefore the standard curve may be prepared by omitting these metals from the procedure. Tungsten produced some interference which was proportional to the amount of tungsten present in the sample aliquot (Table I).

TABLE I

INTERFERENCE BY CHROMIUM AND TUNGSTEN

(0.5-g sample, 2-cm cells, 425 nm)

Metal added			*P*	*Absorbance*	*Error*
Ion	*(mg)*	*(%)*	*(μg)*		*(%)*
Nil	—	—	200	0.560	—
Cr^{3+}	50	10	200	0.553	− 1
Cr^{3+}	50	10	150	0.418	− 0.5
Cr^{3+}	50	10	100	0.280	—
W(VI)	500	100	200[a]	0.530	− 6
W(VI)	250	50	200[a]	0.545	− 3
W(VI)	100	20	200[a]	0.555	− 1

[a] Checked also on 50 and 100 μg P.

Extraction

The volume of solution before the extraction was increased to 150 ml to overcome any precipitation in the filtered organic phase which can be caused by the high salt concentration in the aqueous layer. The filtered organic solution was stable, but to overcome any errors caused by formation of precipitates in the blank, water is recommended as a reference solution. Provided that the correct amount of sulphuric acid was present for the formation of the phosphovanadomolybdate, dilution to 150 ml, or to 165 ml when 15 ml of 50% citric acid was added to complex the arsenic, had no effect on the absorbance.

Study of interferences

No interference was observed from the following concentrations of alloying elements: 10% Cu, Fe, Mo, Mn, Ni, Sn, 5% V, and also when the determination was done in pure thorium and uranium metals. Therefore phosphorus can be determined in niobium, zirconium, titanium and tungsten alloys containing thorium and uranium.

Arsenic interferes seriously but can be complexed after diluting the sample to 150 ml by adding 15 ml of 50% citric acid, then immediately adding 40 ml of IBMK and shaking for 30 sec.

Chromium(III) interferes slightly when present in large amounts, but the interference decreases with the decrease in the phosphorus content (Table I). It has been shown previously that the chromium(III) interference is increased by the presence of fluoride[7].

Tungsten interferes when present in amounts larger than 50 mg per determination (Table I). Tungsten retains some phosphorus in the hydrolytic precipitate and this interference is shown prominently when pure tungsten is analysed for phosphorus.

Reproducibility of the method

Readings on series of 10 standards showed the relative standard deviation at the 5 μg P/ml level (in isobutyl methyl ketone) to be ±0.5%.

Comparison with other methods

The results obtained for some zirconium low-alloy samples are shown in Table II and are in good agreement with results from the modified molybdenum blue pro-

TABLE II

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS IN ZIRCALOYS

Sample[a]	*P found (p.p.m.)*	
	Present method	*Modified molybdenum blue*[b]
V379	6	12
V380	45	50
V381	346	330
V382	158	150
V647	7	10

[a] Samples submitted by Venthon Research Laboratories, France, for interlaboratory comparison analyses.
[b] Ref. 5.

cedure[5]. This modified method was used to determine the phosphorus in zirconium alloys containing titanium and the procedure is as follows:

Dissolve 1 g of sample in 10 ml of water, 5 ml of concentrated nitric acid and 2 ml of 40% hydrofluoric acid, and add 40% hydrofluoric acid to obtain an additional 0.1 ml of 40% hydrofluoric acid per sample aliquot taken for analysis. Add 20 ml of water and 2 ml of saturated potassium permanganate solution. Boil for 2 min and add 1 ml of 10% hydroxylamine hydrochloride. Cool. Transfer to a 100-ml polythene cylinder containing 30 ml of 4% boric acid and dilute to volume. Pipette an aliquot containing 7–12 μg of P and not more than 0.2 g of zirconium into a 250-ml polythene beaker, increase the amount of boric acid to 7.5 ml and continue as in the recommended procedure.

The method described in this paper is superior to the molybdenum blue procedure because large sample sizes are possible and less interference occurs in the blanks.

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

SUMMARY

A method is described for the spectrophotometric determination of up to 0.08% phosphorus in niobium, zirconium, titanium and tungsten and their alloys, based on the extraction of phosphovanadomolybdate by isobutyl methyl ketone. The matrix metals are complexed by fluoride ion and do not interfere in the procedure. The molar absorptivity is 1740 and 3100 at 425 and 400 nm respectively, with a standard deviation of ±0.5%.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du phosphore (jusqu'à 0.08%) dans le niobium, le zirconium, le titane et le tungstène et dans leurs alliages; elle consiste à extraire le phosphovanadomolybdate dans l'isobutylméthylcétone. Les métaux de la matrice sont complexés par le fluorure et ne gênent pas. Le coefficient d'extinction molaire est de 1740 et 3100 à 425 et 400 nm, repectivement, avec une déviation standard de ±0.5%.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben für die spektrophotometrische Bestimmung von bis zu 0.08% Phosphor in Niob, Zirkonium, Titan, Wolfram und deren Legierungen. Das Verfahren beruht auf der Extraktion von Molybdatovanadatophosphat mit Methylisobutylketon. Die Matrixmetalle werden durch Fluoridionen komplexiert und stören die Bestimmung nicht. Der molare Extinktionskoeffizient beträgt 1740 bei 425 nm und 3100 bei 400 nm mit einer Standardabweichung von ±0.5%.

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SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM(III) WITH 5,7-DICHLORO-, 5,7-DIBROMO-AND 5,7-DINITRO-8-HYDROXYQUINOLINE N-OXIDE

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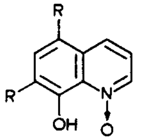
BEAMISH[1] has reviewed the use of the organic reagents for the determination of ruthenium, and has stressed the need for a specific reagent. Many new organic reagents have recently been suggested for the spectrophotometric determination of ruthenium, *e.g.*, 1-nitroso-2-naphthol[2], nitroso-R salt[3,4], 3-nitroso-4-hydroxycoumarin[5], 9-nitroso-10-phenanthrol (phenanthrene quinone monooxime)[6], 2-amino-8-naphthol-6-sulphonic acid[7], 2,3-diaminopyridine[8], 4,7-diphenyl-1,10-phenanthroline[9], salicylic acid[10], thiosalicylic acid[10], Xylenol Orange[11], Chrome Azurol S[12], 1-4,diphenylthiosemicarbazide[13], dinaphthol[14] and 2,4,6-tri(2′-pyridyl)-s-triazine[15]. Though sensitive, these reagents lack specificity.

During studies on 8-hydroxyquinoline N-oxide complexes, it was observed that this reagent forms complexes with all the six platinum metals, and that those with ruthenium(III) and iridium(IV) can be used for the spectrophotometric determination of these metal ions, as the molar absorptivities are fairly high. In an attempt to improve the selectivity of 8-hydroxyquinoline N-oxide (I) by substitution in the ring, the nature of the complexes formed by the platinum metals with some 5,7-disubstituted derivatives of (I) was investigated. The 5,7-dichloro-, 5,7-dibromo- and 5,7-dinitro-8-hydroxyquinoline N-oxides ((II), (III) and (IV)) were found to form intensely coloured complexes with ruthenium(III) only. The colours and wavelengths of maximum absorbance of the three complexes were brownish-green (430 nm), brownish green (420–430 nm) and yellowish brown (410 nm), respectively. However, when the measurements were made at 540–625 nm, the interference of other platinum metals in the spectrophotometric determination of ruthenium(III) was reduced, and ruthenium could be determined in the presence of even 10-fold amounts of the other platinum metals.



(I) R=H
(II) R=Cl
(III) R=Br
(IV) R=NO_2

EXPERIMENTAL

Chemicals and instruments

5,7-Dichloro-8-hydroxyquinoline N-oxide (II), 5,7-dibromo-8-hydroxyquinoline N-oxide (III) and 5,7-dinitro-8-hydroxyquinoline N-oxide (IV) were prepared from 8-hydroxyquinoline N-oxide as described earlier[16,17], and were used as freshly prepared acetone solutions of appropriate concentrations. Stock solution of ruthenium(III) was prepared by dissolving ruthenium trichloride (Johnson–Matthey) in 1 *M* hydrochloric acid (B.D.H. AnalaR); any ruthenium(IV) present was reduced to the tervalent state by boiling with ethanol. The solution was standardised gravimetrically and spectrophotometrically[1]. All other chemicals used were either obtained from Johnson–Matthey, or were of AnalaR grade.

All pH measurements were made with the help of a Beckman pH meter model H 2 with a suitable glass electrode, the pH being adjusted with dilute hydrochloric acid and sodium hydroxide. A Unicam spectrophotometer model SP 600 with 1-cm cells was used for all the absorbance measurements.

All the investigations were carried out in 60% acetone to obtain a homogeneous medium; constant ionic strength was maintained at 0.10 *M* with sodium chloride.

Spectral characteristics of the ruthenium(III) complexes

The absorbance spectra of solutions obtained by heating 1 ml of $4 \cdot 10^{-3}$ *M* ruthenium(III) with a 10-fold excess of reagent in a boiling water bath for 90 min, cooling, and diluting to 25 ml, were measured at different pH values against reagent blanks (Figs. 1–3). The wavelengths of maximum absorbance, the molar absorptivities

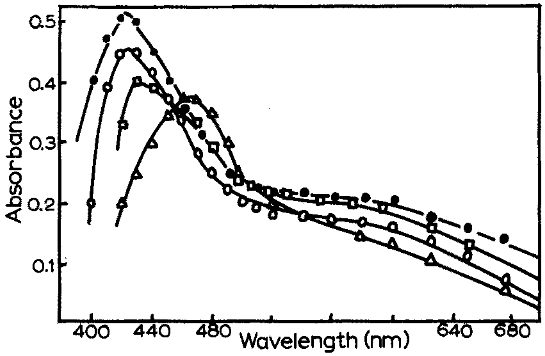


Fig. 1. Absorbance spectra of ruthenium(III)–5,7-dichloro-8-hydroxyquinoline N-oxide, containing 16 p.p.m. Ru(III) at pH 2.0 (○); 3.0, 4.0, 5.2 (●); 7.0 (□); 9.3, 10.3 (△).

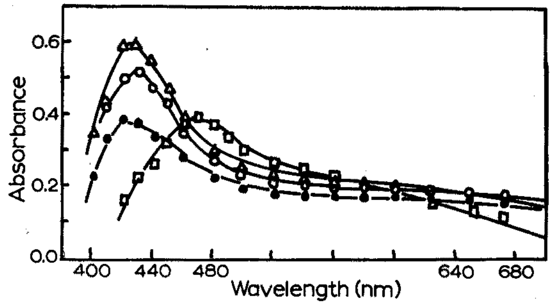


Fig. 2. Absorbance spectra of ruthenium(III)–5,7-dibromo-8-hydroxyquinoline N-oxide, containing 16 p.p.m. Ru(III), at pH 2.5 (●); 3.0, 4.2, 5.0 (△); 6.4 (○); 8.7–10.0 (□).

and the pH range where the absorbance of the solution (measured against a reagent blank) remains constant, are given in Table I; the ranges in which Beer's law is obeyed are also given. Clearly the dinitro derivative provides the greatest sensitivity.

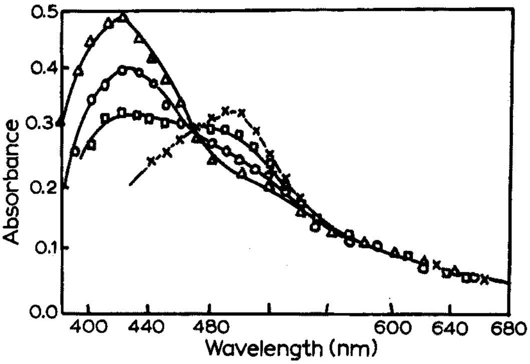


Fig. 3. Absorbance spectra of ruthenium(III)–5,7-dinitro-8-hydroxyquinoline N-oxide, containing 8 p.p.m. Ru(III), at pH 1.5, 2.3, 4.0, 5.0 (△); 5.5 (○); 6.0 (□); 7.2, 8.1 (×).

TABLE I

SPECTRAL CHARACTERISTICS OF RUTHENIUM(III) COMPLEXES WITH SOME 8-HYDROXYQUINOLINE N-OXIDE DERIVATIVES IN 60% ACETONE CONTAINING 0.10 M NaCl AT 35–37°

Derivative	*Wave-length (nm)*	*Molar abs. $\cdot 10^{-3}$ l cm^{-1} mole^{-1}*	*Colour of solution*	*pH range of constant absorbance*	*Range for Beer's law (p.p.m. Ru)*
5,7-Dichloro	430	3.24	Brownish green	2.6–5.5	3.5–32.0
	460–470	2.47	Dark yellow	8.5–10.7	5.5–60.0
5,7-Dibromo	420–430	3.75	Brownish green	2.6– 5.0	2.5–30.0
	470	2.23	Dark yellow	8.3–10.7	6.0–60.0
5,7-Dinitro	410	6.10	Yellow	1.3– 5.2	1.0–15.0
	490	4.00	Yellow	6.0– 8.5	2.0–20.0

Effect of the reagent concentration

For complete colour development, a minimum of 4 times the stoichiometric amount of the reagent was necessary (Fig. 4). For the determination of ruthenium(III), a 10-fold amount of the reagent was used.

Extractability

It was found that from solutions of the ruthenium(III) complexes containing no acetone, the coloured complexes could be extracted moderately by isoamyl alcohol, isobutyl alcohol, cyclohexanol and methyl isobutyl ketone; they were only slightly extracted by ether, ethyl acetate and chloroform, and not extracted by benzene, toluene, petroleum ether or carbon tetrachloride.

Interference of diverse ions

In the determination of 5 p.p.m. of ruthenium(III) with any of the reagents, even 1000-fold amounts of chloride, sulphate, nitrate; 500-fold amounts of perchlorate, and 200-fold amounts of acetate, oxalate, tartrate, citrate, fluoride, phosphate or nitrite did not interfere. The maximum amounts of other ions tolerated are given in Table II. It was found that when measurements were made at 540–625 nm, the

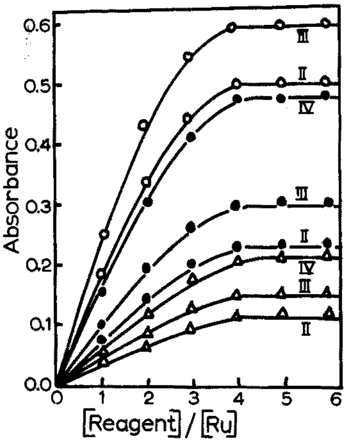


Fig. 4. Effect of reagent concentration on the formation of the ruthenium(III) complexes with reagents (II), (III) and (IV) at the respective wavelengths of maximum absorption. (○) 16 p.p.m. Ru, (●) 8 p.p.m. Ru, (△) 4 p.p.m. Ru.

TABLE II

INTERFERENCE OF FOREIGN IONS IN THE DETERMINATION OF RUTHENIUM(III) WITH 5,7-DICHLORO- (II), 5,7-DIBROMO- (III) AND 5,7-DINITRO-8-HYDROXYQUINOLINE N-OXIDE (IV) IN 60% ACETONE

Foreign ion	*Maximum amount tolerated (in p.p.m.) with reagent*					
	II at		*III at*		*IV at*	
	430 nm^{a}	*600 nm*^{a}	*420 nm*^{b}	*600 nm*^{b}	*410 nm*^{c}	*600 nm*^{c}
Rh(III)	40.0	150.0	26.0	200^{d}	30.0	200^{d}
Pd(II)	15.0	140.0	9.0	200^{d}	10.0	200^{d}
Os(IV)	8.0	150.0^{d}	5.9	150^{d}	7.5	150^{d}
Ir(IV)	3.0	30.0	1.2	20.0	1.5	45
Pt(IV)	75.0	400^{d}	52.0	400^{d}	70.0	400^{d}
Au(III)	25.0	400^{d}	20.0	400^{d}	20.0	400^{d}
Ag(I)	400^{d}	400^{d}	400^{d}	400^{d}	400^{d}	400^{d}
Cu(II)	2.0	4.0	1.2	13.2	12.0	12.0
Ni(II)	2.0	14.0	1.5	15.0	13.5	15.0
Co(II)	15.0	35.0	15.0	35.0	20.0	60.0
Fe(II)	50.0	50.0	50.0	35.0	15.0	45.0
Cr(III)	10.0	70.0	8.0	70.0	8.0	70.0
Hg(II)	200^{d}	200^{d}	200^{d}	200^{d}	200^{d}	200^{d}
Sn(II)	Interferes seriously in all cases.					
Zn(II)	500^{d}	500^{d}	500^{d}	500^{d}	500^{d}	500^{d}

[a] For 15.0 p.p.m. ruthenium(III).
[b] For 20.0 p.p.m. ruthenium(III).
[c] For 5.0 p.p.m. ruthenium(III).
[d] Maximum amount investigated.

sensitivity was reduced, but the tolerance limits for foreign ions increased considerably. Reagent (IV) could then be used for the determination of ruthenium(III) even in the presence of large quantities of most of the other platinum metals investigated.

Recommended procedure for ruthenium(III)

To 1 ml of solution, containing 80–800 p.p.m. of ruthenium(III) in the case of complex formation with 5,7-dichloro-8-hydroxyquinoline N-oxide or with 5,7-dibromo-8-hydroxyquinoline N-oxide, and 25–375 p.p.m. of ruthenium(III) with 5,7-dinitro-8-hydroxyquinoline N-oxide, add a 10-fold excess of the reagent solution, and heat in a boiling water bath for 90 min. Cool and dilute to 25 ml with water and/or acetone to give a 60% acetone medium after ensuring that the pH is in the ranges 2.6–5.5, 2.6–5.0 and 1.3–5.2 for the dichloro, dibromo and dinitro derivatives, respectively. Measure the absorbance at 540–625 nm against water as blank. Determine the concentration of ruthenium(III) from a standard calibration curve prepared under identical conditions.

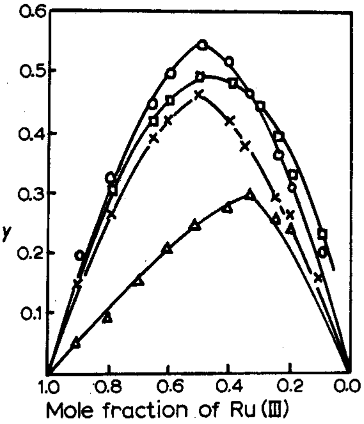
The standard deviation of the procedure was found to be *ca.* 2% for all the reagents.

Note. Because of the common use of concentrated sulphuric acid for the selective dissolution of rhodium in the presence of other platinum metals, the effect of fuming the ruthenium(III) solutions with sulphuric acid as well as fusion of ruthenium trichloride with sodium hydrogen sulphate before complex formation with the proposed reagents was also investigated. It was observed that ruthenium(III) solutions obtained after these treatments did not react with these reagents on heating in the same way as freshly prepared solutions did. However, when such ruthenium solutions were heated with excess of the reagents in the presence of hydrochloric acid, colourations the same as those obtained with standard solutions were found. Accordingly, the reagents can be applied for the spectrophotometric estimation of ruthenium even after fuming with sulphuric acid or fusion with sodium hydrogen sulphate.

MOLAR COMPOSITION OF THE COMPLEXES AND STABILITY CONSTANTS

The molar compositions of the various complexes were determined by the modified method of continuous variations[18] at different pH values and wavelengths. Within the pH range 2–5, ruthenium(III) formed a 1:1 complex with all these ligands, whereas at pH 8–10 for complexes with (II) and (III) and at pH 6–8 for complexes with (IV), the formation of 1:2 complexes was indicated (Figs. 5–7). At intermediate pH values, the Job's curves showed a shoulder and peaks around 1:1 and 1:2 metal:ligand ratios, indicating the formation of more than one complex under these conditions.

The dissociation constants of the ligands were determined spectrophotometrically[19] from the plots of log $((E-e_{HL})/(e_L-E))$ against pH (e_L, e_{HL} and E being the molar absorptivities of the fully ionised, completely undissociated and partially ionised reagent respectively) (Fig. 8). The pK_a values in 60% acetone media containing 0.10 M sodium chloride were determined to be 10.25 ± 0.12, 10.40 ± 0.15 and 5.76 ± 0.12 for reagents (II), (III) and (IV), respectively. The stability constants of the 1:1 complexes (K_1 values) were then determined (i) by HARVEY AND MANNING's method[20] (Fig. 4), and (ii) from formation curves obtained spectrophotometrically for the 1:1 complex (Fig. 9). The values obtained are given in Table III.



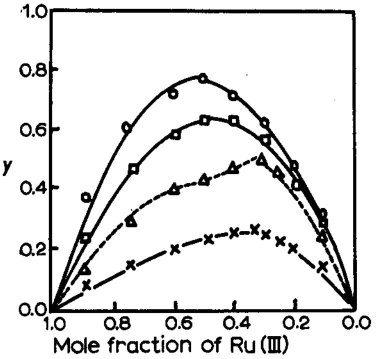
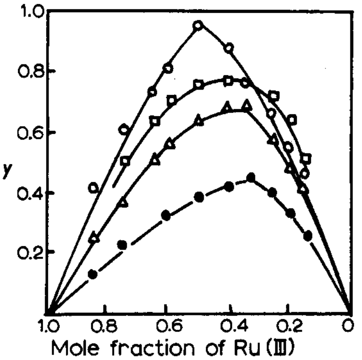


Fig. 5. Job's curves for ruthenium(III)–5,7-dichloro-8-hydroxyquinoline N-oxide system. 430 nm. pH 2.0 (×), 4.0 (○), 6.0 (□), 8.5 (△).

Fig. 6. Job's curves for ruthenium(III)–5,7-dibromo-8-hydroxyquinoline N-oxide system. (——) 420 nm, (– – – –) 470 nm. pH 2.0 (○), 6.0 (□), 9.0 (×, △).



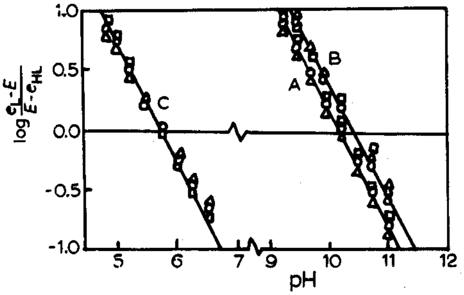


Fig. 7. Job's curves for ruthenium(III)–5,7-dinitro-8-hydroxyquinoline N-oxide system at 480 nm. pH 2.0 (○), 5.5 (□), 7.0 (△), 8.0 (●).

Fig. 8. Plots of log $((e_L - E)/(E - e_{HL}))$ against pH for the reagents (II), (III) and (IV). (A) reagent II, (B) reagent III, (C) reagent IV. λ (○) 420 nm, (△) 450 nm, (□) 480 nm.

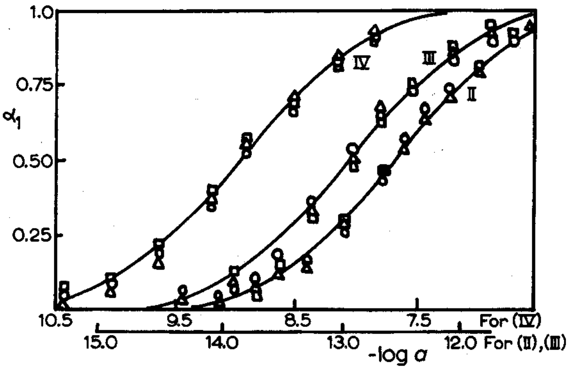


Fig. 9. Degree of formation of the 1:1 ruthenium(III) complex with reagents II, III and IV plotted against log a, at λ = 440 nm (○), 420 nm (△), 460 nm (□).

The stability constants of the 1:2 complexes (K_2 and β_2 being the stepwise and overall stability constants) were determined from the absorbances of the solutions containing both 1:1 and 1:2 complexes, since the relation between the molar absorptivity of such a solution at equilibrium (E) and the stability constants is[19]

$$\frac{E-e_0}{Ea^2} + \frac{E-e_1}{Ea}\beta_1 = \beta_2 - \frac{e_2\beta_2}{E} \tag{1}$$

where e_n is the molar absorptivity of the complex ML_n and a is the free ligand concentration of the anionic form of the ligand. The plot shown in Fig. 10 yields a value for intercept β_2; the values of log β_2 so obtained are given in Table III. It can be seen that the values of log β_n (n being 1 and 2) decrease with decreasing basicity of the ligands.

TABLE III

STABILITY CONSTANTS OF RUTHENIUM(III) COMPLEXES IN 60% ACETONE CONTAINING 0.10 M SODIUM CHLORIDE

Method adopted	*Ru(III)-(II)*	*Ru(III)-(III)*	*Ru(III)-(IV)*
HARVEY AND MANNING'S method: log K_1	12.60 ± 0.07	12.95 ± 0.09	8.91 ± 0.09
BJERRUM'S method: log K_1	12.48 ± 0.07	12.87 ± 0.07	8.99 ± 0.05
Graphical plots of eqn.(1): log β_2	17.86 ± 0.14	18.20 ± 0.12	12.14 ± 0.13
log K_2[a]	5.32	5.29	3.19

[a] For the determination of K_2, the average log K_1 value was used.

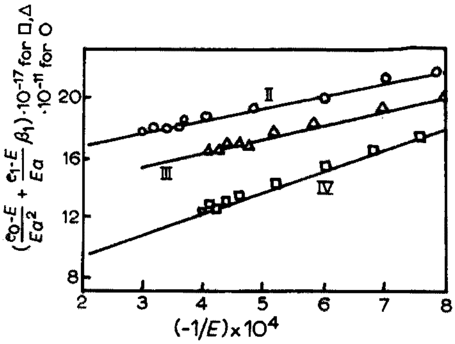


Fig. 10. Plots of $-(E-e_0)/Ea^2 - (E-e_1)\beta_1/Ea$ against $1/E$ for ruthenium(III) complexes with reagents II, III, and IV, at 440 nm.

SUMMARY

The deeply coloured 1:1 and 1:2 (metal:ligand) complexes of ruthenium(III) with 5,7-dichloro-8-hydroxyquinoline N-oxide (II), 5,7-dibromo-8-hydroxyquinoline N-oxide (III) and 5,7-dinitro-8-hydroxyquinoline N-oxide (IV) have been investigated spectrophotometrically in 60% acetone medium, and are suggested for the spectrophotometric determination of ruthenium(III) in presence of other platinum metals.

The stability constants (log β_1 and log β_2) (determined spectrophotometrically) decrease in the order III > II > IV, which is the same as that of the basicity of the ligands.

RÉSUMÉ

Le ruthénium(III) donne des complexes fortement colorés avec l'oxyde dichloro-5,7-hydroxy-8-quinoléine N (II), l'oxyde dibromo-5,7-hydroxy-8-quinoléine N (III) et l'oxyde dinitro-5,7-hydroxy-8-quinoléine N (IV) (métal:ligand 1:1 et 1:2). Ces composés sont proposés comme réactifs pour le dosage spectrophotométrique du ruthénium(III), en présence d'autres métaux du platine. Les constantes de stabilité (log β_1 et log β_2) déterminées spectrophotométriquement diminuent dans l'ordre III > II > IV, correspondant à la basicité des ligands.

ZUSAMMENFASSUNG

Die tiefgefärbten 1:1- und 1:2 (Metall:Ligand)-Komplexe von Ruthenium-(III) mit 5,7-Dichlor-8-hydroxychinolin-N-oxid (II), 5,7-Dibrom-8-hydroxychinolin-N-oxid (III) und 5,7-Dinitro-8-hydroxychinolin-N-oxid (IV) sind spektrophotometrisch in 60%igem Aceton untersucht worden und werden für die spektrophotometrische Bestimmung von Ruthenium(III) in Gegenwart anderer Platinmetalle vorgeschlagen. Die (spektrophotometrisch bestimmten) Stabilitätskonstanten (log β_1 und log β_2) nehmen in der Reihenfolge III > II > IV ab; diese Reihenfolge ist dieselbe wie die der Basizität der Liganden.

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TITRAGES ACIDIMETRIQUES PAR UNE METHODE DE POTENTIOMETRIE SIMPLIFIEE

EMPLOI D'ÉLECTRODES DE ZIRCONIUM ET AUTRES

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(Reçu le 8 novembre, 1969)

Les techniques électrométriques comportant l'usage d'une électrode indicatrice et d'une électrode de référence, ou de deux électrodes indicatrices peuvent être classées en ampérométrie et potentiométrie: potentiel imposé fixe et courant variable ou potentiel variable à intensité nulle ou simplement constante.

Toutes les techniques "sous courant" ont un point commun: on ne peut calculer les courbes de titrage car le phénomène de la polarisation des électrodes entre en jeu. Il est au contraire facile de calculer une courbe de titrage à l'intensité nulle tout au moins si l'on peut appliquer la formule de NERNST (fonctionnement réversible).

L'intérêt d'utiliser des techniques "sous courant" est cependant double: d'abord, comme l'a écrit LINGANE[1], l'équilibre des échanges entre l'électrode et la solution est plus rapide et il devient ainsi possible d'utiliser en analyse des systèmes lents irréversibles; ensuite, la sensibilité est souvent beaucoup plus élevée comme le signale FURMAN[2] d'après les résultats d'ADAMS.

La méthode utilisée par nous se rapproche de la potentiométrie différentielle "sous courant". Elle consiste à mesurer la faible différence de potentiel existant entre deux électrodes indicatrices fonctionnant toutes deux généralement comme cathodes par rapport à une contre-électrode de platine. Les électrodes indicatrices, de plus, ne sont pas des électrodes inattaquables.

Nous avons surtout utilisé des électrodes généralement recouvertes d'une couche d'oxyde telles les électrodes de zirconium ou d'antimoine et limité nos titrages aux titrages acido-basiques.

TRAVAUX ANTÉRIEURS

Potentiométrie sous courant nul

En l'absence d'hydrogène, absorbé à pression normale ou réduite (quinhydrone), l'électrode de platine se montre peu électroactive vis à vis des ions H^+ ou OH^-.

PODUROVSKAYA ET PETRAKOVIC[3] ont néanmoins obtenu, dans l'acétone à 70%, des bons résultats en milieu acide très fort avec le platine "oxydé à l'air". Le tantale, le tungstène, le titane ne sont pas sans intérêt. Leur comportement est celui de "métaux passivés". L'électrode de titane a été récemment étudiée par WINKAUS[4].

Des métaux moins nobles et non passivés, dans les conditions normales d'utilisation, métaux qui, on l'a montré, fonctionnent comme des électrodes à oxyde ont donné de bons résultats: certains métalloïdes comme le tellure ou même l'arsenic également.

SALEM ET AWAD ont essayé des électrodes d'étain, de cadmium et de plomb[5] et ITO ET MUSHA[6] l'électrode de tungstène, employée souvent autrefois couplée au platine.

L'emploi d'électrodes métalliques attaquables pour remplacer l'électrode d'hydrogène n'est d'ailleurs pas nouveau: l'électrode d'antimoine a été longtemps d'un usage courant. Elle a été proposée dès 1925 par KOLTHOFF ET HARTONG[7]. L'électrode de bismuth a été préconisée en milieu alcalin notamment par SCHWABE[8]. Le molybdène en milieu alcalin a également donné des résultats intéressants. Le chrome a été également étudié par TOURKY *et al.*[9].

Il est à remarquer que toutes ces électrodes vraisemblablement à cause de la couche d'oxyde fonctionnent à peu près réversiblement comme une électrode à hydrogène. Le coefficient de proportionnalité entre les différences de pH et les différences de potentiel est voisin de 0.059 V, valeur théorique à 25°. Signalons des résultats intéressants obtenus par KOLTHOFF ET SAMBUCETTI[10] avec une électrode rotative d'aluminium dans les dosages d'ions fluor et même en acidimétrie.

Des électrodes non métalliques comme le graphite ont été proposées par ELVING ET SMITH[11], l'arsenic par TOURKY ET MOUSA[12], le tellure par TOURKY *et al.*[13], également par RICKETTS ET BOWEN[14], ainsi que TOMIČEK ET PUPE[15].

Potentiométrie "sous courant"

Bien que s'appliquant surtout à des titrages d'oxydo-réduction, il n'est point inutile de rappeler quelques observations ou remarques dues à DUYCKAERTS[16]. DUYCKAERTS a étudié les courbes potentiométriques dans le cas où l'électrode "indicatrice" est elle-même "sous tension" l'intensité qui la traverse pouvant être considérée comme constante. Deux faits importants sont à retenir de son étude relative à un titrage par oxydo-réduction.

1. Le point marquant la fin du titrage se trouve décalé en fonction de la "polarisation" de l'électrode.
2. L'erreur sur le titrage est plus forte quand l'électrode est polarisée positivement. Il y a donc un comportement dissymétrique.

BRÉANT[17] donne à partir des courbes potentiel–courant le moyen d'interpréter toutes les courbes de titrage et d'expliquer des faits analogues aux précédents; nous y reviendrons dans notre cas particulier.

Méthode "dead stop end-point"

La méthode de titrage électrochimique connue sous le nom de méthode "dead stop end-point" est déjà ancienne puisqu'elle a été proposée par VAN NAME ET FENWICK[18] en 1925: des électrodes de platine ont seules été utilisées au début.

D'autres dénominations, telles que bi-ampérométrie, polarovoltrie, voltampérométrie ou bi-potentiométrie ont été proposées par certains auteurs[19–22]. Quoiqu'il en soit la polarisation des électrodes y joue le principal rôle, bien qu'il s'agisse plûtot d'ampérométrie à deux électrodes indicatrices (BRÉANT[17]). Toutes ces techniques étant voisines, il n'est pas inutile de rappeler brièvement quelques travaux se rapportant à la méthode "dead stop".

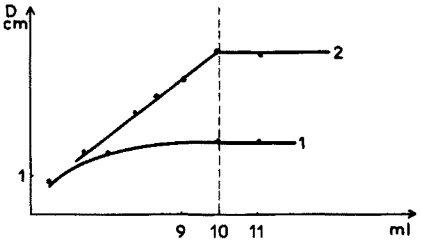
La méthode a fait ses preuves dans les dosages d'oxydo-réduction en iodométrie par exemple (dosage de l'eau par la méthode Karl-Fischer). Depuis les études théoriques de Furman[2] puis dans l'ordre chronologique de: Willard et Fenwick[23], Foulk et Bawden[24], Clippinger et Foulk[25], Delahay[21], Franck[21,26], Kolthoff[27], Lingane[1], Dubois[20], Lacaze et Dubois[28,29], Royon[30], Stone et Scholten[31], l'intérêt qu'on y a porté ne s'est pas démenti.

Nous citerons également les travaux de Bishop[32], Reilley[33], Reilley *et al.*[34], Bertin[35], Dusinsky[36], Enoki et Morisaka[37], Duyckaerts[16], Kies[38], Bishop *et al.*[39,40], Bradbury[41], Evans[42], Gauguin[43], Gauguin et Charlot[44], Vorlicek et Vydra[45], ainsi que les ouvrages de Charlot *et al.*[46], Delahay[21] et Kolthoff et Stenger[47]. Des mises au point récentes accompagnées d'une bibliographie importante ont été faites successivement par Laitinen[22], Laitinen *et al.*[48], et Stock[19]. Nous citerons aussi les travaux très importants de Bishop et Short[40] qui utilisent des électrodes d'antimoine (méthode "dead stop") qui ont donné de bons résultats en acidimétrie: titrages simultanés de deux acides. Ces auteurs ont également utilisé, comme nous l'avons fait, une contre-électrode dans le but d'étudier la polarisation et l'influence du sens du courant polarisant. Ils ont aussi développé la théorie de la surtension des électrodes d'antimoine dont dépend l'allure générale des courbes. Dubois et Lacaze[29] ont obtenu des séparations d'acide avec réactif titrant approprié au milieu. Walisch et Ashworth[49] ont également étudié la possibilité de titrages acidimétriques. Au point de vue technique notons aussi le remplacement du galvanomètre par un oeil électrique et les travaux de Dubois et Walisch[50].

Des solutions ont été proposées pour rendre possible un titrage sensible et précis: la transformation, par exemple d'un titrage acidimétrique en titrage d'oxydo-réduction par les "indicateurs électrométriques" dont l'emploi est très général.

Une revue de ces "indicateurs" a été donnée par Charlot et Trémillon[51]. Citons le travail plus ancien de Ringbom et Wilkman[52]. Des corps, soit oxydants forts comme l'eau oxygénée ou l'ion I_3^-, soit existant eux-mêmes sous deux formes en équilibre comme la quinhydrone et l'hydroquinine, sont actifs. Nous avons nous-mêmes constaté l'efficacité de la quinhydrone (Fig. 1).

Les courbes obtenues ont l'aspect habituel des courbes d'oxydo-réduction (iodométrie, par exemple) et ne présentent pas de maximum marqué (irréversibilité des deux côtés).



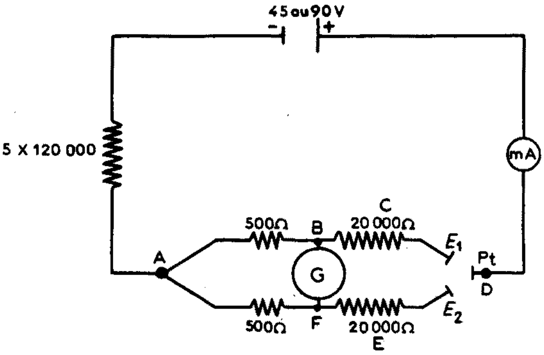


Fig. 1. Efficacité de la quinhydrone. (1) HCl 0.344 *N*, (2) titrage avec quinhydrone.

Fig. 2. Montage.

Nous ne ferons qu'une remarque: en solution très diluée, il peut ne pas être sans inconvénient d'ajouter un indicateur.

Méthode "dead stop" en courant alternatif

Dans la méthode due à FRANCK[26], un courant alternatif est substitué au courant continu. Celui-ci est ensuite redressé et mesuré avec un galvanomètre sensible. FRANCK a observé un comportement particulier des électrodes suivant le pH de milieu dû à l'action des ions H^+ ou OH^- à la surface des électrodes. Des tentatives ont été faites en substituant d'autres électrodes aux électrodes de platine.

Autres méthodes

Nous citerons l'emploi tout récent, d'électrodes de platine "jumelées" en potentiométrie différentielle à courant imposé et une intéressante méthode à courant constant[54].

Technique opératoire

Electrodes. Notre technique qui diffère de la technique ampérométrique à potentiel imposé comporte l'emploi de trois électrodes: deux électrodes "indicatrices" non en platine fonctionnant comme cathodes et une contre-électrode en platine.

Montage. Un montage très simple (Fig. 2) permet d'obtenir un décalage faible entre les deux électrodes indicatrices toutes deux mises sous tension sous un courant de 0.1 mA environ.

Calcul des intensités i en j. Il s'agit des intensités traversant la galvanomètre et le circuit électrolytique comprenant les deux électrodes de zirconium.

L'application des lois de KIRCHOFF aux circuits fermés n'est pas sans intérêt. Les trois résistances du circuit ABF (voir Fig. 2) peuvent être choisies égales; soit ω leur valeur commune avec $\omega \approx 500\ \Omega$; il en est de même des deux résistances placées devant les électrodes de zirconium, soit ϱ leur valeur commune avec $\varrho \simeq 20000$ ohms. Nous appelerons d'autre part R, R_1, R_2, les trois résistances des branches CD, DE, EC: nous avons inclus dans les valeurs de R, R_1, R_2 la résistance due à la couche d'oxyde (éventuel) qui recouvre la surface de l'électrode. Dans le cas du zirconium on observe une résistance très élevée et de l'ordre de $10^5\ \Omega$ plus forte que la résistance du circuit électrolytique. Nous appelons d'autre part I, I', I'' puis, J, J', J'' les intensités traversant les branches AB, BC, CD puis AF, FE, ED et I_e l'intensité traversant le circuit extérieur.

En considérant les intensités aux "noeuds" du circuit et les lois de KIRCHOFF dans les circuits BCEF et CED, on obtient le système de deux équations

$$i(\omega+3\varrho)-R_{\mathrm{j}} = \Delta\varepsilon \qquad (1)$$

$$\frac{3i}{2}(R_1+R_2)+j(R+R_1+R_2) = \frac{I_e}{2}(R_2-R_1) \qquad (2)$$

dont la résolution appelle quelques remarques.

1. La mesure de i donne la mesure de $\Delta\varepsilon$ à un décalage près i étant une fonction linéaire de $\Delta\varepsilon$.

2. Si $i=0$, ce qui est le cas lorsque la mesure s'effectue avec un voltmètre électronique on a plus simplement $j=\Delta\varepsilon/R$.

3. Le cas des électrodes de zirconium est très particulier car la couche de zircone qui se reforme très vite à une très faible conductivité (comparable à celle de l'alumine) est de l'ordre de 10^{-7} mhos. C'est donc l'ordre de grandeur des résistances R, R_1, R_2—on peut d'autre part poser dans ce cas $R = R_1 + R_2$.

Pour $R_2 = 2R_1$ qui correspond à deux électrodes dont l'une a une surface de contact double de l'autre et en négligeant dans l'éqn. (2) le produit $i(R_1 + R_2)$, on trouve $j \approx I_e/24$, c'est-à-dire avec nos valeurs généralement utilisées $j \approx 5 \cdot 10^{-6}$ approximativement cent fois la valeur de i.

Dans nos expériences il s'agit certainement là d'une limite supérieure.

EMPLOI D'ÉLECTRODES DE ZIRCONIUM

Comportement électrochimique

Le zirconium est un métal peu noble mais très fortement "passivé" dans un très large domaine. Valeurs numériques et diagrammes peuvent être extraites des tables ou de l'atlas de POURBAIX[55].

Sur la courbe donnant le potentiel E d'une électrode de zirconium mise sous tension à l'aide d'une contre-électrode en platine et mesuré par rapport à une électrode à calomel de référence en fonction du pH de la solution (diagramme de POURBAIX) on distingue nettement deux domaines de pH. Pour pH < 4 et pH > 10, il existe deux régions pour lesquelles l'électrode peut être attaquée.

Son potentiel standard par rapport à l'électrode à hydrogène correspondant à la dissociation ionique $Zr^{4+} + 4e \rightarrow Zr$ serait de -1.53 V (contre une électrode à hydrogène "normale"). L'électrode de zirconium a été utilisée par MEGREGIAN[56] dans le dosage des fluorures en milieu acide nitrique 0.8 M.

L'électrolyse spontanée du couple Pt–Zr produit un courant dont l'intensité est proportionnelle à la molarité en fluorure.

Nous avons utilisé du zirconium à 99.7% de pureté (Koch-Light). Ce zirconium possède une teinte noirâtre due à la présence d'oxyde. Des échantillons nous ont été également fournis en provenance du laboratoire de Métallurgie de Vitry par le Professeur COLLONGUES que nous remercions. Leur degré de pureté est équivalent: la teinte du métal est plus brillante. Les électrodes des deux provenances nous ont également donné de bons résultats.

Un échantillon contenant 5% de fer également fourni par Vitry nous a permis de faire une étude comparative.

Le zirconium contient toujours une légère proportion de hafnium (de l'ordre de 0.005%) mais les potentiels et les propriétés sont tellement voisins que celui-ci paraît sans influence.

Potentiométrie sous courant nul (contre-électrode à calomel)

Sur la Fig. 3, nous avons représenté deux courbes de titrage acide fort–base forte. L'une donnant le pH, mesuré à l'électrode de verre, l'autre est une courbe de titrage potentiométrique avec l'électrode de zirconium. Une légère translation nous a permis de rattrapper le décalage. On observe une allure quelque peu dissymétrique dans le comportement de l'électrode de zirconium.

En milieu acide les deux courbes se recouvrent pratiquement puis s'écartent en milieu alcalin. Les points de fin de titrage coïncident exactement.

Nous proposons pour expliquer cette anomalie:

(a) un processus d'équilibre en milieu acide qui serait

$Zr + 2\ H_2O \rightleftharpoons ZrO_2 + 4\ H^+ + 4e$

(b) en milieu alcalin:

$Zr + 3\ H_2O \rightarrow ZrO_3^{2-} + 6\ H^+ + 4e$

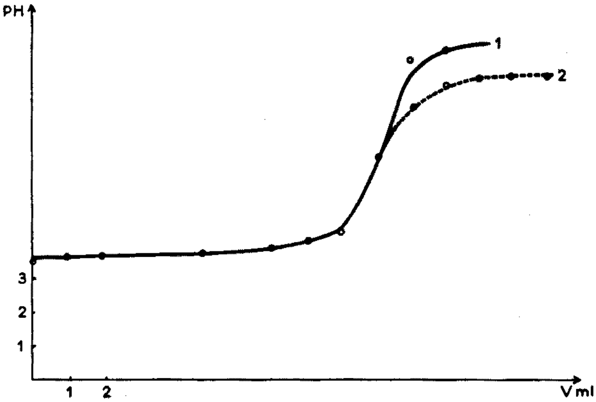


Fig. 3. Potentiométrie sous courant nul. Courbe de titrage acide 10^{-2} *M* avec (1) une électrode de verre, (2) une électrode de Zr.

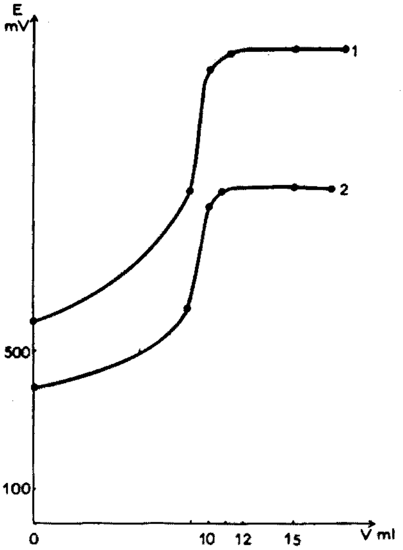


Fig. 4. Courbe potentiométrique du Zr sous courant. Acide 10^{-2} *M*: (1) sans résistance devant la pile, (2) avec résistance (820 kΩ).

Potentiométrie sous courant

On note une très forte influence de l'intensité sur le potentiel (Fig. 4). L'électrode de zirconium est une électrode très polarisable.

Nous avons vu que l'on n'est pas parfaitement maître de choisir l'intensité ou mieux la densité de courant à moins d'utiliser des potentiels de polarisation très élevés qui ne sont pas sans inconvénients.

Apparaît également la dissymétrie signalée. Le décalage du potentiel—même pour des courants tels que ceux que nous avons utilisés, de l'ordre de 10^{-4}—n'est pas négligeable.

Le point correspondant à la fin du titrage comme il est habituel peut se trouver lui aussi légèrement *"déplacé"*.

Résistance "anormale"

En mettant en série avec une cellule comportant une électrode de platine, une électrode de zirconium et de l'acide chlorhydrique 10^{-3} *M* comme électrolyte, une pile de 67 V et des résistances successivement de $7 \cdot 10^2$ et $8 \cdot 10^5$ Ω, on trouve des intensités respectives de $9 \cdot 10^{-5}$ et $4.5 \cdot 10^{-5}$ A. Comme on a le droit de négliger la résistance due à l'électrolyte, il est possible d'avoir une idée de la "résistance" à la surface de l'électrode: on trouve $7 \cdot 10^5$ dans le premier cas et $6.5 \cdot 10^5$ dans le second. Une conséquence de ce phénomène est que l'intensité est loin d'être proportionnelle à la conductibilité du circuit extérieur.

Il faut donc tenir compte de ce fait qui n'est pas particulier à l'électrode de zirconium. La très forte résistance est probablement due à une couche d'oxyde superficielle. Cette couche n'est guère affectée ni par un traitement de la surface au papier de verre ni par une mise "sous tension" de l'électrode, tout au moins pour des intensités de l'ordre de celles utilisées par nous. Quelques mesures rapides nous ont permis de vérifier le peu d'influence du sens du courant ainsi que son intensité.

Les résultats précédents ont été obtenus avec une électrode fonctionnant comme cathode. L'intensité qui traverse la pile lorsque la résistance extérieure est de 700 Ω, le zirconium fonctionnant comme anode est tout à fait du même ordre soit 10^{-4} A.

D'autre part, l'intensité à la suite d'un traitement prolongé de la surface au papier de verre n'a que très peu varié: de $7.8 \cdot 10^{-5}$ à 10^{-4} pour une électrode en forme de ruban et est restée identique pour l'électrode filiforme, soit 10^{-4} A dans les deux cas.

La couche superficielle d'oxyde, qui ne peut être que ZrO_2, aucun autre oxyde n'étant signalé[57], est donc très adhérente et de très faible conductibilité. WILLIS ET ADAMS[58] ont étudié la couche isolante (cinétique).

Variation du potentiel avec le temps

Pour une cathode de zirconium mise "sous tension" avec une intensité de 45 μA en milieu acide fort 10^{-3} *M*, le potentiel par rapport à notre électrode de référence à calomel a passé de 760 mV à 1000 mV en 10 min pour une électrode non traitée au papier de verre.

En frottant au papier de verre une électrode de zirconium, on a d'autre part passé de 600 mV à 400 mV.

Dans ces conditions et avec les surfaces utilisées, variant de 0.5 cm² pour les électrodes filiformes (1 mm de diamètre) à environ 2 cm² pour les électrodes de forme rectangulaire, il n'est pas possible d'utiliser des densités de courant trop élevées. Une intensité de 10^{-4} A parcourant les deux électrodes nous a paru convenable.

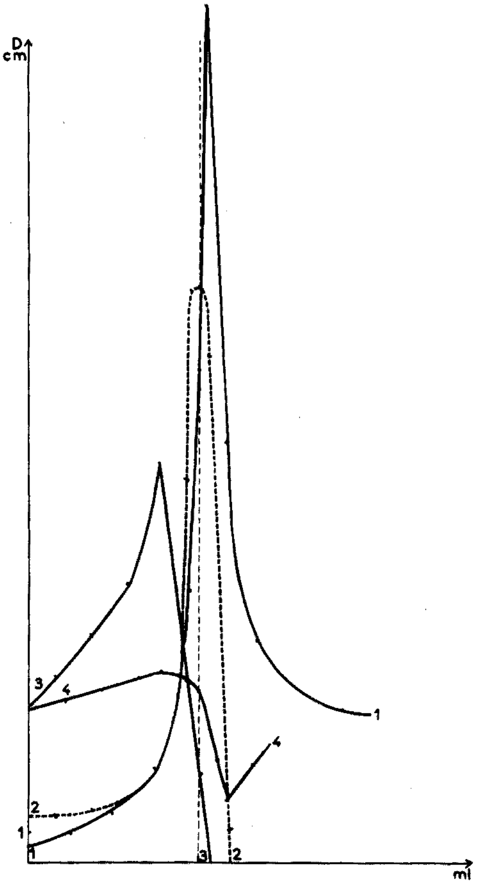
ÉTUDE DIRECTE DE L'INFLUENCE DES DIVERS FACTEURS SUR LES COURBES DE TITRAGE

Nous avons étudié directement sur les courbes de titrage effectuées à l'aide de la technique précédemment décrite: quelle était l'influence de l'intensité et de la polarité. Notre attention s'est portée sur l'écart entre valeur calculée et valeur trouvée pour le titrage soit l'erreur de titrage*.

Influence de la polarité

Bien qu'il ne semble pas qu'il y ait grande différence au point de vue de la sensibilité, il nous est apparu que le fait de travailler avec des électrodes polarisées anodiquement introduit un "décalage" plus important.

Sur la courbe de la Fig. 5, on voit nettement que le "décalage" n'existe pratiquement que si les deux électrodes de zirconium sont polarisées positivement.



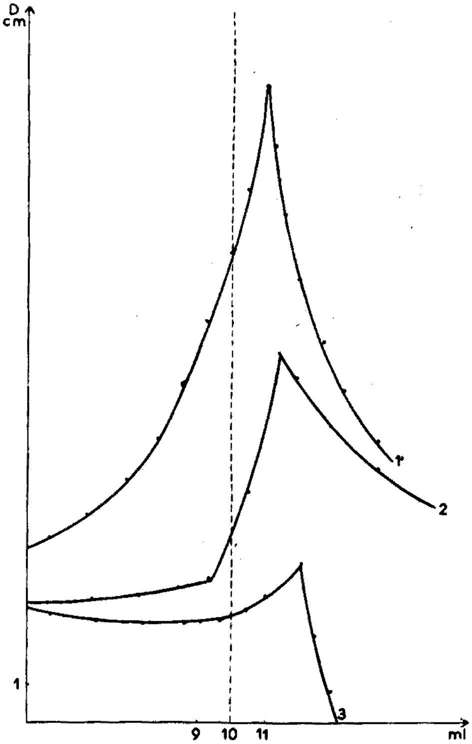


Fig. 5. Influence du sens du courant polarisant. Titrage d'un acide 10^{-2} *M* (dilué 15 fois) par une soude 10^{-2} *M*. (1) Zr^-, (2) Zr^+, (3) Zr^+ après 10 min, (4) Zr^+ après 60 min.

Fig. 6. Décalage en fonction de l'intensité. Acide 10^{-2} *M*. Intensité (1) 0.07 mA, (2) 0.16 mA, (3) 0.28 mA.

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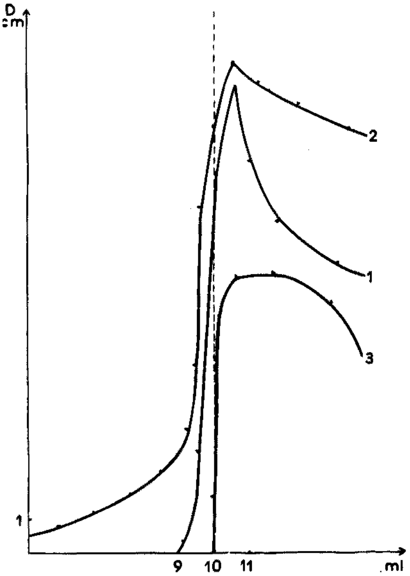
* Nous avons toujours dilué 15 fois les solutions d'acide: 10 ml dans 150 ml et titré avec des solutions de base correspondantes. 1 division de l'échelle vaut $2 \cdot 10^{-7}$ en ordonnées et en abscisses 10% de réactif transformé.

Influence de l'intensité de "polarisation"

Le "décalage" est d'autant plus important que l'intensité de polarisation est forte. Le point de fin de réaction se déplace de 11 à 12 (Fig. 6). L'intensité en mA croît de 0.07 à 0.16 et 0.28 mA.

Il est en outre à remarquer que la "sensibilité" de l'électrode ou plutôt ici des électrodes ne paraît pas augmenter avec l'intensité du courant polarisant. Les pics sont bien marqués et même plus nets pour le courant polarisant le plus faible.

En appliquant les notations de LACAZE ET DUBOIS[28] on peut dire que l'on passe des types $\frac{3}{4}$–1–$\frac{3}{4}$ au type 1–1–$\frac{3}{4}$.



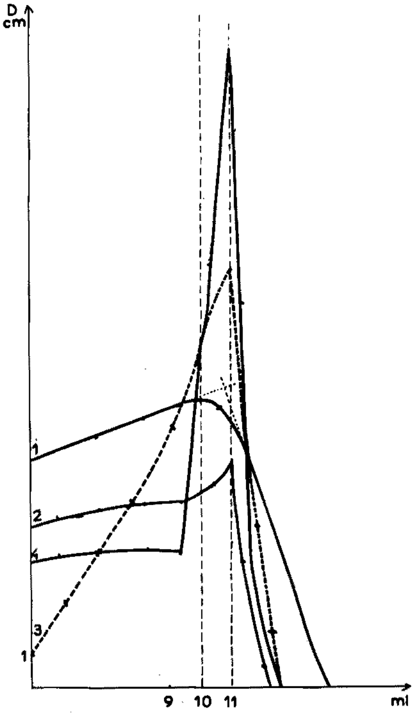


Fig. 7. Vieillissement des électrodes de zirconium contenant 5% de fer: (1) titrage immédiat, (2) titrage après 10 min, (3) titrage après 30 min.

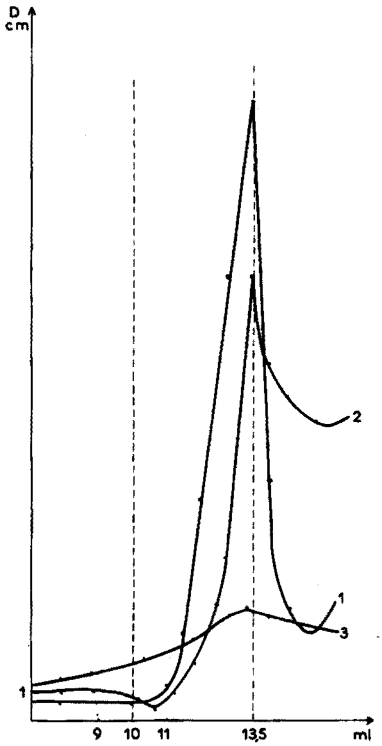
Fig. 8. Influence de l'état de la surface. Titrage d'un acide 10^{-2} M (dilué 15 fois) par une soude 10^{-2} M: (1) fil de Zr (neuf), (2) 1er traitement, (3) 2ème traitement, (4) 3ème traitement.

Influence de la pureté du métal

Il est nécessaire d'employer des électrodes de zirconium pur. Les courbes de titrage correspondant à des électrodes de zirconium avec 5% de fer présentent la particularité intéressante d'une rapide évolution avec le temps. Les électrodes vieillissent vite et deviennent dépourvues de sensibilité (Fig. 7). Sur les courbes de la Fig. 7 correspondant à un titrage acido–basique (dilution de 15, soude 10^{-1} M) on voit que l'évolution demande moins d'une heure.

Influence de l'état de surface

Un traitement des électrodes au papier de verre ou à la meule fine améliore notablement la sensibilité comme l'examen des courbes le montre. Un flambage léger à la flamme d'alcool nous a paru produire d'heureux effets. Il n'est pas nécessaire de traiter les électrodes avant chaque titrage mais il est bon de le faire avant chaque série de mesures.



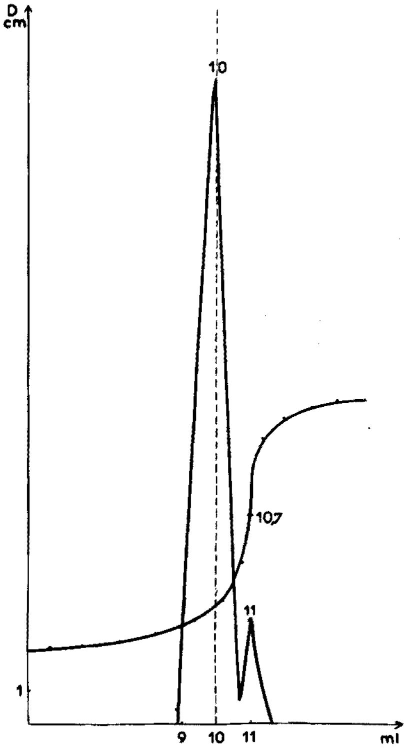


Fig. 9. Vieillissement des électrodes dans l'eau de mer. (1) Titrage après nettoyage (acide 10^{-2} *M* dilué 15 fois), (2) titrage après 4 h, (3) titrage après plusieurs jours.

Fig. 10. Mélange acide fort (10^{-2} *N*) et acide faible (10^{-3} *N*).

La présence d'électrolytes étrangers tels que chlorure de sodium (eau de mer) n'est pas sans modifier le comportement des électrodes. Nous avons noté à la fois une sensibilité accrue et une déterioration assez rapide, des électrodes (Fig. 9).

Lorsque les électrodes fonctionnent comme cathodes, la formation de soude sur l'électrode même n'est certainement pas sans influence; on sait qu'on obtient facilement des zirconates.

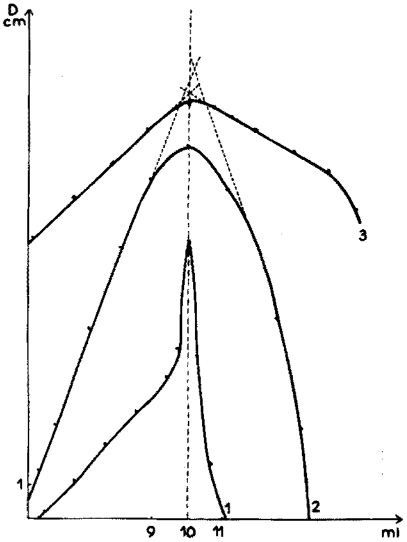
Courbes de titrage

Nous étudierons plus en détail les applications de la méthode dans un prochain mémoire.

A titre d'exemple nous donnons deux courbes de titrage (Figs. 10 et 11) qui permettent de juger de l'efficacité de la méthode dans le titrage de solutions d'acide fort extrêmement dilués et même dans le cas de mélanges. La présence de pics très aigus même en solutions très diluées est également visible sur les courbes précédentes.

On peut juger de l'influence de la dilution. Le dernier titrage correspond à 10 ml d'acide $10^{-3}N$ dilué quinze fois titré par de la soude 10^{-3} N.

Sur la courbe de titrages potentiométriques (Fig. 12) avec acide fort ou faible aux dilutions correspondantes aucun point singulier n'apparaît.



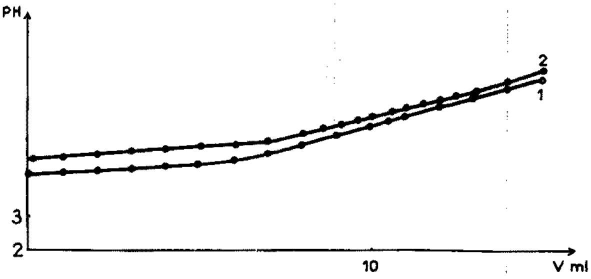


Fig. 11. Influence de la dilution: (1) 10^{-2} N, (2) $5 \cdot 10^{-2}$ N, (3) 10^{-3} N.

Fig. 12. Courbes potentiométriques: (1) H_2SO_4 $10^{-3}N$ par NaOH 10^{-3} N, (2) CH_3COOH 10^{-3} N par NaOH 10^{-3} N.

EMPLOI D'ÉLECTRODES AUTRES QUE CELLES DE ZIRCONIUM

Electrode de platine

Comme nous l'avons déjà dit, l'électrode de platine est peu électroactive en acidimétrie. On obtient des courbes à maximum aplati (Fig. 1) indice d'un fonctionnement réversible, qui n'est pas ici du tout une condition nécessaire pour une bonne sensibilité. Nous avons également observé des phénomènes de "décalage" suivant l'intensité fournie aux deux électrodes. Ceux-ci ont un caractère général. VAN NAME ET FENWICK[18] ont d'ailleurs déjà signalé des faits analogues dans les titrages "dead stop" en iodométrie par exemple, avec deux électrodes de platine.

Electrodes d'antimoine

Elles ont été étudiées dans leur fonctionnement en potentiométrie classique et aussi à l'état "polarisé" et très complètement par BISHOP ET SHORT[40] et STOCK ET PURDY[59]. Nous nous contenterons de donner quelques exemples de courbes de titrages et de montrer les avantages que peut présenter le fonctionnement de deux électrodes d'antimoine toutes deux cathodes.

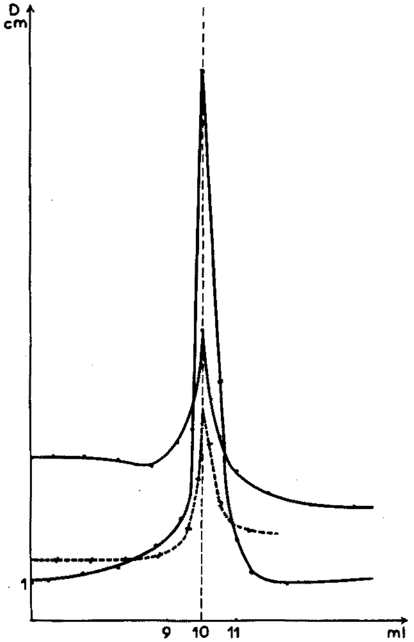
Nous n'avons pas observé d'erreur de titrages lorsque les électrodes sont "cathodes" et ont subi un traitement de surface.

On remarque au contraire que lorsque les électrodes sont positives, le maximum est décalé. Il en est de même pour le tungstène, le tellure, le zirconium.

La nécessité de passer les électrodes au papier de verre ou de les meuler afin de régénérer les surfaces est signalée aussi par BISHOP ET SHORT[40].

Sur la Fig. 13 et bien que les pics soient correctement placés, même pour une électrode vieillie, on voit que la sensibilité s'accroît d'une façon très nette avec un traitement de surface.

Le titrage de l'acide acétique donne également une courbe correcte (Fig. 14).



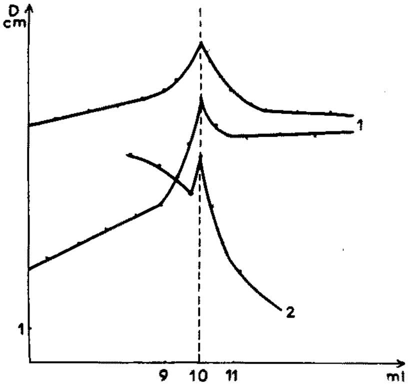


Fig. 13. Influence de l'état de la surface d'électrode Sb. Titrage d'un acide 10^{-2} *M* (dilué 15 fois) par une soude 10^{-2} *M*.

Fig. 14. Titrage de l'acide acétique: (1) sous azote, (2) titrage par baryte.

Enfin sur la Fig. 15 on voit que les deux acidités de l'acide phosphorique apparaissent.

L'aptitude des électrodes d'antimoine à séparer des acides de force différente a été signalée par les auteurs précédemment cités. On voit par exemple nettement deux pics dont l'un correspond à de l'acide sulfurique et l'autre à de l'acide acétique équimoléculaire et $0.66 \cdot 10^{-2}$ *N*. Il est à remarquer que le pic correspondant à la neutralisation de l'acide acétique est de très loin le plus marqué.

Le mélange acide tartrique–acide acétique peut également être "séparé". Il est intéressant de noter que l'allure n'est pas la même suivant qu'on opère en milieu concentré ou dilué ($0.6 \cdot 10^{-2}$ ou $0.6 \cdot 10^{-3}$ *M* env.). Dans un cas, on observera une acidité tartrique et l'acide acétique; dans l'autre, les deux acidités tartriques et le total.

Les résultats sont les mêmes, que le titrage soit effectué sous azote ou non et même dans le cas du mélange acide acétique–acide sulfurique plutôt plus nets sans azote.

On sait que l'antimoine est un élément peu noble qui fonctionne à peu près comme une électrode Sb/Sb_2O_3. D'après KOLTHOFF ET HARTONG[7] le coefficient est à peu près le coefficient "thermodynamique". Entre pH 1 et 12, on obtiendrait:

$$E = -0.0415 - 0.048 \text{ pH pour } 1 < \text{pH} < 5$$

et $$E = -0.009 - 0.0536 \text{ pH pour } 9 < \text{pH} < 12$$

L'ion antimoine(III) n'est pas seul en cause: on aurait suivant les pH SbO^+ puis SbO_2^- en milieu basique.

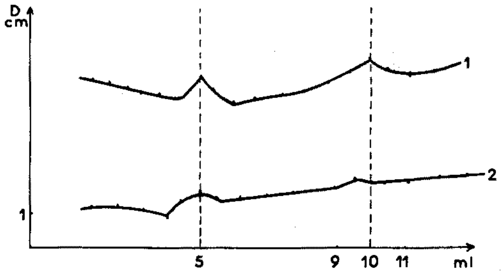


Fig. 15. Titrage de l'acide phosphorique: (1) acide 10^{-1} *M*, (2) acide 10^{-2} *M*.

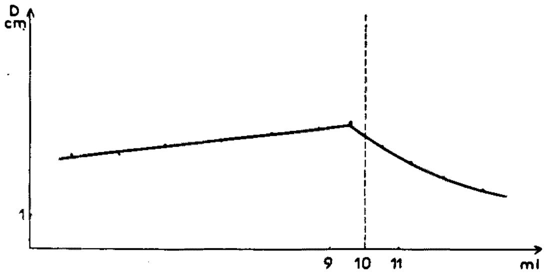


Fig. 16. Electrodes de bismuth: titrage d'un acide 10^{-2} *M* (dilué 15 fois) par une soude 10^{-2} *M*.

Electrode de bismuth

L'électrode de bismuth dont l'usage a donné autrefois de bons résultats en potentiométrie à courant nul et en milieu alcalin[8], est comme l'électrode d'antimoine une électrode à oxyde Bi/Bi_2O_3. On a de même des ions BiO^+. Le diagramme de POURBAIX[55] est beaucoup plus décalé vers les pH alcalins. JOVANOVIC ET BABIC[60] l'ont employé avec succès.

Bien que le point anguleux marquant la fin du titrage soit correctement placé (Fig. 16), il nous a semblé que la sensibilité était très inférieure à celle de l'électrode d'antimoine, tout au moins dans la zone de pH envisagée, où l'on va de l'acide acétique 10^{-2} *N* soit pH $\simeq$ 2.5 à la soude pH $\simeq$ 9.

Electrode de tungstène

Le tungstène n'est pas un élément noble. Son potentiel "standard" par rapport à l'électrode d'hydrogène est de -180 mV[34]. C'est également une électrode à oxyde: métal et WO_2. On note sur la courbe de titrage (Fig. 17) relatif au titrage d'acide 10^{-2} N par la soude un pic peu marqué mais correctement placé. Comme d'habitude, les deux électrodes de tungstène fonctionnent comme cathodes.

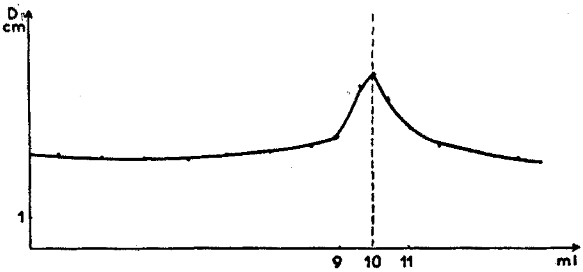


Fig. 17. Electrodes de tungstène: titrage d'un acide 10^{-2} M (dilué 15 fois) par une soude 10^{-2} M.

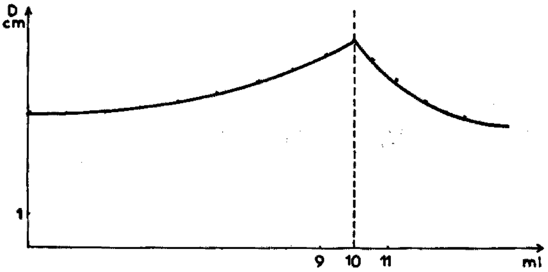


Fig. 18. Electrodes de tellure: titrage d'un acide 10^{-2} M (dilué 15 fois) par une soude 10^{-2} M.

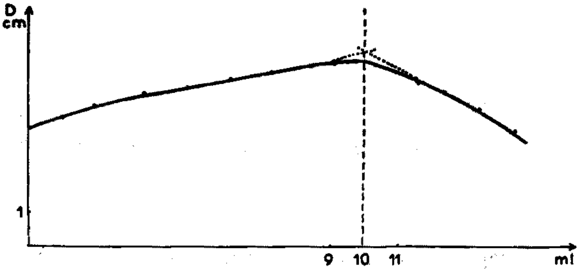


Fig. 19. Electrodes de tantale: titrage d'un acide 10^{-2} M (dilué 15 fois) par une soude 10^{-2} M.

Electrode de tellure

Le tellure a un potentiel particulièrement noble, c'est sans doute aussi une électrode à oxyde. TOURKY *et al.*[13] ont signalé sa bonne stabilité en potentiométrie classique sous courant nul. Nous notons des pics peu marqués mais très correctement placés (Fig. 18) dans le titrage acido-basique. Un décalage net est noté quand les deux électrodes fonctionnent comme cathodes.

Electrode de tantale

Le tantale est un métal à caractère très noble[34], pratiquement inattaquable aux acides sauf à l'acide fluorhydrique ou nitrique concentré. Son potentiel "standard" est de 251 mV. On note la présence d'un oxyde Ta_2O_5. Une courbe de titrage effectuée dans des conditions identiques aux précédentes, c'est-à-dire acide 10^{-2} N par soude 10^{-2} N, présente un pic peu marqué quoique correctement placé (Fig. 19).

Conclusions pratiques

Ce sont donc les électrodes de métaux relativement peu nobles comme l'antimoine, ou des métalloïdes comme le tellure qui se sont révélés les plus intéressants à notre point de vue. L'état de la surface qui doit être fréquemment passée au papier de verre ou meulée joue un rôle prépondérant.

Aucun autre métal étudié, ne nous a donné une sensibilité comparable à celle due à l'emploi des électrodes de zirconium. L'antimoine présente cependant une apitude particulièrement intéressante à la séparation analytique.

Il est intéressant de noter que pour le tellure, par exemple, on a intérêt à faire fonctionner les électrodes comme anodes (Fig. 20).

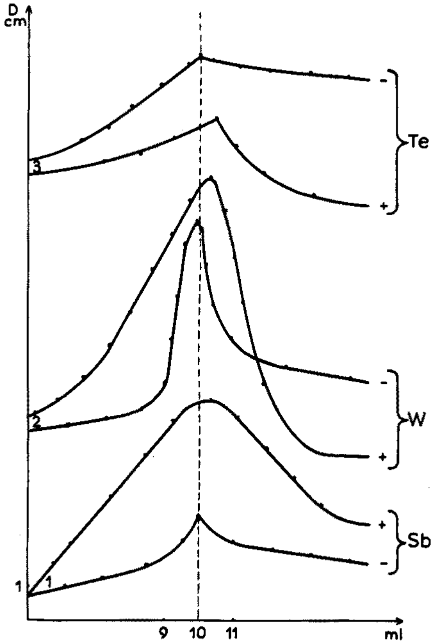


Fig. 20. Influence du sens du courant polarisant.

CONCLUSIONS GÉNÉRALES

Notre attention s'est surtout portée sur l'emploi des électrodes de zirconium qui présentent des particularités remarquables:

(*a*) Apparition sur les courbes de titrage de pics très aigus dissymétriques comme on peut le prévoir d'après les courbes potentiométriques sous courant.

(*b*) L'erreur de titrage due au décalage des courbes de titrage, en fonction de l'intensité appliquée reste négligeable, car le courant traversant les électrodes ne dépasse pas 0.1 mA. Ce décalage ne peut être complètement compensé même dans la méthode de "dead stop end-point" où les deux électrodes sont de signe contraire car il y a souvent dissymétrie.

(*c*) Présence d'une couche d'oxyde très résistante.

Parmi les électrodes présentant de l'intérêt on peut signaler l'antimoine et le tellure remarquable par sa stabilité.

Les électrodes d'antimoine ont donné d'excellents résultats dans les séparations d'acide. Les électrodes restant sous courant d'azote ont été appliqués à quelques titrages.

Signalons pour terminer que dans certaines séparations d'acides faibles et forts, les électrodes d'antimoine et de zirconium se complètent car avec le zirconium c'est l'acide le plus fort qui apparaît le plus net à l'inverse de ce qui se passe avec l'antimoine.

Certaines de ces séparations font d'ailleurs certainement intervenir la formation de complexes: les complexes des sels de zirconyle sont très stables. La comparaison des courbes de pH habituelles et de nos courbes montre que lorsque les constantes d'acidité sont voisines la présence des pics ne peut être uniquement due aux variations de pH.

RÉSUMÉ

Notre méthode diffère de la méthode classique (dead stop) par l'utilisation d'électrodes autres que celles de platine. Un montage très simple permet le fonctionnement de deux électrodes "indicatrices" comme cathodes, une contre-électrode en platine sert d'anode. L'intensité traversant le circuit étant imposée il s'agit plutot d'une méthode de "potentiométrie dérivée" sous courant. Les électrodes de zirconium ont particulièrement retenu notre attention. Elles se sont révelées très éfficaces dans le dosage d'acides forts très dilués. Les électrodes d'antimoine et de tellure ne sont pas non plus sans intérêt.

SUMMARY

The proposed method differs from the classical "dead stop" procedure in that electrodes other than platinum electrodes are used. The simple set-up includes 2 indicating electrodes as cathodes, with a platinum counter electrode. With an applied potential, the method is essentially derivative potentiometry. Zirconium electrodes are given particular attention, and are shown to be particularly effective in the determination of very dilute strong acids. Antimony, bismuth, tungsten and tellurium electrodes are also discussed.

ZUSAMMENFASSUNG

Die vorgeschlagene Methode unterscheidet sich dadurch vom klassischen "Dead-Stop"-Verfahren, dass andere als Platin-Elektroden verwendet werden. Der einfache Aufbau besteht aus 2 Indikatorelektroden als Kathoden mit einer Platin-Gegenelektrode. Bei einem angelegten Potential ist die Methode im wesentlichen eine Derivativpotentiometrie. Zirkonium-Elektroden verdienen besondere Beachtung;

es wird gezeigt, dass sie besonders günstig sind für die Bestimmung von sehr verdünnten starken Säuren. Antimon-, Wismut-, Wolfram- und Tellur-Elektroden werden ebenfalls diskutiert.

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ANALYSIS OF MIXTURES OF AMINES BY DIFFERENTIAL KINETICS

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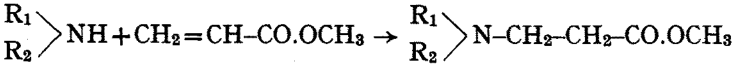
Differential reaction rate techniques have been utilised for the analysis of various mixtures of organic compounds having the same functional group[1]. HANNA AND SIGGIA[2] analysed mixtures of primary and secondary amines by this technique; in their method the amines are allowed to react with phenyl isothiocyanate in dioxane medium and the reaction is followed by potentiometric titration of the unreacted amines with perchloric acid in glacial acetic acid. More recently, GREINKE AND MARK[3] described methods for the analysis of amines by differential reaction rates with methyl iodide, by means of the conductivity method. None of these methods, however, can resolve a mixture of primary amines in the presence of secondary and tertiary amines. In the present work, the reaction with salicylaldehyde has been used for the analysis of mixtures of primary amines in the presence of secondary and tertiary amines. The addition of secondary amines to methyl acrylate has been utilised for the resolution of mixtures of such amines in the absence of primary amines.

The reactions involved in the two cases may be represented by eqns. (1) and (2) respectively.

$$R\,NH_2 + C_6H_4(OH)CHO \rightarrow RN{=}CH(OH)C_6H_4 + H_2O \qquad (1)$$



$$\left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle NH + CH_2{=}CH\text{-}CO.OCH_3 \rightarrow \left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle N\text{-}CH_2\text{-}CH_2\text{-}CO.OCH_3 \qquad (2)$$

The method, in either case, consists in measuring the rate at which the mixture of primary or secondary amines at a known total concentration reacts with a known concentration of the added reagent (salicylaldehyde or methyl acrylate). The initial concentration of the slower reacting component can be graphically obtained from the latter portion of the usual plot for a second-order reaction, and hence, the total initial concentration of the mixture being known, the concentration of each component may be obtained.

EXPERIMENTAL

Materials

Piperidine, morpholine, diethylamine, diethanolamine, triethylamine and triethanolamine were of analytical-reagent grade (Merck) and were used without further treatment. Di-*n*-butylamine, di-*n*-propylamine, monoethanolamine, *n*-butylamine, benzylamine and *tert.*-butylamine (laboratory reagent, B.D.H.) were purified by treatment with potassium hydroxide pellets and distillation in all-glass apparatus.

Solutions of the amines in methanol (analytical reagent, Merck) were standardized by titrating with standard hydrochloric acid in *n*-butanol, with thymol blue as indicator. Amine solutions in chloroform (analytical reagent, Merck) were standardized against perchloric acid in dioxane, with methyl violet as the indicator.

Salicylaldehyde (laboratory reagent, B.D.H.) was distilled twice under reduced pressure in all-glass apparatus. Standard solutions (0.3–0.4 *M*) in chloroform were prepared by weighing.

Methyl acrylate (laboratory reagent, Rohm and Haas) was purified by the usual method[4]. Standard solutions in methanol were prepared by weighing.

Dioxane (laboratory reagent, Riedel) was purified by overnight treatment with potassium hydroxide pellets, refluxing with sodium metal for 6 h and distillation over sodium. Only freshly distilled samples were used.

Perchloric acid solutions in dioxane were standardized with potassium hydrogen phthalate (extrapure, Merck) in glacial acetic acid (analytical reagent, Merck), with methyl violet as the indicator.

Hydrochloric acid in *n*-butanol (analytical reagent, B.D.H.) was standardized against a standard methanolic solution of mercury(II) acetate[5], prepared from mercury(II) oxide (extra pure, Merck).

Procedures

Resolution of primary amine mixtures. Mix measured volumes of the two amines in chloroform solutions in a reagent bottle and rapidly add a known volume of salicylaldehyde solution in chloroform.

The total concentration of the amines in the reaction mixture was roughly 0.08 *M*, that of salicylaldehyde being nearly twice the amine concentration.

Temperature control was unnecessary[1,2]. Pipette out 5-ml aliquots of the reaction mixture at suitable time intervals into a flask containing 1 ml of acetic anhydride to acetylate the unreacted primary amines. Within 5–6 min, titrate the yellow solution with 0.05 *M* perchloric acid in dioxane, with methyl violet as indicator.

The acid titre gives the amount of the Schiff's base formed and hence is a direct measure of the primary amine that has reacted. The Schiff's base also reacts slowly with acetic anhydride, as indicated by the gradual disappearance of the yellow color and decreased acid titre. A time of 2 min sufficed for complete acetylation of the unreacted amines. Hence, titration was generally started 3 min after the addition of acetic anhydride, and the solution should be titrated within 5–6 min; during this period very little reaction occurs between acetic anhydride and the Schiff's base.

On titration with perchloric acid, the yellow color gradually fades; 1–2 drops of methyl violet are added when the color is light yellow, whereupon a red color is obtained. At the end-point, the color changes to bluish violet; the change is not very sharp, but can be detected without difficulty.

Primary amine mixtures in the presence of secondary and tertiary amines. Use the procedure described above. Secondary amines do not react with salicylaldehyde, but on treatment with acetic anhydride they are acetylated along with the unreacted primary amines. Hence, the acid titre still corresponds to the Schiff's base formed.

Tertiary amines do not react with salicylaldehyde or acetic anhydride. The calculated titre corresponding to the tertiary amine present must be subtracted from the experimental acid titre to obtain the amount of Schiff's base formed.

The amounts of primary, secondary and tertiary amines in the initial mixture may be separately determined by the usual methods[1,6].

Resolution of secondary amine mixtures. Mix measured volumes of the secondary amines in methanol and add a known volume of a methanolic solution of methyl acrylate. The concentration of the reagent in the reaction mixture should be roughly twice the total amine concentration. Pipette out 5-ml aliquots at suitable time intervals into a flask containing 1–2 ml of acetic anhydride. After 5 min, titrate the solution with standard hydrochloric acid in *n*-butanol, with thymol blue as indicator. The acid titre is a direct measure of the tertiary amine formed, as the addition product[7]. If the reaction appears to be inconveniently fast (as with piperidine), it can be slowed down by using methanol–benzene as the reaction medium[7].

Proceed in the same way for mixtures of secondary amines in the presence of a tertiary amine. The experimental acid titre in this case corresponds to the addition product plus the tertiary amine initially present in the mixture, the amount of the latter being determined separately.

The method fails when primary amines are present in the mixture.

Calculation

The second-order kinetics for the addition of secondary amines to methyl acrylate was established by MALLIK AND DAS[7]. In course of the present studies, the reaction of salicylaldehyde with primary amines in chloroform was also found to be second order. In either case, therefore, a plot of log $(b-x)/a-x)$ against time should yield two intersecting straight lines for a binary mixture, where a and b represent the initial concentrations of the total amines and the reagent respectively and x is the concentration of the product formed. To obtain more points for this plot than available from direct experiment, a smooth curve was first drawn by plotting x against t, from which any convenient number of values of x at different values of t could be read off. It should be noted that for resolution of mixtures of primary amines in the presence of secondary or tertiary amines, a denotes the total concentration of primary amines only. Similarly, for mixtures of secondary amines, a denotes the total concentration of secondary amines alone.

The amount of the faster reacting component in the mixture was calculated by adopting both the "intercept" and the "time-axis" methods[1].

RESULTS

Mixtures of primary amines

Kinetic studies on the reaction between salicylaldehyde and some individual primary amines in chloroform medium at room temperature (*ca.* 30°) indicated second-order reaction. The relative rates of reaction for the four primary amines studied were in the order:

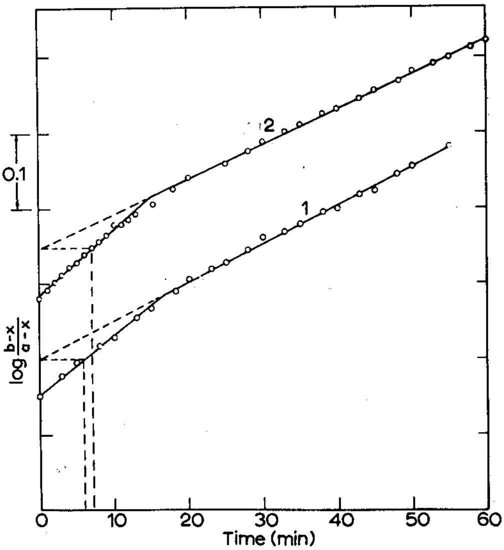
n-butylamine >	monoethanolamine >	benzylamine >	*tert.*-butylamine
(1.2)	(1.1)	(0.35)	(0.12)

The figures in parentheses give the approximate second-order rate constants (l mole^{-1} min^{-1}) at room temperature.

A graph for a typical binary mixture (*n*-butylamine + benzylamine) is shown in Fig. 1, which also shows the graph for another binary mixture (*n*-butylamine +

tert.-butylamine) in the presence of a secondary amine (morpholine). The analytical results, calculated by both the intercept and time-axis methods, are shown in Tables I and II.

For one of the mixtures (benzylamine + *tert.*-butylamine), the result obtained for the faster reacting component (benzylamine) involved a large error. In this case, however, the two straight lines in the graph were not very well defined. The rate



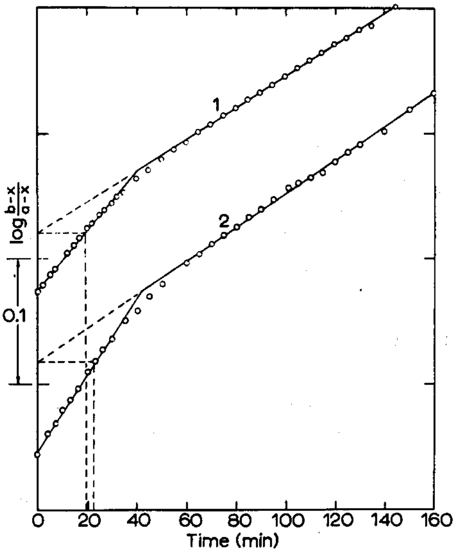


Fig. 1. Reactions of salicylaldehyde with mixtures of primary amines in chloroform medium. (1) *n*-Butylamine + benzylamine, (2) *n*-butylamine + tertiary butylamine in the presence of morpholine.

Fig. 2. Reactions of methyl acrylate with secondary amines in methanol medium. (1) Di-*n*-propylamine + diethanolamine, (2) di-*n*-propylamine + diethanolamine in the presence of triethylamine.

TABLE I

DETERMINATION OF THE FASTER REACTING COMPONENT IN BINARY MIXTURES OF PRIMARY AMINES

Component determined	*Amount present (%)*	*Amount found (%)*	
		Time-axis	*Intercept*
n-Butylamine[a]	29.4	28.6	28.0
Monoethanolamine[a]	24.7	25.0	25.1
	39.6	41.2	40.7
n-Butylamine[b]	27.6	–	26.9
	28.4	–	28.2
Benzylamine[b]	25.3	23.3	23.5
	20.1	21.7	21.6
Monoethanolamine[b]	32.6	–	31.2
	30.9	–	30.2

[a] In mixture with benzylamine. [b] In mixture with *tert.*-butylamine.

TABLE II

DETERMINATION OF *n*-BUTYLAMINE IN THE PRESENCE OF *tert.*-BUTYLAMINE AND A SECONDARY OR TERTIARY AMINE

n-Butylamine present (%)	23.2	20.1	24.1	23.2
Secondary or tertiary amine (%)	15.8[a]	27.1[a]	27.2[b]	15.8[c]
n-Butylamine found (%)				
Time-axis	23.0	19.4	23.7	22.9
Intercept	22.7	19.4	23.5	22.7

[a] Morpholine. [b] Triethanolamine. [c] Triethylamine.

constants for these two amines, as approximately determined at room temperature, were found to differ by a factor of less than 3. This ratio probably represents the extreme limit that permits the resolution of primary amine mixtures by this method, but obviously another parameter is involved—the mole ratio of the two components in the mixture. It may be noted from Table II that fairly good results were obtained for mixtures of *n*-butylamine in the presence of *tert.*-butylamine as well as a secondary or tertiary amine.

Resolution of secondary amine mixtures

Mallik and Das[7] kinetically studied the addition of morpholine and piperidine to methyl acrylate in methanol. In course of the present work, the rates of addition of other secondary amines were studied at room temperature and second-order kinetics established. The rates of the reaction were in the following order, the rate constants (l mole^{-1} min^{-1}) at room temperature being shown in parentheses:

Piperidine $\gg$ morpholine > diethylamine > di-*n*-butylamine > di-*n*-propylamine >
(15.3) (0.92) (0.60) (0.37) (0.31)
diethanolamine
(0.063)

A graph for a typical binary mixture (di-*n*-propylamine + diethanolamine) is shown in Fig. 2, which also shows the graph for a mixture of the same amines in the presence of a tertiary amine (triethylamine). The amounts of the faster reacting components in several binary mixtures, calculated by both the intercept and time-axis methods, are shown in Table III.

For mixtures containing piperidine (which reacts rather too quickly), it was found convenient to slow down the rate by allowing the reaction to occur in 1:1 or 1:2 methanol–benzene medium, instead of pure methanol. For mixtures containing amines with rate constants differing by a factor of 10 or more (*e.g.* morpholine and diethanolamine, or diethylamine and diethanolamine), the first portion of the graph showed deviations from linearity, and the time-axis method was not reliable enough. For such mixtures, however, good results were obtainable from the intercept method, since the second portion of the graph, corresponding to the slower reacting component, was a good straight line. On the other hand, for morpholine with di-*n*-butylamine, where the ratio of the rate constants was about 2.5, the graph showed two good straight lines, and the results calculated by both the methods were in fairly good agreement with the theoretical values. No resolution could be effected for morpholine and

TABLE III

DETERMINATION OF THE FASTER REACTING COMPONENT IN BINARY MIXTURES OF SECONDARY AMINES

Component determined	*Amount present (%)*	*Amount found (%)*	
		Time-axis	*Intercept*
Piperidine[a]	63.1	–	63.3
	38.4	38.9	40.1
	36.8	–	37.7[g]
	22.6	20.1[f]	22.0[f]
	22.6	21.6[f]	22.9[f]
Piperidine[b]	33.2	32.1	33.6
	48.2	46.2	50.4
Diethylamine[c]	25.4	–	26.4
	22.6	21.7	22.3
Piperidine[c]	32.4	32.9	33.1
	32.2	–	32.5
Morpholine[c]	33.4	30.9	33.8
	33.4	30.2	33.6
	18.9	–	18.4
	10.4	11.0	11.8
Morpholine[d]	19.5	19.9	19.7
	27.3	27.0	27.4
Di-*n*-butylamine[c]	21.8	21.6	21.5
	25.1	25.0	24.7
Di-*n*-propylamine[c]	21.5	21.4	21.2
Piperidine[e]	30.3	–	30.7
Piperidine[d]	32.8	–	33.9

[a] In presence of morpholine. [b] In presence of diethylamine. [c] In presence of diethanolamine. [d] In presence of di-*n*-butylamine. [e] In presence of di-*n*-propylamine. [f] In 1:2 methanol–benzene. [g] In 1:1 methanol–benzene.

diethylamine where the rate constants differed by a factor of only 1.5.

For mixtures of morpholine and diethanolamine, where the rate constants were in a ratio of nearly 15, several determinations were carried out, the percentage of the faster reacting component (morpholine) being varied over 10–36 in the mixture. Analyses in triplicate (with 33.4% morpholine) showed that the intercept method gave excellent results ($33.6\pm0.1\%$); however, with a low percentage (10.4%) of morpholine, results were not satisfactory.

Ternary mixtures

In the analysis of a typical mixture containing piperidine, morpholine and di-*n*-butylamine, a graph with three straight-line portions was obtained. The middle line on extrapolation gave piperidine, whereas the intercept of the third line gave piperidine + morpholine. Thus, if the total concentration of bases is known from direct titration, all three can be determined. The result for piperidine (the fastest reactant) was calculated with greater accuracy by separately plotting only the first two straight-line portions of the graph on a larger scale with a greater number of points. Results of analysis of ternary mixtures are shown in Table IV.

TABLE IV

ANALYSIS OF MIXTURES OF PIPERIDINE (A), MORPHOLINE (B) AND DI-*n*-BUTYLAMINE (C)

% A		*% B*		*% C*		*% (A + B)*		
Present	*Found*	*Present*	*Found*	*Present*	*Found*	*Present*	*Found*	
							Time-axis	*Intercept*
15.0	14.8	23.9	24.0	61.1	61.2	38.9	39.5	38.8
15.0	15.7	26.4	24.4	58.6	59.9	41.4	40.0	40.1

TABLE V

DETERMINATION OF DI-*n*-ALKYLAMINE IN THE PRESENCE OF DIETHANOLAMINE AND TRIETHYLAMINE

Component determined	*Amount present (%)*	*Amount found (%)*	
		Time-axis	*Intercept*
Di-*n*-butylamine[a]	21.0	21.1	20.9
Di-*n*-propylamine[b]	22.8	23.0	23.0

[a] 19.5% triethylamine present. [b] 10.9% triethylamine present.

Mixtures of secondary amines in the presence of a tertiary amine

Two sets of binary mixtures (di-*n*-butylamine with diethanolamine, and di-*n*-propylamine with diethanolamine) each in the presence of triethylamine were analysed. The results (Table V) show that the method is highly satisfactory for the determination of the fastest reacting component.

CONCLUSION

In the case of mixtures of secondary amines, the method is applicable in the presence of tertiary, but not primary, amines. Attempts were made to remove primary amines with salicylaldehyde before treatment with methyl acrylate which reacts with both primary and secondary amines, but the method failed. In the absence of primary amines, the method gives excellent results.

The method described above for the resolution of mixtures of primary amines has the distinct advantage over other methods[2,3] based on differential kinetics in that mixtures of primary amines can be analysed in the presence of secondary and tertiary amines; this is not possible by the other methods.

The intercept method, in general, yields better results than the time-axis method.

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SUMMARY

The reaction between salicylaldehyde and primary amines in chloroform is utilised for analysis of binary mixtures of primary amines by the differential rate technique. The method is applicable in the presence of secondary as well as tertiary amines. The difference in the rates of addition of secondary amines to methyl acrylate in methanol is utilised for resolution of binary and ternary mixtures of secondary amines. The method is applicable in the presence of tertiary, but not primary, amines. In either case, the second-order reaction is followed by non-aqueous titration, and the resolution is effected by graphical extrapolation from the usual second-order plots.

RÉSUMÉ

La réaction entre salicylaldéhyde et amines primaires dans le chloroforme est appliquée à l'analyse de mélanges binaires d'amines primaires par la technique de vitesse différentielle. Cette méthode est applicable en présence d'amines secondaires et tertiaires. La différence dans les vitesses de réaction des amines secondaires avec le méthylacrilate, dans le méthanol est utilisée pour l'analyse de mélanges binaires et tertiaires d'amines secondaires. Cette méthode peut être utilisée en présence d'amines tertiaires, mais non en présence d'amines primaires. Dans ces cas, la réaction de second ordre est suivie d'un titrage non-aqueux; la résolution est effectuée par extrapolation graphique.

ZUSAMMENFASSUNG

Die Reaktion zwischen Salicyladehyd und primären Aminen in Chloroform wird angewendet für die Analyse von binären Gemischen von primären Aminen mit Hilfe einer differentialen Reaktionsgeschwindigkeitsmethode. Das Verfahren ist anwendbar in Gegenwart von sowohl sekundären als auch tertiären Aminen. Die Differenz zwischen den Geschwindigkeiten der Addition von sekundären Aminen an Methylacrylat in Methanol wird benutzt für die getrennte Bestimmung von sekundären Aminen in binären und ternären Gemischen. Die Methode ist anwendbar in Gegenwart von tertiären, nicht aber primären Aminen. In jedem Fall wird die Reaktion zweiter Ordnung durch nichtwässrige Titration verfolgt; die Auflösung wird durch graphische Extrapolation der für zweite Ordnungen üblichen Auftragungen erreicht.

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DETERMINATION OF SOME FIRST TRANSITION METAL GROUP ELEMENTS BY ELECTRON SPIN RESONANCE

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Recently results concerning the determination of manganese(II) and copper(II) in their pure solutions and in the presence of each other by means of e.s.r. methods have been reported[1,2]. In these papers, some limitations of the methods, which used for an analytical evaluation the heights of peaks recorded, in the presence of diverse ions and ligands, were discussed. Our previous work on these assays indicated that this method might be used for the determination of other ions of the first transition metal group. In this paper the results achieved on the investigations of Cr(III), VO(II), Fe(III), Co(II) and Ni(II) ions are reported. The method is based on the linear relationship that exists between the concentrations of these ions and the amplitude of the absorption curve, if the line width is held constant.

In this study, the effect of many substances (cations, anions, and organic molecules) on the spectra of the paramagnetic species has been investigated, and precise and accurate analytical methods have been developed for the determination of chromium(III), vanadyl(II) and iron(III). Some results have been achieved in the determination of these ions in the presence of each other. These results will be reported in a separate paper[3].

EXPERIMENTAL

Apparatus

E.s.r. spectra were taken with the Varian E-3 e.s.r. spectrometer with a modulation frequency of 100 kHz. A standard quartz aqueous solution sample cell Varian Type V-4548 was used in all analyses. Use of this type of cell minimized the relatively high dielectric loss due to water as solvent, projecting into the r.f. electric field of the cavity.

Reagents

Standard solutions of Cr(III), VO(II), Fe(III), Co(II), and Ni(II), were prepared by dissolving the reagent-grade chloride, perchlorate, nitrate or sulfate salts in triply distilled water. For the investigation of iron(III), the solutions used were prepared by dissolving anhydrous iron(III) chloride in reagent-grade, dried acetone, acetonitrile or ethanol. Solutions of all diverse substances (see Table II) were prepared by dissolving reagent-grade chemicals in triply distilled water. The different chromium(III)

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salts were analyzed titrimetrically and their chromium contents were adjusted to equal concentrations.

Procedure

General operation. The instrument and the cell were tuned as described in a previous publication[1]. The tuning procedure had a reproducibility of about ±0.4% on the peak heights. The magnitude of the time constant depended on the receiver gain used. The scan time used depended on the time constant chosen; the peak-to-peak scan time had to be equal to, or larger than, 7–10 times the time constant used to avoid distortion of absorption lines.

All studies were performed in an air-conditioned room, thermostatted at 21±1°.

Determination of the ions. Stock solutions containing Cr(III), VO(II), Ni(II) or Co(II) in water (or in the case of iron(III), organic solvents) were placed in the cell in the E-3 spectrometer. A frequency $\nu_0 = 9.434$ GHz, and a field range of ±1000 G for chromium(III), ±500 G for vanadyl(II) or cobalt(II), or ±250 G for iron(III) was used in all measurements. The H_0 used depended on the average values of each ion in solutions: 3368 G for vanadyl(II), 3365 G for chromium(III), 3323 G for iron(III), and 3150 G for cobalt(II). An e.s.r. spectrum of cobalt(II) was observed only in the presence of an excess of cyanide ions, and no spectra could be obtained with nickel(II). Because the chromium, iron and cobalt ions in aqueous solution exhibit a more or less broad spectrum, without resolution, the single lines were used for these ions. In the case of vanadyl(II) ion, the characteristic 8-line spectrum was observed; this is due to vanadium nucleus having a nuclear spin 7/2. For the evaluation of vanadium, the third or fourth line from downfield was used ($I = -3/2$ or $-1/2$). These two lines were the narrowest and had the greatest peak height. The measured peak heights (mm) were divided by the modulation amplitude (usually 10 G) and the receiver gain, and were plotted *vs.* the concentrations of the individual ions. By these methods linear calibration curves for the ions were obtained.

RESULTS AND DISCUSSION

Table I shows for each of the ions investigated the useful concentration range for analysis and also the "relative intensity" values (a term introduced previously[2],

TABLE I

E.S.R. DETERMINATION OF VARIOUS IONS

Ions	*Upper limit (M)*	*Lower limit (M)*	*Relative intensity (ion : Mn(II))*	*Precision (%)*	*Error (%)*
Cr(III)	$1 \cdot 10^{-1}$	$8 \cdot 10^{-5}$	1:21	± 0.4	2.2
VO(II)	$5 \cdot 10^{-2}$	$1 \cdot 10^{-5}$	1:6.4	± 0.6	1.8
Fe(III)	$1 \cdot 10^{-1}$	$8 \cdot 10^{-6}$	1:4.5	± 0.4	2.5
Co(II)[a]	$5 \cdot 10^{-1}$	$1 \cdot 10^{-6}$	—	—	—
Ni(II)[b]					

[a] Not good for quantitative analysis (see text).
[b] No e.s.r. signal observed.

which describes the intensity of the signal for each ion compared to that observed for manganese(II) under the same experimental conditions). Different ions exhibiting paramagnetic properties have different intensities at the same concentration because of complicated processes occurring in solutions of these ions. Nickel(II) has a very short relaxation time. Furthermore, in the crystals of hydrated nickel ion the axial spin–spin term is rather large ($D \approx 2$ cm^{-1}); this value is too large to be averaged out in solutions[4]. We have failed to achieve appropriately longer relaxation times and a smaller D (ligand field splitting) value by complexation with any of the ligands listed in Table II.

In the case of cobalt(II), an e.s.r. spectrum could only be achieved when excess of potassium cyanide was used as a complexing agent. The olive-green solutions of the cobalt cyanide complex have a relatively intensive, narrow single absorption line. Unfortunately, this spectrum could not be used for quantitative analytical purposes, because the intensity of the signal has a significant dependence upon time, and even worse, is a function of the excess cyanide concentration. The correlations are presented in Fig. 1. The exact nature of this phenomenon will be investigated in the future. This phenomenon might be useful for the detection of cobalt(II), because of all the iron group elements only the vanadyl(II) has a spectrum (8 lines) in the presence of excess cyanide ion. With the others, namely, Mn^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, and Ti^{3+}, no e.s.r. spectrum is observed in the presence of cyanide. Iron(II or III) cyanide has only a very broad and very weak spectrum in the presence of cyanide.

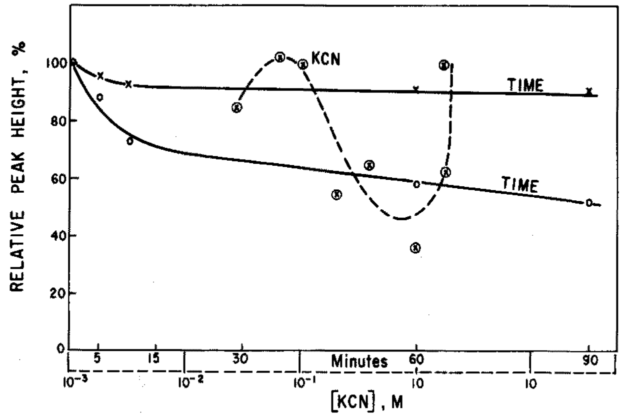


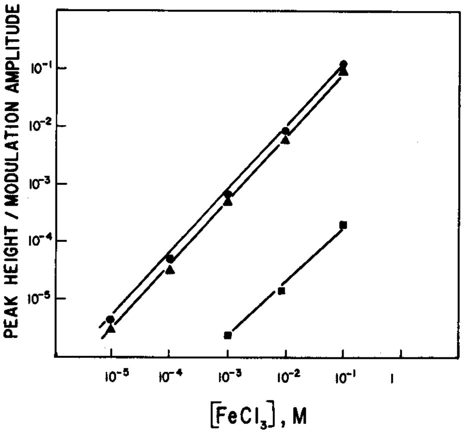
Fig. 1. The changes of the peaks heights of cobalt(II)–cyanide complex as a function of time, and the concentration of KCN. $Co^{2+} = 5 \cdot 10^{-3}$ *M*. (○) 0.1 *M* KCN, time axis; (×) 1.8 *M* KCN, time axis; (⊗) KCN axis.

To prepare a calibration curve for chromium(III), four different salts with the same concentration were used. The intensity of the e.s.r. signal of these compounds was found to be similar, except at higher concentrations. Above a concentration of 10^{-2} *M*, non-linearity between signal intensity and concentration exists in the case of chromium(III) chloride and potassium chromium sulfate. In the cases of the perchlorate and nitrate salts, linearity was observed up to 10^{-1} *M*. These phenomena are best explained as ion-pairing effects[5] caused by sulfate and chloride ions, rather than as dipole–dipole interactions. Theoretically one would expect a resolved 4-line e.s.r. spectrum of chromium(III) since ^{53}Cr with 9.55% abundance has a nuclear spin of 3/2. The hyperfine splitting does not appear in aqueous solutions at room temperature due to line broadening. This is because the anisotropic g values, existing in the solid (crystal) state, are not averaged out perfectly, and the ligand field splitting constant has a value of 0.05 cm^{-1}.

The vanadyl(II) ion is one of the most frequently investigated inorganic paramagnetic species[6]. Its spectrum consists of 8 lines, due to a nuclear spin of 7/2. These lines are not equally broad, because of the relaxation time, which depends on the nuclear spin values, and the anisotropy of the g value[7]. For analytical purposes the fourth line from downfield which corresponds to a value of $I = -1/2$, was used. A good spectrum of vanadium ion was observed only when the (V=O) group was present. In aqueous solution, vanadium ion in all oxidation states except vanadium(V) has a relatively small energy level difference between the ground and excited states, and consequently a spectrum is observed only at low temperatures. The existence of V=O binding introduces a larger splitting in the energy levels. To prove this, if one makes a solution of vanadyl(II) ion basic the structure of the vanadyl ion is destroyed and the signal disappears. Therefore, it is necessary to work at a pH of about 3.

Iron(III) ion has a very broad single signal in aqueous solution with about 1000 G. Its height is thus very small, and the e.s.r. spectrum can be used for analytical purposes only with serious limitations. This broad line is characteristic of the hydrated form of iron(III). SWANSON AND LAURIE have pointed out[8] that iron(III) ion in non-aqueous solutions has much narrower lines, which are more useful for analytical purposes. These authors have proved that this phenomenon is correlated with the formation of iron tetrachloride anions in non-aqueous solution. The best solvents are acetone and acetonitrile. Ethanol is a better solvent than water, but not as good as acetone or acetonitrile.

In Fig. 2 are presented the iron(III) calibration curves, obtained in different solvents. Addition of lithium chloride shifts the equilibrium toward formation of the



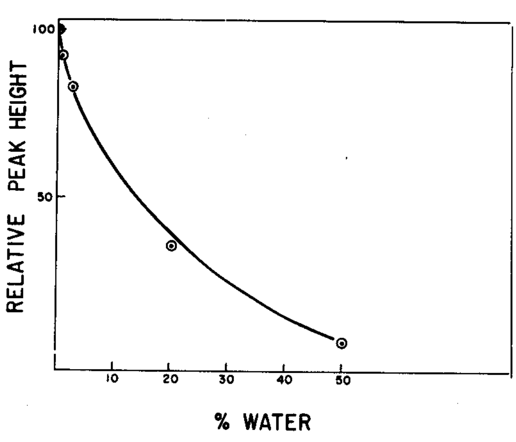


Fig. 2. Calibration curves for iron(III) chloride in different organic solvents. (●) Acetone, (▲) acetonitrile, (■) ethanol.

Fig. 3. Change of the peak height of the e.s.r. spectrum of iron(III) chloride in acetone with increasing water content. $FeCl_3 = 10^{-2}$ M.

iron tetrachloride ion and better results are obtained. The water content of the solvents has a drastic effect, decreasing the height of the signals. Therefore, it is important to use carefully dried solvents. The effect of the water content of solvents is shown in Fig. 3.

All of the calibration curves obtained were prepared by averaging 5–6 measurements. The reproducibility of the data was between 0.4–0.6%, and when the calibration curves were used for the determination of the individual ions, an accuracy of 2.5–4% was achieved in the concentration ranges mentioned in Table I.

The effect of the diverse ions on the peak heights

In Table II are listed the maximum concentrations of the diverse substances that can be added with no effect on the height or shape of the e.s.r. curves. In the case of chromium(III) every diverse substance caused a decrease in the magnitude of the curves, but the effects were different, depending on the nature of the compounds added to the solutions. Essentially the same results were obtained with H_3O^+, Zn^{2+}, Mg^{2+}, Na^+, K^+, or Ca^{2+} with the same anions. The anions affecting the amplitude of the spectra of chromium(III) may be placed into two groups. In the first group are inorganic compounds whose effect is independent of the concentration of chromium(III); the same effect was observed at concentrations of chromium(III) of $5\cdot10^{-2}$ and $5\cdot10^{-3}$. The effect of these ions, which is negligible at concentrations lower than those listed in Table II, may be attributed to the physical factors mentioned previously[2]. Those compounds which hydrolyze in water to yield basic solutions, *i.e.*, that precipitate $Cr(OH)_3$, exhibit a greater effect on the e.s.r. spectra; but this effect can be easily avoided by using perchloric acid to keep the pH at about 3–4.

TABLE II

EFFECT OF DIVERSE SUBSTANCES ON THE E.S.R. SPECTRA OF CHROMIUM(III) AND VANADYL(II) IONS

Diverse substances	*Maximum tolerable concn. (M)*[a]		*Diverse substances*	*Maximum tolerable concn. (M)*[a]	
	Cr(III)[b]	*VO(II)*[b]		*Cr(III)*[b]	*VO(II)*[b]
HCl	$5\cdot10^{-2}$	$5\cdot10^{-2}$	K_2 oxalate	$5\cdot10^{-4}$	$2\cdot10^{-4}$ [c]
CH_3COOH	$1\cdot10^{-1}$	$1\cdot10^{-1}$	KNa tartrate	$5\cdot10^{-4}$	$1\cdot10^{-4}$ [c]
$HClO_4$	$1\cdot10^{-1}$	$1\cdot10^{-1}$	EDTA	$2\cdot10^{-4}$	$2\cdot10^{-4}$ [d]
HNO_3	$1\cdot10^{-1}$	$6\cdot10^{-2}$	KCN	$2\cdot10^{-4}$	$2\cdot10^{-4}$ [d]
H_3PO_4	$2\cdot10^{-2}$	$2\cdot10^{-2}$	NH_3	$5\cdot10^{-3}$	$5\cdot10^{-4}$ [c]
H_2SO_4	$2\cdot10^{-3}$	$2\cdot10^{-2}$	Ethylenediamine	$1\cdot10^{-4}$	$5\cdot10^{-4}$
HCl	$5\cdot10^{-2}$	$4\cdot10^{-1}$	$Ca(NO_3)_2$	$2\cdot10^{-1}$	$5\cdot10^{-1}$
KBr	$8\cdot10^{-2}$	$3\cdot10^{-1}$	$CaCl_2$	$5\cdot10^{-2}$	$2\cdot10^{-1}$
KI	$1\cdot10^{-1}$	$5\cdot10^{-1}$	$MgCl_2$	$5\cdot10^{-2}$	$1\cdot10^{-1}$
KSCN	$2\cdot10^{-1}$	$5\cdot10^{-2}$	$Zn(NO_3)_2$	$2\cdot10^{-1}$	$5\cdot10^{-1}$
KNO_3	$1\cdot10^{-1}$	$3\cdot10^{-1}$	$ZnSO_4$	$8\cdot10^{-4}$	$2\cdot10^{-2}$
Na_2SO_4	$5\cdot10^{-4}$	$2\cdot10^{-2}$	$MgSO_4$	$8\cdot10^{-4}$	$2\cdot10^{-2}$
K_2HPO_4	$8\cdot10^{-4}$	$1\cdot10^{-1}$	*p*-Dioxane	1% vol	2%
KH_2PC_4	$1\cdot10^{-3}$	—	Acetonitrile	2%	4–5%
Na acetate	$5\cdot10^{-4}$	$5\cdot10^{-4}$	Methanol	3%	2%
$NaClO_4$	$1\cdot10^{-1}$	$4\cdot10^{-1}$	Acetone	2%	2%
Na citrate	$1\cdot10^{-4}$	$2\cdot10^{-4}$ [c]	Dimethylformamide	1%	1%

[a] Maximum concentration that can be added with no effect on the e.s.r. spectra.

[b] $Cr(NO_3)_3 = 10^{-2}$ *M*, $VOSO_4 = 10^{-2}$ *M*.

[c] Spectrum with some new features appeared in presence of excess of these ligands.

[d] Intensively narrow spectra. With relatively high peaks.

Members of the second group (citrate, oxalate, EDTA, tartrate, ethylenediamine, potassium cyanide, ammonia) show an effect that is dependent on the concentration of chromium(III). E.s.r. spectra cannot be obtained at higher concentrations of cyanide, ammonia or ethylenediamine because of precipitation. In the case of citrate, the spectrum did not totally disappear, and furthermore, at higher concentrations, the height of the signal started to increase.

The diverse substances produced more complicated effects on the e.s.r spectra of vanadyl(II) (Fig. 4). The univalent anions decreased the height, as usual.

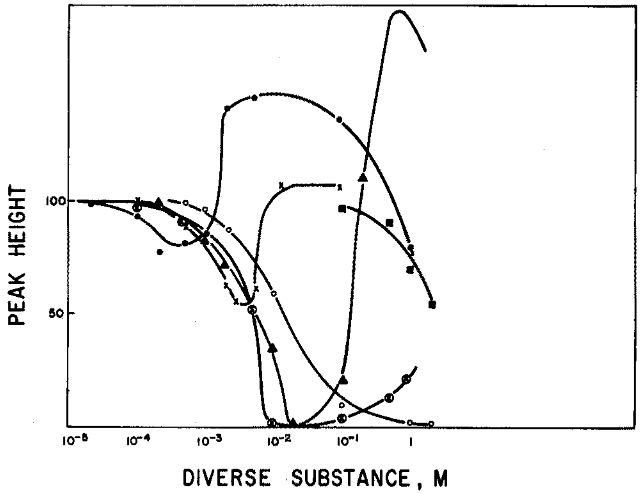


Fig. 4. Some selected curves, showing the effects of different compounds on the heights of the fourth peak of vanadyl as a function of the concentration of diverse substances. (VO^{2+}) = 10^{-2} *M*. (▲) KCN, (⊗) tartrate, (■) HCl, (●) oxalate, (×) EDTA, (○) Na acetate.

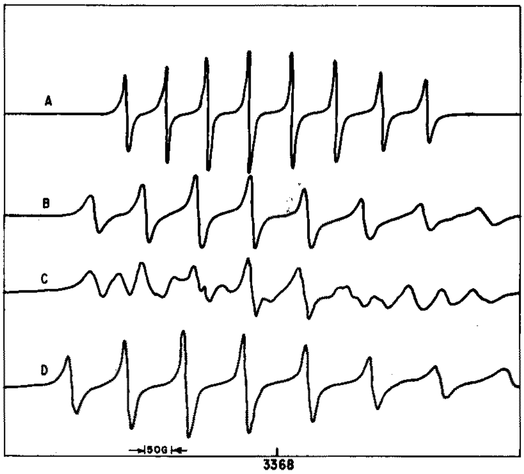


Fig. 5. Some selected e.s.r. spectra of vanadyl ions in the presence of (A) KCN, (B) EDTA, (C) KNa tartrate, (D) water. The spectra are taken at the same concentrations of VO(II) = $1 \cdot 10^{-2}$, with excess of the ligands. All experimental conditions were the same, except for varying receiver gain. $H_0 = 3368$ G ± 500 G.

It has already been pointed out that at basic pH the spectrum disappears, owing to the well known effect of destroying the V=O structure. Polydentate ligands caused a narrower spectrum (*i.e.* the coupling constant was smaller). Some of these effects are shown in Fig. 5. Of particular interest is the EDTA. If this ligand is used in stoichiometric amounts or in excess, the spectrum becomes narrower with a bandwidth of about 100 G. With less than a stoichiometric amount a mixed spectrum of vanadyl(II) and the vanadyl(II)–EDTA complex was observed, together with separated lines. One can obtain a similar spectrum by complexing vanadyl(II) with potassium cyanide, but the lines are narrower than in the case of EDTA. Something similar to this occurs in the complexation with oxalate. The hydroxycarboxylic acid type ligands (citrate, tartrate) produced a special type of spectrum. The spectra disappeared, when the ligands were present at concentrations equal to that of vanadyl(II). With a large excess of the ligands, a new spectrum appeared with different *hfs* coupling constants. Instead of 8 lines, one can observe more, depending on the circumstances (about 20–24 lines more or less overlapping each other (Fig. 5)). Such observations have been made by DUNHILL[9] in the case of copper(II) and citrate ion, and an explanation of these phenomena was given as a function of pH and the structure of the complex ions. Citrate, DL-tartrate, DL-malate and glycolate complexes of vanadyl and copper(II) ions were found to give spectra with special features. A further investigation of the nature of these complexes is under way and the results will be published at a later date.

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SUMMARY

An e.s.r. method is described for the determination of chromium(III), vanadyl(II), and iron(III). The measurement is based on the linear relationship that exists between the peak heights of the spectra of these ions and their concentration. Iron(III) ion has a very broad line in aqueous solution, but in organic solvents its line becomes much narrower, and suitable for analytical purposes. Nickel(II) has no observable spectra in aqueous solution; cobalt(II) has a relatively sensitive signal only in the presence of excess cyanide ion. The reproducibility of the calibration curves is about ±0.4–0.6%. The accuracy of the determination varies between 2 and 4%. The effect of about 30 different diverse substances (anions and ligands) on the peak heights was studied. The maximum concentrations of these ions that have no effect on the e.s.r. spectra are summarized.

RÉSUMÉ

On décrit une méthode e.s.r. pour le dosage du chrome(III), du vanadyle(II) et du fer(III). Elle est basée sur la relation linéaire qui existe entre les hauteurs des pics des spectres de ces ions et leur concentration. Le fer(II) présente une raie très large en solution aqueuse, mais en solvants organiques cette raie devient beaucoup plus étroite et convient pour des analyses. Le nickel(II) ne donne pas de spectre observable en solution aqueuse; le cobalt(II), en présence d'un excès de cyanure présente un signal relativement sensible. La reproductibilité des courbes est d'environ ±0.4–0.6%. L'exactitude des dosages varie entre 2 et 4%. On a examiné l'influence de 30 substances environ (anions et ligands) sur les hauteurs des pics.

ZUSAMMENFASSUNG

Es wird eine e.s.r.-Methode für die Bestimmung von Chrom(III), Vanadyl(II) und Eisen(III) beschrieben. Die Messung beruht auf der linearen Beziehung zwischen den Peak-Höhen der Spektren dieser Ionen und deren Konzentration. Eisen(III)-Ionen ergeben in wässriger Lösung eine sehr breite Linie, in organischen Lüsungsmitteln wird die Linie jedoch viel schmaler und eignet sich so für analytische Zwecke. Nickel(II) hat in wässriger Lösung keine beobachtbaren Spektren; Kobalt(II) ergibt nur in Gegenwart eines Überschusses an Cyanid-Ionen ein verhältnismässig empfindliches Signal. Die Reproduzierbarkeit der Eichkurven beträgt etwa ±0.4–0.6%. Die Genauigkeit der Bestimmung schwankt zwischen 2 und 4%. Der Einfluss von etwa 30 verschiedenartigen Substanzen (Anionen und Liganden) auf die Peak-Höhen wurde untersucht. Die höchsten Konzentrationen dieser Ionen, die keinen Einfluss auf die e.s.r.-Spektren haben, werden zusammengestellt.

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SOME SELECTIVE DETERMINATIONS OF IRON GROUP ELEMENTS IN THE PRESENCE OF EACH OTHER BY ELECTRON SPIN RESONANCE METHODS

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Depending on the properties and nature of e.s.r. methods, one can utilize the following possibilities for the selective measurements of individual paramagnetic species in the presence of each other if one wants to avoid the use of some suitable separation methods. Firstly, if a constant frequency is used, the paramagnetic substances can have a relatively large difference on their g values; hence the resonance absorption will take part at different H values. If the difference of H values is large enough, one can obtain separated spectra by a sweeping of the magnetic field. In this case, one must determine by experiment the limitations by dipole–dipole interactions, by ion-pairing effects, etc. When the distance between the lines is limited, one must determine at what concentrations of the ions partial overlapping of spectra becomes serious from an analytical viewpoint.

The second possibility is to use a reagent with which all the ions present in the solution react, but with which all the products of the reaction lose their original paramagnetic properties, except for the compound to be analyzed. Naturally, the complexation reaction causing the elimination of the paramagnetic properties has to be fast and quantitative, and cannot have an adverse effect on the compound to be determined. In a previous paper[1] copper(II) and manganese(II) were determined in the presence of each other, by both of the principles mentioned above. The reagent used was ethylenediamine. The study on the other members of the iron group elements has been continued[2] and their behavior with different ligands has been examined. Some selective determinations of mixtures of paramagnetic ions are possible without prior separation.

EXPERIMENTAL

Apparatus

Varian E-3 e.s.r. spectrometer was used with a standard quartz aqueous solution sample cell (Varian type V-4548).

Reagents

Standard copper(II), vanadyl(II), chromium(III), manganese(II), cobalt(II), nickel(II) and iron(III) solutions were prepared by dissolving reagent-grade salts of

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these ions (perchlorate or nitrate, and in the case of copper(II) and vanadyl(II), sulphate) in water. For the complexations reagent-grade ethylenediamine, 0.1 *M* ethylenediaminetetraacetic acid, disodium salt (EDTA), and 2.0 *M* potassium cyanide were used.

Procedure

The instrument and the cell were used as described previously[2,3]. During the measurements different field settings were used, depending on the ions to be determined. These values are shown in Table I, together with the field range values. The lines used for quantitative evaluations were also given previously[1,2]. The concentrations were determined by using calibration curves prepared as previously described[1], except for vanadyl, which will be discussed later in this paper. For the determination of copper(II) in the presence of different iron group elements, ethylenediamine was used as ligand. In the presence of ethylenediamine, the e.s.r. spectra of all ions disappeared, except that of copper(II). For the selective determination of vanadyl ions, excess of EDTA (0.1 *M* in aqueous solution) was used. In the presence of excess of EDTA, e.s.r. spectra of only the vanadyl–and copper(II)–EDTA complexes were obtained; fortunately, these spectra were separated along the magnetic field.

TABLE I

DETERMINATION OF COPPER(II) IN THE PRESENCE OF SOME OTHER PARAMAGNETIC IONS

Diverse ions	*Allowable amount present*[a]	*Field setting (G)*	*Field range (G)*	*Precision (%)*	*Error (%)*
VO^{2+}	10 times higher than Cu^{2+} [b]	3150	± 500	± 0.5	2.4
Cr^{3+}	10 times higher than Cu^{2+}	3150	± 500	± 0.5	2.4
Co^{2+}	No limitations[c]	3150	± 500	± 0.5	2.4
Ni^{2+}	No limitations	3150	± 500	± 0.5	2.4
Fe^{3+}	No limitations	3150	± 500	± 0.5	2.4

[a] Ethylenediamine used in excess; the evaluation is based on the calibration curve for the Cu–ethylenediamine complex.
[b] When the concentration of vanadyl is higher than $5 \cdot 10^{-2}$ *M*, see text.
[c] Except by anions belonging to the cations[1].

The following is an example of the determination of ions in the presence of each other.

Pipette into a volumetric flask 1–2 ml of the test solution of copper and vanadyl. Add 1 ml of ethylenediamine and dilute to the mark with distilled water. Wait for 3–5 min, shaking the flask periodically, and filter. The resulting solution is ready for analysis. Record the e.s.r. spectrum of the solution (the spectrum should have four lines). From the height of the third peak, determine the copper content by means of a calibration curve. For the determination of vanadyl, pipette a second 1-ml aliquot to another volumetric flask and dilute to the mark with 0.1 *M* EDTA solution. After the e.s.r. measurement, measure the height of the fourth line and from a calibration curve determine the concentration of vanadyl. Several combinations of ions that can be determined are summarized in Tables I–III.

RESULTS AND DISCUSSION

Determination of copper(II)

The determination of copper(II) in the presence of other iron group elements is based on the fact that copper(II) has a relatively well resolved four-line spectrum after complexation with ethylenediamine, but the e.s.r. spectra of other ions disappear in the presence of excess ethylenediamine. The correlation between the heights of the peaks of the copper(II)–ethylenediamine spectrum and the concentration of copper(II) is linear, as reported earlier[1]. Vanadyl does not interfere in concentrations up to $5 \cdot 10^{-2}\ M$. At concentrations higher than this, it is necessary to wait for 10–15 min, shaking the solution periodically, until the vanadyl is oxidized to vanadium(V). One can follow this process since the violet-brown turbid solution becomes clear and the violet-bluish color of the copper–ethylenediamine complex appears. In the presence of chromium(III) and iron(III), one obtains a precipitate after treatment with ethylenediamine. This precipitate, most probably the hydroxides of chromium(III) and iron(III), can be very easily removed by filtration. Nickel(II) and cobalt(II) do not interfere in the determination of copper(II) either with or without complexation with ethylenediamine. In Table I are summarized the results and the limitations of the determination of copper(II) as its ethylenediamine complex in the presence of other iron group elements. In the presence of copper(II) one can determine with some limitations vanadyl and chromium(III) in the same way as manganese(II). The limitations are only the relative concentrations of the other ions and copper(II). Copper(II) has a spectrum with a "tail" in the direction of higher magnetic field and this disturbs the lines that have been chosen for the quantitative determination of other ions at high concentrations of copper(II). In addition, the effects of anions that belong to copper(II) must be considered, because these might affect the peak intensity[1]. In the presence of copper(II) vanadyl and chromium(III) can be determined only with some limitations. Table II shows the results.

TABLE II

DETERMINATION OF CATIONS IN THE PRESENCE OF COPPER(II) WITHOUT COMPLEXATION

Ion determinable	*Tolerable concentration of Cu^{2+}*	*Field setting (G)*	*Field range (G)*	*Precision (%)*	*Av. error (%)*
VO^{2+}	$10 \times VO^{2+}$	3668	± 1000	± 0.5–0.6	2.1
Cr^{3+}	$1/10\ Cr^{3+}$	3365	± 1000	± 0.5–0.6	4.0
Co^{2+}[a]	No disturbances. Cu(II) reacts with KCN	3223	± 500	± 0.5–0.6	2.8
Ni^{2+}	Not determinable	3500	± 1000		
Fe^{3+}	In water solution practically not determinable. Can be determined in non-aqueous solution[3] containing KCN[2]	3500	± 1000		

Determination of vanadyl in the presence of other paramagnetic ions

It has been reported[2] that vanadyl(II) ion gives with the ligands EDTA or potassium cyanide a relatively narrow, unchanged, 8-line resolved spectrum, if the ligand is present in excess. These reactions have been studied in detail from aspects of the quantitative analysis. When EDTA is used in excess, a linear relationship can be obtained between the peak height and the concentrations of the vanadyl–EDTA complex. The experiments with cyanide showed that the height of the peaks depends on the relative amounts of the excess of cyanide, if the concentration of vanadyl is held constant, and that the peak heights decrease with time. This decrease was extremely fast in the presence of manganese(II). Consequently, EDTA was chosen as a specifically acting ligand to eliminate the spectra of other iron group elements. In the presence of EDTA, the e.s.r. signals of manganese(II), chromium(III) and iron(III) disappear, but the spectrum of copper(II) (reported previously) becomes a bit better resolved than in its hydrated form. Some shifting of the spectrum in the direction of higher magnetic field is observed with a value of about 100 G. However, there is some difference between the *g* values and this creates a separation between the spectra of

TABLE III

DETERMINATION OF VANADYL IN THE PRESENCE OF SOME OTHER PARAMAGNETIC IONS[a,b]

Diverse ions	*Allowable amount present*	*Precision (%)*	*Av. error (%)*
Mn^{2+}	Mn^{2+} can be 10 × higher than VO^{2+}	0.5–0.6	2.7
Cu^{2+}	Cu^{2+} can be 2 × higher than VO^{2+}	0.5–0.6	3.8
Cr^{3+}	Cr^{3+} can be 5 × higher than VO^{2+}	0.5–0.6	2.8
Ni^{2+}	No limit	0.5–0.6	1.8–2
Co^{2+}	No limit[c]	0.5–0.6	1.8–2
Fe^{3+}	No limit	0.5–0.6	1.8–2

[a] In the presence of excess EDTA.
[b] Field setting and field range are constant at 3368 G ± 500 G.
[c] Depends on the anions.

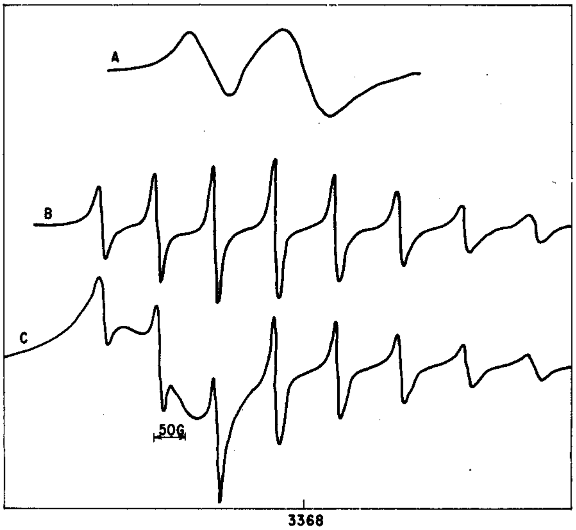

Fig. 1. Some selected e.s.r. spectra useful for the determination of ions in the presence of each other. $H_0 = 3368$ G ± 500 G. (A) 10^{-2} *M* CuSO$_4$ and 10^{-2} *M* Cr(NO$_3$)$_3$; (B) 10^{-3} *M* VOSO$_4$ in the presence of EDTA, CuSO$_4$ = 10^{-3} *M*; (C) 10^{-3} *M* VOSO$_4$ in the presence of EDTA, CuSO$_4$ = 10^{-2} *M*.

the copper–EDTA and vanadyl–EDTA complexes. At a frequency $\nu_0 = 9.433$ GHz, H_0(VO–EDTA) $-$ H_0(Cu–EDTA) ≈ 230 G, and the intensity of the spectrum of the vanadyl–EDTA complex is 20 times higher than that of the copper–EDTA complex. Only in the case of relatively high concentrations of copper compared to vanadyl is there any error in the determination of vanadyl.

Some of the results obtained with EDTA complexation are summarized with the limitations of each procedure in Table III. Some selected spectra are presented in Fig. 1.

The same results in the determination of chromium(III) ion could not be achieved. In the presence of this ion, copper and vanadyl can be determined but not manganese(II). The chromium(III) itself can be determined only in the presence of limited amounts of copper(II) since there is a relatively large separation along the magnetic field. But when copper(II) is present in high concentrations, the error of the chromium(III) determination becomes large, because of an interference caused by tailing in both spectra (Table II). The determinations of the ions mentioned have been studied in the presence of cobalt(II) and nickel(II); these ions do not have spectra in aqueous solution (the reasons for this phenomenon have been discussed[1]) and hence do not interfere in the determination of other ions. The ion-pairing effect caused by the anions of these cations is important, however. No direct interactions between the cobalt(II) or nickel(II) and the other ions which are determinable by e.s.r. methods, were observed.

We are planning to continue research in this field, by using more specifically acting ligands, combined with good separation methods (for example, chromatography, extractions, etc.).

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SUMMARY

The selective determination of iron group elements in the presence of each other by e.s.r., without previous separation is described. The method is based on the difference of *g* values that exists, and on the use of specific complexations. For the determination of copper, ethylenediamine is used, which by complexation eliminates the spectra of all the iron group elements except copper. For the selective measurement of vanadyl ion in the presence of different ions, EDTA complexation is successfully used. The only ion, besides vanadyl, with a spectrum after reaction with EDTA is copper, but the spectra are separated by their different *g* values. Some limitations of the measurement methods are shown and discussed.

RÉSUMÉ

On décrit un dosage sélectif des éléments du groupe du fer, en présence les uns des autres, par résonance de spin, sans séparation. La méthode est basée sur la différence des valeurs *g* et sur la formation de complexe. On utilise l'éthylènediamine pour le cuivre, qui par formation de complexe élimine les spectres de tous les éléments du groupe du fer, à l'exception du cuivre. On peut mesurer sélectivement l'ion vanadyle en présence d'autres ions, en utilisant l'EDTA comme complexant. Seul le cuivre donne un spectre, mais ceux-ci sont séparés grâce aux différentes valeurs de *g*.

ZUSAMMENFASSUNG

Es wird die selektive Bestimmung von nebeneinander vorliegenden Elementen der Eisengruppe durch e.s.r. ohne vorhergehende Trennung beschrieben. Die Methode beruht auf der Differenz der *g*-Werte und auf der Anwendung spezifischer Komplexbildungsreaktionen. Für die Bestimmung von Kupfer wird Äthylendiamin benutzt, das die Spektren aller übrigen Elemente der Eisengruppe durch Komplexierung eliminiert. Für die selektive Messung von Vanadyl-Ionen in Gegenwart verschiedener anderer Ionen wird die Komplexierung durch EDTA mit Erfolg angewendet. Das einzige Element, das ausser Vanadyl-Ionen nach der Reaktion mit EDTA ein Spektrum zeigt, ist Kupfer; jedoch können die Spektren auf Grund ihrer verschiedenen *g*-Werte voneinander unterschieden werden. Einige Grenzen der Messmethoden werden aufgezeigt und diskutiert.

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SHORT COMMUNICATIONS

Complex formation in concentrated sulfuric acid between carminic acid and germanium(IV) or boric acid

Carminic acid is a member of a group of hydroxyanthraquinones which react with boric acid in concentrated sulfuric acid, and has been extensively used in the spectrophotometric determination of boron. Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone)[1] and diaminochrysazin (4,5-diamino-1,8-dihydroxyanthraquinone)[2] have also been widely used in the photometric determination of microgram quantities of boron, and the stability constants of the boron–quinalizarin complex[3] and the boron–diaminochrysazin complex[4] have been reported.

A series of contributions by LANGMYHR *et al.* has described the analytical applications and complex formation in concentrated sulfuric acid of 1,1′-dianthrimide with boron[5] and germanium[6,7]. The 1,1′-dianthrimide reagent requires extensive periods of heating under controlled conditions to produce complexes with these elements. The present paper deals with complex formation between boric acid or germanium(IV) and carminic acid, a reagent which does not require heating.

Equipment

Extinction measurements were made with a Bausch and Lomb Spectronic 505 recording spectrophotometer. The cell compartment of the instrument contained a jacket through which water maintained thermostatically at 25° was circulated. The silica cells used had paths of 0.1, 0.5, 1.0 cm.

All glassware used for volumetric purposes was of the "soft glass" type (Kimble brand). For storage and ordinary handling of acid solutions, Corning alkali-resistant ("boron-free") glass No. 7280 was used.

Reagents and standard solutions

Carminic acid was obtained from Eastman Kodak, and the germanium dioxide from British Drug House and also from Sargent Scientific. The boric acid, sulfuric acid and fuming sulfuric acid were of reagent-grade quality.

Standard solutions of boric acid and of carminic acid were prepared by weighing out the proper amounts and dissolving in 93% sulfuric acid. The solubility of germanium dioxide in 93% sulfuric acid is too low to obtain a standard solution by the direct method. Instead a solution was prepared in 1% sodium hydroxide in which germanium dioxide dissolves readily. This standard solution was stored in a plastic bottle. To prepare a $1 \cdot 10^{-3}$ M solution of germanium in 93% sulfuric acid, the requisite volume of the solution in sodium hydroxide was pipetted into a volumetric flask and 96% and 15% fuming sulfuric acids were added. There was no evidence of any precipitation in this solution at the end of 4 months. For all the reactants, solutions of other concentrations were prepared by dilution of the standard solutions with 93% sulfuric acid.

Effect of concentration of sulfuric acid

It has been reported[8] that maximum sensitivity is achieved in 93% sulfuric acid media for some of the analytical methods for boron which use hydroxyanthraquinones in concentrated sulfuric acid. To check the effect of acid concentration on the germanium–carminic acid complex, solutions were prepared in which the germanium was in ten-fold excess and the concentration of the sulfuric acid was varied from 91 to 96%. The absorbances were read at 602 nm and at 540 nm. In neither set did the total change with sulfuric acid concentration exceed 4%. In this range the sulfuric acid concentration was not critical and the 93% acid was chosen to conform to the concentration used in boron determinations.

The germanium–carminic acid complex

The absorption curve of a solution of carminic acid in 93% sulfuric acid showed two peaks of almost equivalent height at 540 and 505 nm and a third lower peak at 335 nm. The lowest absorbance over the range 320–650 nm was between 590 and 650 nm. Carminic acid solutions with a 10-fold excess of germanium had a peak at 356 nm and a sizeable difference in absorbance between complex and reagent above 590 nm; the peak at 505 nm decreased while the peak at 540 nm disappeared. Preliminary studies of the complex reaction showed that several hours were required at room temperature to reach equilibrium.

The absorbances of a set of solutions of constant total concentration of $1 \cdot 10^{-4}$ M were measured for the continuous variation method. Readings were made at 347, 540 and 602 nm. At each wavelength the continuous variation curve showed a rounded maximum which had its highest point at a molar fraction of 0.55. Since the maximum occurred at the same fraction for three widely spaced wavelengths, it would seem that only one complex is present.

TABLE I

STABILITY CONSTANT OF THE GERMANIUM COMPLEX

Solution number	*Germanium concentration* $(\cdot 10^{-4}M)$[a]	*Extinction*[b] *at 602 nm*	*Stability constant* $(\cdot 10^{4})$
G1	6	0.252	3.29
G2	5	0.250	3.45
G3	4	0.246	3.44
G4	3	0.240	3.52
G5	2	0.225	3.49
G6	1	0.190	3.87

[a] A constant concentration ($0.5 \cdot 10^{-4}$ M) of carminic acid was used.

[b] All extinctions read against a blank which was $0.5 \cdot 10^{-4}$ M in carminic acid.

If the presence of a complex of the form Ge_mA_n is assumed, the quotient n/m may be determined by the straight-line method of HOLME AND LANGMYHR[9]. Table I gives some data for the germanium–carminic acid system at 602 nm. A straight line was obtained for $n/m = 1$. The same data may be used to determine the value of n by the straight-line method of KLAUSEN AND LANGMYHR[10]. With this second method a straight line was obtained for $n = 1$. Therefore the complex formed has the formula GeA.

The boron–carminic acid complex

The absorbance curve of the boron–carminic acid complex exhibited the same features as those found with germanium and carminic acid. The only difference occurred at the peak in the region 340–360 nm which was lower for boron than for germanium. Application of the above methods showed that the quotient n/m was unity and that $n=1$. The complex has therefore the formula BA.

The stability constant

To calculate the stability constant, two methods were chosen—the method of HOLME AND LANGMYHR[9] and the method of ROSE AND DRAGO[11].

In the HOLME AND LANGMYHR method the constant is obtained from the expression

$$K = \frac{\dfrac{Ea}{E_0 m}}{\left(b - \dfrac{n}{m}\dfrac{E}{E_0}a\right)^n \left(a - \dfrac{E}{E_0}a\right)^m}$$

where a and b are the initial concentrations of the reactants, E is the measured extinction and E_0 is the upper extinction limit. For both complexes $m=1$ and $n=1$. Table I gives an example.

The method of ROSE AND DRAGO requires a value for the extinction coefficient ε_A of carminic acid; it is assumed that the extinction coefficient ε_c of the complex is not known. Because of solubility limitations for germanium in sulfuric acid it was not possible to add a very large excess of germanium to the carminic acid and obtain the extinction coefficient on the assumption that all the carminic acid had been used in the complex. Instead a series of values were assigned to ε_c and by the use of the equation

$$K^{-1} = \frac{E}{(\varepsilon_c - \varepsilon_A)} - a - b + \frac{ab(\varepsilon_c - \varepsilon_A)}{E}$$

the corresponding values of K^{-1} were calculated. A plot of K^{-1} against ε_c gave a straight line. With a series of concentrations, all lines should intersect at the values of K^{-1} and ε_c.

The data in Table I, when treated by this method and with $\varepsilon_A = 1.4 \cdot 10^3$ gave a point of intersection of all six lines at $K^{-1} = 0.28 \cdot 10^{-4}$ and $\varepsilon_c = 6.7 \cdot 10^3$. From this the stability constant is $3.58 \cdot 10^4$.

Both methods were used to calculate the stability constants from extinctions measured at 540 nm and at 356 nm for germanium and 360 nm for boron. Some values were obtained from solutions in which the concentration of the carminic acid was $0.25 \cdot 10^{-4}$ *M* or $1.25 \cdot 10^{-4}$ *M*.

Results and discussion

The calculated values of K and ε_c, and their standard deviations σ_k and σ_ε, respectively, are given in Table II. The average K value for the boron complex is $1.94 \cdot 10^{-4}$, and that for the germanium complex is $3.79 \cdot 10^4$.

Boron and carminic acid form a 1:1 complex with a stability constant similar to that of boron with other hydroxyanthraquinones; *e.g.* for quinalizarin[3], $K = 8.7 \cdot$

TABLE II

STABILITY CONSTANTS FOR THE COMPLEXES OF GERMANIUM(IV) OR BORIC ACID WITH CARMINIC ACID

	Complex GeA				*BA*			
	K	σ_k	ε_c	σ_ε	*K*	σ_k	ε_c	σ_ε
Method of Holme and Langmyhr								
602 nm	35200	2000			20300	1080		
540 nm	38000	6000			22900	2700		
360 nm					20500	1500		
356 nm	37000	4900						
Method of Rose and Drago								
602 nm	38000	2000	6700	40	17900	840	6400	100
540 nm	41000	8500	3800	37	18200	2200	4500	50
360 nm					16700	2160	12200	100
356 nm	38500	9000	14700	360				

10^4 and for diaminochrysazin[4], $K = 3.55 \cdot 10^3$. The boron in solution in 93% sulfuric acid is assumed to be in the form $B(HSO_4)_4^-$. A search of the literature produced no information on the form of germanium(IV) in concentrated sulfuric acid. In 100% sulfuric acid, lead(IV) exists as $H_2Pb(HSO_4)_6$ and its anions[12]. From the similar spectra of the complexes GeA and BA, it would be expected that the germanium(IV) in 93% sulfuric acid is in a form similar to boron or lead, namely $Ge(HSO_4)_4$.

However, in preliminary experiments with germanium(IV), it was found that it reacted at room temperature with alizarin and quinalizarin, it required heating to react with chrysazin, and it did not react with 1-amino-4-hydroxyanthraquinone or diaminochrysazin. All of these reagents react with boron at room temperature. Thus, as an analytical reagent carminic acid could determine the total of boron and germanium(IV), while diaminochrysazin could be used to determine boron only.

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Determination of aluminum in alkyl aluminum compounds
Part II. Hydrolysis of the reactivity titration solution

In a recent publication[1] the determination of trialkyl aluminum and dialkyl aluminum hydride in pyrophoric aluminum organic mixtures was described. In order to complete the actual reactivity analysis, a separate sample must first be analyzed for aluminum[2].

The present communication describes a significant extension of the earlier method[1] in that aluminum as well as the reactivity can be determined on the same sample. This extension reduces the time required for an actual analysis from 25–30 min to 15 min, and, just as important, reduces the possibility of error from air contamination of the septum-covered sample by eliminating multiple punctures of the septum.

Procedure

(*PRECAUTION*. Pyrophoric alkyl aluminum compounds are extremely hazardous and must be handled with care).

Reactivity determination. Sample the alkyl aluminum as described previously[3], weigh, and add to a nitrogen-purged, dry 2 or 4 oz. rubber-septum-covered narrow-necked bottle containing 10–20 ml of dry xylene (distilled from calcium hydride in an all-glass apparatus, only a heart cut being used) and 0.5 ml of a 0.5% (w/v) solution of phenazine in xylene[1] by carefully uncapping the hypodermic needle, inserting it through the septum and depressing the plunger. Withdraw the needle and cap it, and titrate the mixture for trialkyl aluminum and dialkyl aluminum hydride reactivity as previously described[1].

Aluminum determination. Transfer the titrated solution to a 500-ml Erlenmeyer flask. Wash the bottle twice with five 10-ml portions of acetone and twice with five 10-ml portions of water, adding each wash to the flask. Add 5–10 ml of concentrated hydrochloric acid, at least a 5-ml excess of 0.05 *M* cyclohexanediaminetetraacetic acid (CDTA) solution[2], and 200 ml of isopropanol, and heat nearly to boiling. Add 1.0 ml of 1% (w/v) dithizone solution in acetone to the hot mixture. Adjust to pH 4.5 (yellow-green) with 1:4 ammonia and/or hydrochloric acid, and pH 4.5 ammonium acetate buffer. Titrate the excess of CDTA with standard 0.05 *M* zinc sulfate solution[2]. The end-point is very sharp from green to red. If a two-phase system occurs after addition of isopropanol, add more of the alcohol.

Discussion and results

Before the investigation of phenazine as an indicator for determining total and/or dialkyl aluminum hydride reactivity, the controlled deactivation procedure for determination of aluminum was the simplest, most rapid and most precise procedure available. Controlled deactivation by ether complexation of alkyl aluminum compounds does pose minor hazards, on account of ether flammability if proper precautions[2] are not followed.

At the outset of this investigation, it was felt that if aluminum as well as reactivity could be determined from the phenazine–xylene–pyridine titration mixture, there would be less chance for sample alteration from multiple puncturing of the septum-covered sample. A study of phenazine, xylene, and pyridine interference separately and collectively in the titration of *standard* aluminum solutions in the described manner showed no bias. However, a two-phase system was observed that made the end-point questionable. Additionally, when the *reactivity titration samples* were analyzed for aluminum, there was a 0.2% high bias regardless of the aluminum level in the samples. Addition of enough alcohol to form a single-phase system plus an additional 50 ml, eliminated the bias and also eliminated the questionable end-point.

The results obtained by the controlled deactivation method[2] and the proposed phenazine–xylene–pyridine complexation modification are compared in Table I. The data show equivalent results and no bias by either method. The accuracy of the compleximetric aluminum determination and the precision of the controlled deactivation procedure have been described[2]. From the comparative data, the proposed modification for aluminum determination in alkyl aluminum compounds should be as precise as the controlled deactivation procedure. Several hundred samples have been analyzed by the proposed method without difficulty and range from very pure to very complex mixtures without interference or matrix effect.

TABLE I

ALUMINUM RESULTS OBTAINED ON VARIOUS ALKYL ALUMINUM COMPOUNDS BY CONTROLLED DEACTIVATION AND THE PROPOSED METHOD

Sample	*% Aluminum*		Δ
	Controlled deactivation	*Proposed modification*	
195–1	13.50	13.52	+ 0.02
–2	14.88	14.96	+ 0.08
–3	16.16	16.19	+ 0.03
196–1	10.02	10.00	– 0.02
–2	12.07	11.99	– 0.08
198–1	11.77	11.73	– 0.04
–2	13.20	13.29	+ 0.09
–3	14.76	14.71	– 0.05
–4	14.61	14.48	– 0.13
199–1	9.44	9.47	+ 0.03
–2	9.46	9.48	+ 0.02
–3	7.35	7.39	+ 0.04
–4	8.26	8.15	– 0.11
–5	6.74	6.75	+ 0.01
190–1	27.92	27.90	– 0.02
–2	23.66	23.64	– 0.02
191–3	26.86	17.00	+ 0.14
–4	22.50	22.55	+ 0.05
135–2	27.49	27.50	+ 0.01

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The spectrophotometric determination of iridium with N,N'-di(2-naphthyl)-*p*-phenylenediamine

Methods for the spectrophotometric determination of iridium in aqueous media are numerous[1], but most of the available methods lack sensitivity or selectivity or both, and there are objectionable interferences from most of the noble metals.

In the course of investigations in this laboratory, it was observed that N,N'-di(2-naphthyl)-*p*-phenylenediamine formed a red colouration with iridium(IV) which could be extracted into chloroform and used for the spectrophotometric determination of small amounts of iridium. A review of the literature showed that this reagent has not been used previously. An investigation of the optimum conditions for the formation and extraction of the colour formed was therefore made, and a quantitative procedure was developed.

Apparatus and reagents

All spectral measurements were made with a Unicam SP600 spectrophotometer in 1.00-cm cells.

Ammonium chloroiridate solution (100 μg Ir ml^{-1}). Dissolve 0.224 g of ammonium chloroiridate (Johnson–Matthey, spectrographically pure) in 1 l of 1 *M* hydrochloric acid.

All other chemicals used were of analytical-reagent grade.

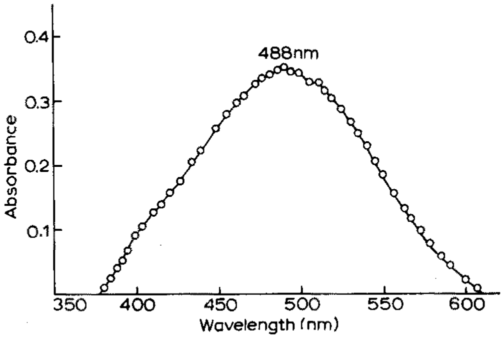

Fig. 1. Absorbance spectrum of the iridium complex.

Optimum conditions for colour formation, its extraction and properties

The red colour was formed by treating 10–200 μg of iridium in a 20-ml volume with 0.5 ml of a 0.1% (w/v) solution of N,N'-di(2-naphthyl)-*p*-phenylenediamine in acetone. The colour was readily extracted into chloroform. The most suitable pH range was 2.0–5.0. The extract has its absorbance maximum at 488 nm (Fig. 1), and the absorbance was found to be stable for at least 2 h. Beer's law was obeyed over the range 10–180 μg of iridium per 20 ml of solution.

General procedure

Transfer the iridium solution from a microburette to a separating funnel and dilute to 20 ml with distilled water. Add 0.5 ml of 0.1% (w/v) N,N′-di(2-naphthyl)-*p*-phenylenediamine in acetone. Extract with three 3-ml portions of chloroform and transfer each extract to a dry 10-ml volumetric flask. Make up to the mark with chloroform, and measure the absorbance at 488 nm against a blank treated in the same way.

Tests on amounts of iridium in the range 20–150 μg showed that the errors obtained with this procedure lay in the range 0.5–1%.

Effect of diverse ions

The results showed that 100-fold amounts of Rh^{3+}, Pt^{4+}, Os^{4+}, Ru^{3+}, Pd^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, Sr^{2+}, Cd^{2+}, Fe^{2+}, Hg_2^{2+}, Sb^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^- and CH_3COO^- caused no interference in the determination of iridium. Gold interfered seriously. The precision of the results in these tests was ±1%. Results for iridium in the presence of various other metals are shown in Table I.

TABLE I

DETERMINATION OF IRIDIUM IN PRESENCE OF OTHER IONS

Iridium (μg)		*Other elements present (mg)*	*Iridium (μg)*		*Other elements present (mg)*
Present	*Found*		*Present*	*Found*	
25	25.2	Pt 1.50	30	30.0	Os 1.00
	25.0	Rh 3.00		29.8	Ni 3.00
	25.1	Cu 2.50		30.2	Rh 2.50
50	50.4	Os 3.50	40	39.9	Co 4.00
	50.1	Rh 1.00		40.2	Pd 2.00
	50.3	Ru 0.50		40.2	Pt 0.50
70	70.5	Hg 5.00	60	59.6	Cu 5.00
	70.3	Pt 0.50		60.0	Rh 1.50
	70.1	Pd 1.00		59.8	Pd 0.50

As a final check on the method, various amounts were analysed. The results are shown in Table I.

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The reaction of iron(III) and chlorokojic acid

Chlorokojic acid (2-chloromethyl-5-hydroxy-4H-pyran-4-one) was first reported to react with iron(III) to give a purple colour[1]; it reacts with some (unnamed) metal ions to give complexes[2] and has been reacted with polyvinyl alcohol to give a resin which retains, among others, the iron(III) ion[3].

In view of the fact that 5-hydroxy-γ-pyrones including pyromeconic, comenic, meconic, and kojic acids form rather similar series of red or orange complexes with iron(III), one would expect a corresponding behaviour from chlorokojic acid. In fact, a red precipitate is formed. This paper presents information on the nature of the precipitate and on preliminary investigations of the effects of other metal ions on the precipitation.

Apparatus

The thermal analysis equipment (Dupont Model 900 DTA and Model 950 TGA) was routinely operated at a heating rate of 20° min^{-1} in an atmosphere of dried air. A Leeds and Northrup 7401 pH meter with micro glass and silver chloride electrodes was used.

Reagents

Iron(III) perchlorate stock solution was prepared from the yellow hydrated salt (G. Frederick Smith Co.) and gravimetrically standardized. Sufficient perchloric acid to prevent precipitation of hydrolysis products was added to all iron solutions.

Chlorokojic acid (Aldrich Chemical Co.) was sublimed under vacuum at 140–150°; the resulting white powder was recrystallized from hot ethanol to give white needles, m.p. 162.5–164° (lit.[1] 166–167°).

Other chemicals were reagent grade. All water was deionized.

Experimental

When chlorokojic acid in warm 95% ethanol was added to an acidic solution of iron(III) perchlorate, a red precipitate formed. Elemental analysis for carbon, hydrogen and chlorine in the reagent [$H(C_6H_4O_3Cl)$] and on the precipitate [$Fe(C_6H_4O_3Cl)_3$] showed that the compounds were pure.

To test for completeness of precipitation, a solution of 0.3 g of chlorokojic acid in 20 ml of warm 95% ethanol was added to 25.00 ml of iron stock solution (24.17 mg of iron). The reaction was allowed to proceed for 30 min and then 30 ml of acetic acid–sodium acetate buffer (pH 4.45) was added to bring the final pH to 4.2. The solution was left overnight and filtered on a tared F-porosity porcelain filtering crucible. The granular precipitate was washed with five 10-ml portions of cold water, sucked dry for 2 min and oven-dried at 110° for 60 min. Crucibles were weighed after standing 5 min in air, 15 min in a desiccator over silica gel, and 1 min in the balance. Three determinations gave an average recovery of 99.83% of the original iron with an average deviation of 0.08%, based on the theoretical factor 0.1045.

Qualitative tests of reactivity between chlorokojic acid and various metal ions were made by adding 5 ml of the acetate buffer to 1 ml of 0.02 *M* metal salt (as perchlorate unless specified) plus 1 ml of 0.1 *M* chlorokojic acid in warm ethanol, and comparing the solution with a similar one without the chlorokojic acid. Negative results were found with Ba^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Cr^{3+} (as nitrate). Silver, aluminium(III) and vanadium(IV) gave purple, orange and yellow colours, respectively. Precipitates were formed with copper(II) (green) and strontium(II) (white). Quantitative recoveries of 24.17 mg of iron(III) were achieved in the presence of 27.5 mg Mn^{2+}, 30 mg Ni^{2+}, 25.5 mg VO^{2+} or 30 mg Co^{2+}; 10 mg of chromium(III) caused high results.

Discussion

The red precipitate appears to be iron(III)-tris(chlorokojate). The removal of iron(III) from mildly acidic solution by forming this compound is virtually quantitative. Thermogravimetric analysis showed that the precipitate can be dried at temperatures up to 200° and weighed as such, giving a favourable gravimetric factor for iron (0.1045). If the temperature is raised to above 750°, a residue corresponding to the expected weight of Fe_2O_3 remains.

Of the ions added which did not themselves precipitate with the reagent, the most notable interference was found with chromium, though chromium(III) was not quantitatively coprecipitated.

It appears that chlorokojic acid may prove to have analytical uses based on its reaction with iron(III).

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Concentration et séparation de l'uranium sur résines échangeuses d'ions

L'utilisation de résines échangeuses d'ions permet d'augmenter la sélectivité d'une méthode d'analyse, suivant la stabilité et la nature des complexes obtenus.

On a ainsi pu réaliser la séparation de l'uranium d'avec les éléments coexistant dans ses minerais, en utilisant des résines échangeuses d'anions et l'acide aminoacétique comme agent complexant. La méthode est basée sur l'affinité de l'uranium pour le ligand mentionné[1,2] formant un complexe négatif très stable, retenu par un anionite fortement basique; tandis que les cations: Cu(II), Cd(II), Pb(II), Co(II), Ni(II), Mn(II) et Zn(II) passent dans l'effluent, leurs combinaisons complexes étant moins stables[3–9]. La méthode a été développée aussi pour la séparation d'avec le fer(II) qui coexiste en proportion appréciable dans les minerais d'uranium et interfère dans presque tous les procédés de dosage de l'uranium.

Partie expérimentale

On a employé des colonnes anioniques Dowex 2-X4 (20–50 mesh) et Vionit AT-1, de 80 × 10 mm, dont le débit correspond à un flux de 0.6 ml/min.

On a utilisé le nitrate d'uranyle, $UO_2(NO_3)_2 \cdot 6H_2O$ (Riedel p.a) en solution $10^{-2}\,M$ et dosé l'uranium au moyen de thioglycolate d'ammonium en milieu basique, à l'aide d'un spectrophotomètre Pulfrich[10]. Les éléments: Cu(II), Pb(II), Co(II), Ni(II), Mn(II), Zn(II) et Fe(II), en solutions $5 \cdot 10^{-2}\,M$, ont été dosés par titrage avec l'EDTA, en solutions tamponnées en présence de murexide ou de violet de pyrocatéchol, à l'exception du fer, analysé par spectrophotométrie avec l'α,α'-dipyridyle.

Les mesures de pH ont été effectuées à l'aide d'un pH-mètre MV-11S Clamann & Grahnet.

On a examiné l'influence de la concentration du complexant en dosant l'uranium dans l'effluent recueilli après passage des échantillons contenant une quantité déterminée d'uranium et différentes concentrations d'acide aminoacétique: $5 \cdot 10^{-3}\,M$, $10^{-2}\,M$, $5 \cdot 10^{-2}\,M$, $10^{-1}\,M$, $5 \cdot 10^{-1}\,M$ et $1\,M$. Les résultats indiquent un maximum pour la concentration $10^{-1}\,M$ de ligand.

On a examiné également l'influence du pH de la solution, en maintenant constantes la concentration en uranium dans l'échantillon et la concentration optimum $10^{-1}\,M$ en agent complexant. Pour un pH < 3.4 l'uranium n'est pas retenu sur la colonne; pour l'intervalle de pH 3.4–4.9 cette fixation augmente nettement, aboutissant à une valeur maximum entre les pH 4.9–6.0. L'augmentation du pH (>6) est accompagnée d'une précipitation de diuranate.

L'étude de la variation de la quantité d'uranium retenue sur la résine, par rapport à la quantité correspondante contenue dans l'effuent a été effectuée pour des échantillons à concentrations variables en uranium, maintenant constantes la concentration du ligand et le pH de la solution. Les courbes ont été tracées à pH 5.4 pour quatre concentrations en agent complexant: $10^{-2}\,M$, $5 \cdot 10^{-2}\,M$, $10^{-1}\,M$ et $1\,M$.

On remarque une augmentation prononcée de la quantité d'uranium retenue par la résine, pour un domaine de concentration totale en uranium, relativement étroit. Le domaine est plus étendu pour la concentration optimum en glycine ($10^{-1}\,M$).

Applications analytiques

Dans la partie expérimentale, on a établi les conditions les plus favorables pour une fixation totale de l'uranium sur la résine utilisée. Dans ces conditions les éléments: Cu(II), Cd(II), Ni(II), Co(II), Mn(II), Zn(II) et Pb(II) ne sont pas retenus.

En vue d'établir l'efficacité de la séparation de l'uranium d'avec les éléments mentionnés, on a examiné des mélanges binaires: en solution d'acide aminoacétique $10^{-1}\,M$, à un pH de 5.4 et des quantités variables d'éléments étrangers; la quantité d'uranium introduite a été retrouvée.

Par contre la séparation de l'uranium d'avec le fer(II) a posé certains problèmes, le fer formant avec la glycine une combinaison peu soluble. Pour éviter cet inconvénient, on a introduit l'α,α'-dipyridyle, donnant avec le fer une combinaison complexe soluble, stable et électropositive, non retenue sur la colonne d'anionite. Ce réactif présente l'avantage de ne pas réagir avec l'uranium en présence de glycine et en même temps permet le dosage spectrophotométrique du fer directement dans l'effluent, sous forme de $[Fe(dip)_3]^{2+}$, rouge.

Les résultats obtenus sont présentés dans le Tableau I.

TABLEAU I

Elément	*U(VI)*	*Cu(II)*			*Cd(II)*			*Pb(II)*			*Co(II)*		
Ajouté (mg)	1.19	1.59	3.17	15.98	2.81	5.60	28.10	5.18	10.36	51.79	1.46	2.90	14.67
Trouvé (mg)	1.19	1.60	3.20	15.88	2.80	5.62	27.81	5.16	10.36	51.80	1.32	2.93	14.69
Elément	*U(VI)*	*Ni(II)*			*Mn(II)*			*Zn(II)*			*Fe(II)*		
Ajouté (mg)	1.19	1.46	2.93	14.67	1.37	2.75	13.73	1.63	3.26	16.44	1.39	2.79	4.78
Trouvé (mg)	1.19	1.42	2.87	14.77	1.40	2.79	13.78	1.68	3.31	16.34	1.39	2.76	4.79

A la suite des résultats concordants obtenus, cette méthode a été appliquée à un mélange complexe contenant l'uranium en présence de tous les éléments mentionnés. On a constaté que le réactif α,α'-dipyridyle n'empêche pas la séparation, sa structure déterminant la formation de combinaisons complexes électropositives, non retenues sur les résines fortement basiques employées.

TABLEAU II

Résine		*Dowex 2-X4*			*Vionit AT-1*	
Initial	ml solution	300	600	600	300	600
	mg U	0.59	1.19	2.38	0.59	1.19
Final	ml solution	25	25	25	25	25
	mg U	0.59	1.188	2.382	0.60	1.189

Afin de vérifier la séparation, et en même temps la fixation totale de l'uranium sur la résine, on a procédé à une élution à l'aide d'une solution chlorhydrique à 2% et à un dosage spectrophotométrique en présence de thioglycolate d'ammonium. Les traces des éléments mentionnés interfèrent avec ce réactif, le dosage de l'uranium n'est donc pas possible sans une séparation intégrale. La concordance entre la quantité initiale d'uranium introduite dans le mélange et retrouvée après l'élution, confirme l'efficacité de la méthode.

Cette méthode permet également la concentration de l'uranium dans des solutions même très diluées et sa récupération dans un volume très réduit.

Le Tableau II donne les résultats concernant la séparation de l'uranium et sa concentration dans des solutions très diluées.

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The determination of impurities in high-purity cadmium by spectrography or polarography after distillation of cadmium

Little seems to have been published on the analysis of high-purity cadmium metal. Direct methods of analysis are insufficiently sensitive for many elements, except for copper and silver which can be determined spectrographically. Solvent extraction with tributyl phosphate in $2.5\ M$ hydroiodic acid media has been used to separate cadmium before the polarographic determination of copper, iron, nickel and lead[1]. A spectrographic method has been developed to determine many elements after solvent extraction with sodium diethyldithiocarbamate[2], but the reproducibility of the method was not good, owing to variable residual amounts of cadmium after extraction. Another possibility of separation of impurities is a vacuum distillation of cadmium metal at high temperatures[3]. The present communication deals with a method for the high-temperature distillation of cadmium before the spectrographic or polarographic determination of the nonvolatile impurities.

Experimental

Preparation of standard samples for analyses. Standards containing known quantities of impurities were not available, hence the samples used were analysed by other procedures for comparison. The impurities in cadmium metal were determined spectrographically and polarographically, first by a direct method and secondly after the extraction of cadmium with tributyl phosphate[1].

The standard samples were prepared from pure cadmium metal (99.9999%; VEB spuren Metalle, Freiburg/S.A.). A weighed quantity of metal was dissolved in 1:1 hydrochloric acid solution, evaporated to dryness and redissolved in $0.2\ M$ hydrochloric acid solution. The solution was transferred into a volumetric flask and standard solutions of the elements to be determined as impurities were added. The samples were dissolved in the same way as the standards.

The hydrochloric and nitric acids used were distilled from quartz apparatus.

Polarographic method. A square-wave polarograph (MK-III) was used. The supporting electrolytes were: $0.5\ M$ phosphoric acid for copper and lead; a mixture containing $0.5\ M$ sulfuric acid, $1\ M$ manganese(II) sulfate, $0.1\ M$ hydrochloric acid and $8\cdot10^{-4}\ M$ methylene blue for bismuth; and 12% (v/v) ammonia solution con-

TABLE I

SPECTROGRAPHIC WORKING CONDITIONS AND ANALYTICAL LINES USED

Spectrograph	Jarrell Ash, 3.4 m, with a plane grating. Dispersion 5 Å/mm, first order.
Excitation source	a.c. arc, current 7 A; $V = 240$ V; C = 0.005 μF; H = residual.
Slit width	15 μ.
Exposure time	30 sec.
Plate	Eastman Kodak SA-1.
Illumination	Cylindrical lenses, 2-step sector beside the slit.
Development	Kodak D. 19; 4 min/20°.
Analytical lines[a]	Fe 3020 Å, Ni 3050 Å, Bi 3067 Å, Ag 3282 Å, Cu 3247 Å, Pb 2833 Å, Tl 2709 Å, Sb 2599 Å.

[a] All with Mo 3170 Å.

taining 0.01 M sodium hydroxide and a few drops of 1% potassium hexacyanoferrate(II) solution for thallium.

Spectrographic method. Molybdenum was used as internal standard. The standard and sample solutions were transferred to flat graphite electrodes (National Carbon Co.), previously treated with a polystyrene solution in benzene. The working conditions are given in Table I. Straight-line calibration graphs were found for 0.1–5 p.p.m. Pb, 0.2–5 p.p.m. Ag, and 0.2–5 p.p.m. Cu.

Distillation method. The apparatus used is shown in Fig. 1.

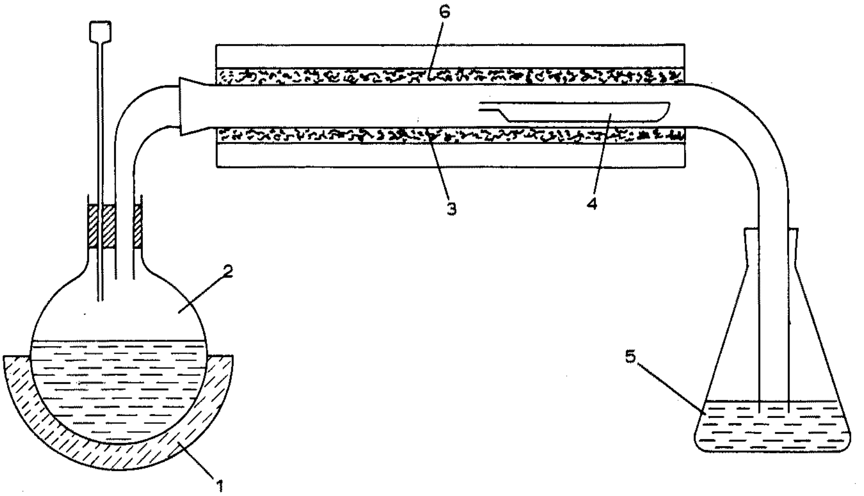

Fig. 1. Distillation apparatus. (1) Heater, (2) bulb with water, (3) quartz tube, (4) quartz vessel for samples, (5) flask for collection of condensate in water, (6) furnace (i.d. 2.9 cm).

The furnace was heated electrically to 630°. On passage of steam through the tube, the cadmium metal evaporated and was collected in water in the flask; 1 g of metallic cadmium could be evaporated in 40–45 min. The residue after distillation of a 1-g sample was 2–3 mg; this was dissolved as described above and the required elements were determined.

To prepare suitable standard samples, cadmium metal (99.9999% purity) was weighed and powdered Cu, Ni, Bi, Pb and Sb metals were added. The sample was then distilled and the elements were determined.

Results and discussion

The results of analyses are given in Table II. The results for antimony were very low, indicating that antimony was also evaporated. Bismuth, lead, nickel and iron could be determined satisfactorily.

Repeated evaporations of the cadmium in the super-heated steam showed that 99.9–99.5% of the metal evaporated. A small part of cadmium remained in the boat mostly as the oxide. The use of nitrogen as the carrier gas was completely unsatisfactory.

Cadmium metal samples purified by the amalgamation method were analysed by the direct spectrochemical and polarographic methods, as well as by the distillation method; comparative results are shown in Table III. It is obvious that the results of different methods are in good agreement, that the proposed method is satisfactory for impurities in cadmium metal, and that lead, bismuth, copper and silver do not evaporate during distillation. Antimony and thallium were found to be partially evaporated along with the cadmium metal, as is indicated by the vapour pressures of these metals (Table IV). The vapor pressures of the other metals at 630° are insignificant (Table IV). The results obtained also show that cadmium does not carry other elements and that its behaviour does not depend on the properties of the other metals. There was no apparent relationship between the concentration of cadmium and the concentrations of elements being determined, with regard to the evaporation process.

The proposed method of metal distillation has certain advantages. Extraction of cadmium requires large amounts of the extractant, so that contamination problems can readily arise from the chemicals used; even purified reagents contain impurities such as iron, magnesium, etc., at levels which are unsuitable for high-purity metal analysis. Atmospheric contamination may also be considerable in

TABLE II

DETERMINATION OF IMPURITIES IN KNOWN SAMPLES AFTER DISTILLATION OF CADMIUM

Element	*Added (p.p.m.)*	*Recovery*			
		Spectrographic		*Polarographic*	
		(p.p.m.)	*(%)*	*(p.p.m.)*	*(%)*
Bi	1580	1390	89	1430	90.8
Fe	945	940	99	—	
Pb	2360	2150	90.8	2180	92.5
Sb	1850	580	31.4	—	
Ni	1670	1590	95.5	1602	96.2

TABLE III

COMPARATIVE ANALYSES OF CADMIUM METAL

Sample	*Pb*		*Bi*		*Cu*		*Ag*	
	A[a]	*B*[b]	*A*	*B*	*A*	*B*	*A*	*B*
1	100	116	21.5	20.4	7.1	7.7	12	10.8
2	2.6	4.0	—	—	6.1	6.8	3.5	2.9
3	240	256	—	—	8	11	—	—

[a] Direct determination, or after TBP extraction.
[b] After distillation of cadmium.

TABLE IV

TEMPERATURES AT WHICH THE METAL VAPOUR PRESSURES REACH DIFFERENT LEVELS

Element	*1 mm Hg*	*100 mm Hg*	*760 mm Hg*
Mn	1292	1792	2151
Sb	886	1223	1440
Bi	1021	1271	1420
Cd	394	611	765
Fe	1787	2360	2735
Pb	973	1421	1744
Ni	1810	2364	2732
Ag	1357	1865	2212
Tl	825	1196	2457
Cu	1628	2207	2595

extraction processes, unless special working conditions are provided. With the distillation method, only small amounts of reagents are needed and a contaminated atmosphere has less effect. Moreover, the efficiency of the separation can readily be improved by using larger samples or by repeated distillations. Of course, elements with higher vapor pressures than that of cadmium cannot be determined, but a larger number of elements can be determined after distillation than after the extraction method.

The reproducibility of the direct polarographic method was found to be 3–10%, and the reproducibility of the direct spectrographic method 4–11% (standard deviation). The reproducibility of these methods after the distillation method was found to be 1–6%. The limits of detection were lowered by about 20-fold for the distillation method compared to the direct method.

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Über die Verwendung von Oxazinen in der Analytik
III. Mitteilung. Indirekte spektralphotometrische Bestimmung von Silber mit Nilblau

In einer früheren Arbeit[1] berichteten wir darüber, dass Nilblau zur spektralphotometrischen Bestimmung von Jodid geeignet ist. Nilblau bildet in schwach saurem Medium mit Jodid einen Farbkomplex aus, der sich mit Chloroform extrahieren lässt und bei 626 nm gemessen werden kann.

Es war nun zu erwarten, dass bei konstanter Jodidmenge durch Kationen, die schwerlösliche Jodide bilden, eine Extinktionsverminderung hervorgerufen wird. Das zu bestimmende Kation hat dabei im wesentlichen zwei Bedingungen zu erfüllen.

1. Das Löslichkeitsprodukt des entsprechenden Jodids muss kleiner sein als 10^{-15}, da ansonsten der nicht erfassbare Anteil des Kations zu gross wird und die Abnahme der Extinktion nicht linear erfolgt.

2. Der gebildete Niederschlag muss kolloidal sein, damit eine saubere Phasentrennung erreicht werden kann.

Quantitative Messungen mit verschiedenen Kationen liessen erkennen, dass nur Silber diesen Bedingungen genügt. Dies ermöglichte die Ausarbeitung einer indirekten spektralphotometrischen Silberbestimmung.

Geräte und Reagenzien

Alle Messungen erfolgten mit einem Spektralphotometer der Firma Zeiss Type PMQ II. Nilblausulfat (Nile blue A: G. F. Smith Chemical Co., Columbus, Ohio) oder Nilblauchlorid (Merck Nr. 1291). Kaliumjodid, Silbersulfat, Schwefelsäure, Chloroform und diverse Salze zur Ermittlung des Fremdioneneinflusses, zur Analyse Merck.

Reagenslösung. Nilblauchlorid oder Nilblausulfat 0.005 %-ig in 0.25 *N* Schwefelsäure.

Jodidlösung. 78.5 mg Kaliumjodid werden mit Wasser zu 1 l gelöst. Diese Lösung wird mit Wasser 1:10 verdünnt; sie enthält 60 μg J^-/10 ml.

Silberstandardlösung. 72.3 mg Silber(I)-sulfat werden mit Wasser zu 1 l gelöst. Diese Lösung wird mit Wasser 1:10 verdünnt; sie enthält *ca.* 5 μg Ag/ml. Der genaue Gehalt wurde potentiometrisch mit Natriumchlorid ermittelt.

Arbeitsvorschrift

Zur Aufstellung der Eichkurve werden in einem 100-ml Schütteltrichter verschiedene Mengen der Silberstandardlösung (5–35 μg Ag) mit je 10.0 ml Jodidlösung und Reagenslösung versetzt und das Volumen mit Wasser auf 50 ml ergänzt. Man extrahiert dreimal mit je 5 ml Chloroform, sammelt die Extrakte in einem 25-ml-Messkolben und füllt mit Chloroform bis zur Marke auf. Die Extinktion wird in 1-cm Glasküvetten bei 626 nm gegen Chloroform gemessen (Extinktionswert *A*). Man erhält eine Eichkurve *A* wie Figur 1 zeigt.

Um das bei photometrischen Verfahren gewohnte Bild einer Eichkurve zu erhalten, misst man einen Blindwert (ohne Silber) gegen Chloroform (Extinktionswert *B*) und erhält durch Subtraktion einen Extinktionswert *C*: $C = B - A$. Mit Hilfe der Extinktionswerte *C* gelangt man zu einer Eichkurve *C* wie in Figur 1 ersichtlich ist. Dieselben Resultate ergeben sich, wenn man den Blindwert gegen die Probe misst.

Zur Bestimmung von Silber in einem Probematerial wird eine entsprechende Menge aufgeschlossen und zweimal mit Schwefelsäure bis fast zur Trockene abgeraucht. Nach dem Verdünnen mit Wasser bringt man die Lösung mit Natronlauge auf ein pH von 2–3 und ergänzt auf ein definiertes Volumen. Mit 30 ml dieser Probelösung (5–35 µg Ag enthaltend) verfährt man dann nach der angegebenen Arbeitsvorschrift weiter.

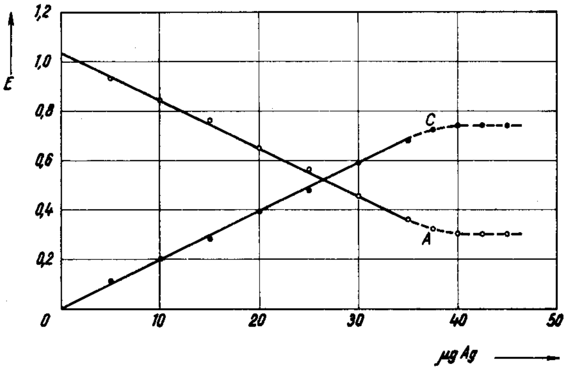

Fig. 1. Eichkurven für die Bestimmung von Silber mit Nilblau (Erläuterungen siehe Text). (○) Extinktionswert *A*. (●) Extinktionswert *C*.

Statistische Prüfung der Methode

Das Analysenverfahren wurde nach GOTTSCHALK[2] statistisch getestet. Zur Prüfung wurde die angegebene Silberstandardlösung benützt. Nach der Arbeitsvorschrift gelangten 21 Proben sieben verschiedener Konzentrationen (0.20 bis 1.40 µg Ag/ml Chloroform) zur Messung. Die Korrelationsrechnung ergab:

$$\tau_r = 1.72 < t(95) = 2.09$$

Das Lambert–Beersche Gesetz wird mithin im untersuchten Konzentrationsbereich streng erfüllt. Durch Ausgleichsrechnung ergaben sich weiters

Verfahrenskonstante: $\omega = 19.06 \pm 0.14$ n mol ml^{-1}.
molarer Extinktionskoeffizient[3]: $\varepsilon_{626} = 52470 \pm 350$ l mol^{-1} cm^{-1}.
Standardabweichung: $s_K = \pm 0.157$ n mol ml^{-1} $\equiv$ ± 0.017 µg ml^{-1}.
Grenzwerte der Varianzen: $V_o = \pm 1.2$ Rel.-%, $V_u = \pm 8.5$ Rel.-%.
Empfindlichkeit[3] ($E = 0.001$): 0.0021 µg cm ml^{-1}.
Die Fehlerbereiche für statistische Sicherheiten von 99 und 99.9% sind

$$T(99) = \pm 0.447 \text{ n mol ml}^{-1} \equiv \pm 0.048\ \mu\text{g ml}^{-1},$$

$$T(99.9) = \pm 0.604 \text{ n mol ml}^{-1} \equiv \pm 0.065\ \mu\text{g ml}^{-1}.$$

Die Bestimmungsgrenze unter den angegebenen Bedingungen (1-cm Küvette, $\lambda = 626$ nm) beträgt

$$b_N = T\sqrt{2}\ (99.9) = 0.854 \text{ n mol ml}^{-1} \equiv 0.092\ \mu\text{g ml}^{-1}.$$

TABELLE I

EINFLUSS VERSCHIEDENER IONEN AUF DIE BESTIMMUNG VON SILBER MIT NILBLAU

Ion	*Zugegeben als*	*µg erlaubt*	*Ion*	*Zugegeben als*	*µg erlaubt*
Al^{3+}	$Al_2(SO_4)_3$	800	Fe^{3+}	$Fe_2(SO_4)_3$	1000
AsO_4^{3-}	Na_3AsO_4	1000	Hg^+	Hg_2SO_4	0
Bi^{3+}	$(BiO)_2SO_4$	1000	K^+	K_2SO_4	1000
BO_3^{3-}	Na_3BO_3	1000	Mg^{2+}	$MgSO_4$	1000
Ca^{2+}	$Ca(CH_3COO)_2$	1000	Mn^{2+}	$MnSO_4$	300
Cd^{2+}	$CdSO_4$	1000	Na^+	Na_2SO_4	1000
CH_3COO^-	$NaCH_3COO$	1000	NH_4^+	$(NH_4)_2SO_4$	1000
$C_4H_4O_6^{2-}$	$Na_2C_4H_4O_6$	120	Ni^{2+}	$NiSO_4$	400
$C_2O_4^{2-}$	$K_2C_2O_4$	1000	NO_3^-	KNO_3	100
Cl^-	KCl	3	Pb^{2+}	$Pb(CH_3COO)_2$	1000
ClO_4^-	$KClO_4$	100	PO_4^{3-}	Na_2HPO_4	1000
CrO_4^{2-}	Na_2CrO_4	400	SO_4^{2-}	K_2SO_4	1000
Co^{2+}	$CoSO_4$	1000	Tl^+	Tl_2SO_4	800
Cu^{2+}	$CuSO_4$	600	Zn^{2+}	$ZnSO_4$	1000

Beeinflussung durch Fremdionen

Die Halogenide und einige andere Anionen stören die Silberbestimmung stark. Diese Störungen können durch zweimaliges Abrauchen der Probe mit Schwefelsäure beseitigt werden, da Sulfat keinen Einfluss auf die Bestimmung ausübt. Nun wurde die Beeinflussung verschiedener Kationen studiert. Lösungen verschiedener Konzentrationen der einzelnen Kationen wurden sowohl mit als auch ohne Silber (20 µg) nach der angegebenen *Arbeitsvorschrift* behandelt und gemessen. Ein Fehler bis zur doppelten relativen Standardabweichung wurde toleriert. Der Störeinfluss von Ionenkonzentrationen grösser als 1 mg wurde nicht untersucht. Die erhaltenen Ergebnisse werden in Tabelle I aufgezeigt.

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Determination of chromate by precipitation of silver chromate from homogeneous solution

The many advantages of homogeneous precipitation methods (PFHS) are well known and have been carefully reviewed by GORDON, SALUTSKY AND WILLARD[1]. Chromate is generally determined as barium chromate or lead chromate. For the precipitation of barium chromate from weakly acidic solution, sulphate, fluoride and oxalate should be absent. The solubility of lead chromate and the reported stability of the salt to drying and ignition[2] would appear to recommend this compound for the gravimetric determination of chromium. However, lead chromate is trimorphic, forming a stable monoclinic modification and unstable rhombic and tetragonal forms; the rhombic form tends to be stabilized by and to occlude excess lead, hence in the precipitation of chromate, the precipitate frequently deviates from the correct composition, and an empirical factor is advisable[3]. Furthermore, the insolubility of many other lead salts, *e.g.* sulphate, renders the method rather unsuitable for quantitative work. Similarly, in the determination of chromate as mercury(I) chromate, many other ions interfere.

The quantitative precipitation of barium chromate from homogeneous solution can be done by urea hydrolysis[4] as well as by complexation and replacement methods[5]; the urea hydrolysis method has been applied to a wide variety of materials[6]. HOFFMAN AND BRANDT[7] precipitated lead chromate from homogeneous solution by slowly oxidising chromium(III) to chromate with bromate in an acetate-buffered solution; either lead or chromate can be quantitatively precipitated by this procedure. FIRSCHING[8] used volatilization of ammonia from the silver–ammonia complex to separate and determine equimolar mixture of chloride, bromide and iodide. The same general idea had been applied to the determination of phosphate[9].

The purpose of the work described below was to establish the suitability of this method for the determination of chromate, in presence of sulphate. Chromium(III) could be determined after oxidation in alkaline medium with sodium peroxide in presence of diverse ions, by the PFHS method.

Reagents and equipment

B.D.H. Analar potassium chromate and ammonium hydroxide were used. Twice recrystallised silver nitrate (Johnson and Johnson) was used for preparing the silver–ammonia complex. All other chemicals were of E. Merck extrapure grade.

A Carl Zeiss P.M.Q.II model spectrophotometer was used for absorbance measurements.

Determination of chromate by PFHS

Add 0.5 ml of concentrated ammonia solution and 25 ml of 1.0 M ammonium nitrate solution to a sample containing about 0.8 mmole of potassium chromate, and adjust the volume to *ca.* 100 ml. Prepare the precipitant by diluting to about 75 ml a mixture of 5 ml of 1.0 M silver nitrate solution and 3 ml of concentrated ammonia solution. Add this solution to the chromate solution in one portion. Add concentrated ammonia solution dropwise to remove any turbidity.

Heat the beaker on a steam bath for 4–5 h, maintaining the volume by occasional additions of distilled water. The completeness of precipitation is indicated by the disappearance of the yellow colour of the supernate at room temperature. The pH of the supernate was found to be between 7 to 7.5 as indicated by pH paper. Filter the precipitate on a G4 sintered glass crucible and wash with small amounts of ice-cold distilled water. Dry at 120° in an oven for about 30 min and weigh.

The filtrate was collected and the amount of unprecipitated chromium determined by developing the violet colour with 1,5-diphenylcarbohydrazide and measuring the absorbance at 540 nm[10].

Determination of chromium(III) in chrome alum

Oxidise a sample of chrome alum to chromate by treating with sodium peroxide in the cold in presence of 2–3 *M* sodium hydroxide. Destroy the excess of peroxide by boiling and dilute with water to 500.0 ml. Neutralise a 50.0-ml aliquot with 1:1 nitric acid, and add a slight excess of concentrated ammonia solution. Then determine the chromate by the above procedure.

Determination of chromium(III) in presence of diverse cations

Oxidise with sodium peroxide as described above. Filter the precipitated metal hydroxides and wash several times with water till the filtrate is colourless. Neutralise an aliquot of the filtrate and make slightly ammoniacal as described above. Heat the solution on a steam bath for about 2 h, filter again to remove metal hydroxides, if necessary, and determine the chromate by the recommended procedure.

Results and discussion

Table I reports data collected in a typical series of determinations by the recommended procedure. In every case the particle size was much larger than that obtained by direct precipitation. When examined under a polarising microscope, the precipitate obtained by direct mixing was found to be an amorphous powder, while the precipitate obtained by homogeneous precipitation belonged to the monoclinic system. Filtration and washing were also facilitated by the increased particle size obtained in the recommended procedure. The percentage error ranged from 1.10 to 1.80 when the determination was carried out by directly mixing dilute solutions of potassium chromate and silver nitrate.

TABLE I

DETERMINATION OF CHROMATE AS SILVER CHROMATE

No. of detns.	*Range found*	*Weight of silver chromate (mg)*			*Amount of Cr in filtrate: Mean (μg)*
		Mean found	*True value*	*Deviation from true value (%)*	
10	269.4–273.4	271.2	271.6	− 0.15	120

Table II shows that chromium(III) in chrome alum can be readily oxidised in alkaline solution to chromate and determined as silver chromate. Chromium(III) can also be separated and determined in the presence of Mg(II), Mn(II), Fe(III), Cu(II), Ti(IV), Zr(IV), Ni(II) and Co(II) (Table III). However, when these ions are present in very large excesses, the filtration of the hydroxides becomes very time-consuming.

TABLE II

DETERMINATION OF CHROME ALUM AS SILVER CHROMATE

No. of detns.	*Weight of silver chromate (mg)*		*Deviation from true value (%)*	*Amount of Cr in filtrate: Mean (µg)*
	Mean found	*True value*		
5	311.2	311.8	− 0.19	140

TABLE III

DETERMINATION OF CHROMIUM(III) IN PRESENCE OF DIVERSE IONS

(0.804 mmole of Cr^{3+}; 41.8 mg taken)

Diverse ions taken (mmole)	*Weight of silver chromate (mg)*			*Deviation from true value (%)*	*Amount of Cr in filtrate: Mean (µg)*
	No. of detns.	*Mean found*	*True value*		
$Mg(NO_3)_2$ (2.0), $Mn(NO_3)_2$ (1.0), $Fe(NO_3)_3$ (1.0), $Cu(NO_3)_2$ (1.0), $Ti(SO_4)_2$ (1.0), $Zr(NO_3)_4$ (1.0), $Ni(SO_4)$ (1.0), $Co(NO_3)_2$ (1.0)	4	263.6	266.8	− 1.2	160

TABLE IV

EFFECT OF SULPHATE IONS ON THE DETERMINATION OF CHROMATE AS SILVER CHROMATE

No. of detns.	*Substance*		*Weight of silver chromate (mg)*		*Deviation from true value (%)*	*Amount of Cr in filtrate: Mean (µg)*
	Taken	*mmoles*	*Mean found*	*True value*		
5	$(NH_4)_2SO_4$	100.0	331.4	332.0	− 0.18	145
5	Na_2SO_4	200.0	333.2	332.0	+ 0.36	150

TABLE V

EFFECT OF VARYING EXCESSES OF SILVER(I) ON THE PRECIPITATION OF SILVER CHROMATE

No. of detns.	*Silver(I) mmoles*	*Weight of silver chromate (mg)*		*Deviation from true value (%)*
		Mean found	*True value*	
3	2.0	270.4	271.6	− 0.44
3	5.0	271.0		− 0.22
3	10.0	270.8		− 0.29
3	20.0	271.2		− 0.15
3	30.0	270.4		− 0.44
3	40.0	272.2		+ 0.22
3	50.0	272.6		+ 0.37

Table IV shows that chromate can be determined well in the presence of a large excess of sulphate.

The excess of silver(I) is not critical. When the quantity of silver nitrate was varied from 2.0 to 50.0 mmoles, the determination of 0.8 mmole chromate was reproducible within 0.4 mg. A value of five mmoles was selected for routine use. No weight loss of the silver chromate precipitate after heating for 5 h at 120° was found.

This method would not be satisfactory if arsenate, tungstate, vanadate, chloride, etc. were present. The very favourable gravimetric factor of silver chromate is, however, an advantage. Very few PFHS methods involve determination of anions[11].

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ANNOUNCEMENT

COLLOQUE SUR L'ELECTROCHIMIE EN MILIEUX NON AQUEUX

Organisé sous le patronage de
L'UNION INTERNATIONALE DE CHIMIE PURE ET APPLIQUÉE
8–10 juillet 1970 à Paris (France)

PROGRAMME PROVISOIRE

Président honoraire: PR. I. M. KOLTHOFF
Président: PR. G. CHARLOT

Conférences plénières

Pr. A. BARD	Electrochemistry of organic compounds in aprotic solvents. Methods and applications.
Pr. G. CAUQUIS	Oxydation électrochimique des composés aromatiques azotés au sein des solvants organiques.
Pr. J. J. LAGOWSKI	Solvation phenomena in basic solvents.
Pr. A. J. PARKER	Ionic equilibria in protic and dipolar aprotic solvents.
Pr. H. STREHLOW	Solvatation des ions en milieu non aqueux.
Pr. B. TREMILLON	Le concept de solvo-acidité et son étude électrochimique dans deux milieux ionisés fondus typiques: les hydroxydes alcalins et les mélanges d'halogénures d'aluminium et de sodium.

Aucune communication ne sera présentée au cours du Colloque, mais seulement une quinzaine d'exposés de mises au point (30 minutes) sur les thèmes suivants:

(A) Solvatation. Solvation.
(B) Méthodes électrochimiques d'analyse en milieu non aqueux.
Electroanalytical methods in non-aqueous media.
(C) Etude électrochimique des équilibres ioniques: acide–base, oxydoréduction, complexation, etc.
Electrochemical investigations of ionic equilibria: acid–base, redox, complexation, etc.
(D) Réactions électrochimiques en chimie organique.
Organic electrode reactions.

Traduction simultanée Français ⇌ Anglais. Le nombre des participants est limité à deux cents (200) personnes.

Organisateur local: Dr. J. BADOZ-LAMBLING, Lab. Chimie Analytique, E.S.P.C.I., 10, rue Vauquelin, Paris-5^{e}.

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Short Communications

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