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Papers will be published in English, French or German.

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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.

For multi-author references, **all** authors must be named, and initials given, in the reference list, although the use of, for example, SMITH *et al.*, is desirable in the text.

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 50, No. 2, May 1970

THE DETERMINATION OF PLATINUM BY ATOMIC ABSORPTION SPECTROSCOPY

PART I. AIR–ACETYLENE FLAMES

The atomic absorption determination of platinum in air–acetylene flames is thoroughly studied and reasons for the cationic and anionic interferences are discussed. A superior analytical method is proposed in which lanthanum is used to suppress interferences; the method has been successfully applied to synthetic mixtures and a commercial platinum metal concentrate.

A. E. PITTS, J. C. VAN LOON AND F. E. BEAMISH,
Anal. Chim. Acta, 50 (1970) 181–194

THE DETERMINATION OF PLATINUM BY ATOMIC ABSORPTION SPECTROSCOPY

PART II. NITROUS OXIDE–ACETYLENE FLAMES

Platinum can be successfully determined by atomic absorption spectroscopy with nitrous oxide–acetylene flames. Although the sensitivity is less than that obtained with air–acetylene flames, all potential interferences are eliminated; high concentrations of precious metals are tolerated.

A. E. PITTS, J. C. VAN LOON AND F. E. BEAMISH,
Anal. Chim. Acta, 50 (1970) 195–199

COMPLEX EXTRACTION OF VANADIUM FOR ATOMIC ABSORPTION SPECTROSCOPY

DETERMINATION OF MICROGRAM QUANTITIES OF VANADIUM IN LAKE WATERS

Thirteen chelating agents have been investigated for their suitability for extraction of vanadium for atomic absorption spectroscopy. Dichloro-oxine was found to extract vanadium(IV), vanadium(V) and 90% of vanadium(III). The complex formed was very stable and gave high sensitivity for atomic absorption. A method combining extraction and atomic absorption has been developed for the determination of vanadium in lake water with a sensitivity of 0.3 p.p.b.

Y. K. CHAU AND K. LUM-SHUE-CHAN,
Anal. Chim. Acta, 50 (1970) 201–207

A COMPARISON OF THE USE OF CUPFERRON AND OXINE IN THE SUBSTOICHIOMETRIC DETERMINATION OF MOLYBDENUM BY NEUTRON ACTIVATION

Extraction into chloroform with substoichiometric amounts of 8-hydroxyquinoline and cupferron has been used for the determination of molybdenum in germanium dioxide. The effect of interfering metal ions on both methods of extraction has been studied. A substoichiometric isotope dilution method with cupferron is feasible for milligram quantities of molybdenum but not for microgram quantities.

N. K. BAISHYA AND R. B. HESLOP,
Anal. Chim. Acta, 50 (1970) 209–217

DETERMINATION OF TRACES OF CHLORINE IN ORGANIC LIQUIDS. A COMBUSTION–MICROCOULOMETRIC METHOD

The Dohrmann microcoulometric titration technique has made it possible to develop a method for the rapid determination of trace amounts of chlorine in organic liquids. The sample (1–100 μl) is vaporized in a stream of helium and then fed to an oxygen atmosphere where it undergoes combustion. The hydrochloric acid formed is titrated with the aid of a silver coulometer cell. In its most sensitive form the method has a precision (repeatability) of *ca.* 0.05 p.p.m. of chlorine.

W. LÄDRACH, F. VAN DE CRAATS AND THE LATE P. GOUVERNEUR,
Anal. Chim. Acta, 50 (1970) 219–228

CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF THE OXYGEN–METAL RATIO IN MIXED URANIUM–PLUTONIUM OXIDES

A method has been developed for the determination of the oxygen–metal ratio in mixed oxides of uranium and plutonium. The sample is treated with hot concentrated phosphoric acid. Plutonium(IV), uranium(VI), total plutonium and total uranium are then determined by controlled-potential coulometric procedures. The ratio is calculated from the equation:

$$\frac{\mathrm{O}}{\mathrm{M}} = 2 + \frac{[\mathrm{U(VI)}] - 0.5[\mathrm{Pu(III)}]}{[\mathrm{U}] + [\mathrm{Pu}]}$$

N. E. BÄRRING AND G. JÖNSSON,
Anal. Chim. Acta, 50 (1970) 229–236

Molecular Vibrations and Mean Square Amplitudes

by SVEN J. CYVIN

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

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

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

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

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

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

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

7x10″, viii + 430 pages, 157 tables, 45 illus., 1968, Dfl. 75,00, £10

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SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF RARE EARTHS IN PLUTONIUM—USE OF TRILAURYLAMINE

A spectrographic method for the estimation of some rare earths (Gd, Sm, Dy, Er and Ce) in plutonium samples is described. The rare earths were separated from 100 mg of plutonium by extracting plutonium with trilaurylamine. After concentration of the solution, the spectrum was photographed on a Hilger large quartz spectrograph, with scandium as internal standard. The estimation ranges are Gd 10–100 p.p.m., Sm 50–300 p.p.m., Dy 5–100 p.p.m., Er 5–200 p.p.m. and Ce 100–600 p.p.m. The overall standard deviation is 14%. The method is applicable to samples containing calcium and iron upto 1000 p.p.m. The resolving power and line interferences are discussed.

R. K. Dhumwad, M. V. Joshi and A. B. Patwardhan,
Anal. Chim. Acta, 50 (1970) 237–242

N-BENZOYL-*o*-TOLYLHYDROXYLAMINE AS A GRAVIMETRIC REAGENT FOR URANIUM(VI)

N-Benzoyl-*o*-tolylhydroxylamine has been used for the gravimetric determination of uranium(VI) by direct weighing of the complex. Uranium(VI) is precipitated quantitatively in the pH range 5.0–7.5 and its separation from a large number of metal ions is described. The composition of the complex has been formulated as $UO_2(C_{14}H_{12}O_2N)_2 \cdot C_{14}H_{13}O_2N$ in conformity with analysis, n.m.r. and mass spectra. The gravimetric factor for the conversion of the metal-complex to the metal is 0.2509, smaller than that for other reagents for uranium.

M. K. Das and A. K. Majumdar,
Anal. Chim. Acta, 50 (1970) 243–247

THE DETERMINATION OF TERBIUM(III) IN BORATE GLASSES

A procedure for the determination of terbium(III) in sodium borate–boric acid glasses is described. The emission and excitation spectra and the decay times are measured. The concentration dependence of the terbium(III) fluorescence can be described by two straight lines intersecting at 1% concentration. Concentrations in the ranges 0.001–1% (w/w) and 1–5% (w/w) can be determined.

R. Reisfeld, Z. Gur-Arieh and E. Greenberg,
Anal. Chim. Acta, 50 (1970) 249–254

ADHESION AND ADHESIVES

2nd, completely revised, edition

edited by R. Houwink and G. Salomon

Volume 1

Adhesives

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

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

CONTENTS:

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

Volume 2

Applications

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

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

CONTENTS:

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

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A DIRECT SPECTROPOLARIMETRIC DETERMINATION OF MAGNESIUM(II), CALCIUM(II), STRONTIUM(II), AND BARIUM(II) WITH D-(−)-*trans*-1,2-CYCLOHEXANEDIAMINE-TETRAACETIC ACID

A rapid titrimetric method was developed for magnesium(II), calcium(II), strontium(II), and barium(II), with the stereospecific ligand, D-(−)-*trans*-1,2-cyclohexanediaminetetraacetic acid (D(−)-CDTA), as titrant. A photoelectric polarimeter was used to monitor continuously the optical rotation of the solution during titration; the titrant and metal complexes formed are optically active and serve as self-indicators. The observed rotation is linear with respect to concentration of the metal complexes and D(−)CDTA, hence the end-point can be established by straight-line extrapolation. The most sensitive wavelength for spectropolarimetric analysis (365 nm) was determined from the optical rotatory dispersion curves. The range of average deviation from visual chelometry for the four metals titrated was 0.00−0.17%.

J. R. Baker and K. H. Pearson,
Anal. Chim. Acta, 50 (1970) 255–260

A COMPARATIVE STUDY OF VARIOUS COMPLEXING AGENTS (POLYOLS) IN THE TITRATION OF BORIC ACID

Boric acid reacts with several polyols to form complexes which are acidic enough to be titrated directly with alkali hydroxide solution. A detailed potentiometric study has shown that sorbitol gives slightly sharper end-points than the more commonly used mannitol, but both are satisfactory for the titration of $5 \cdot 10^{-2}$–$5 \cdot 10^{-4}$ M boric acid. Fructose, glycerol and invert sugar are not satisfactory for less than 10^{-3} M boric acid solutions, and very large concentration of the latter two reagents are needed. Ethylene glycol has limited application; glucose and sucrose cannot be used. The pK values of the complexes formed increase in the order sorbitol $<$ mannitol $<$ fructose $\ll$ glycerol $<$ ethylene glycol.

R. Belcher, G. W. Tully and G. Svehla,
Anal. Chim. Acta, 50 (1970) 261–268

SOLVENT EXTRACTION OF COPPER(II) BY SCHIFF'S BASES

The solvent extraction of copper(II) by a number of quadridentate Schiff's bases has been investigated. All but one of the reagents are capable of extracting copper(II) quantitatively from aqueous solution and the possibility of using these reagents for determination of copper(II) by absorption spectrophotometry and by atomic absorption spectrophotometry is described. Spectrophotometric determinations are not sensitive but the atomic absorption method allows determinations in the p.p.b. range, similar to ammonium pyrrolidinedithiocarbamate.

J. Aggett and R. A. Richardson,
Anal. Chim. Acta, 50 (1970) 269–275

INTRODUCTION TO NUCLEAR CHEMISTRY

by D. J. Carswell

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

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

STATISTICAL THERMODYNAMICS

An Introduction to its Foundations

H. J. G. Hayman

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

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

THE STRUCTURE OF INORGANIC RADICALS

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

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

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

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

FUNDAMENTALS OF METAL DEPOSITION

by E. Raub and K. Müller

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

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

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THE EXTRACTION OF INDIUM FROM AQUEOUS HALIDE AND THIOCYANATE MEDIA BY SOLUTIONS OF LIQUID ANION EXCHANGERS IN ORGANIC SOLVENTS

The distribution of indium(III) at tracer levels between aqueous solutions containing chloride, bromide, iodide and thiocyanate ions and solutions of the corresponding tetra-*n*-hexylammonium salts in 1,2-dichloroethane has been studied and the composition of the extracted ion-pairs is discussed. The effect of the cations H^+, Li^+ and Na^+ on extractions from chloride media is reported, together with the results of changing the organic solvent when indium is extracted from hydrochloric acid by solutions of tri-*n*-hexylamine hydrochloride.

H. M. N. H. IRVING AND A. D. DAMODARAN,
Anal. Chim. Acta, 50 (1970) 277–285

IONIC EQUILIBRIA IN MIXED SOLVENTS
MONOPROTIC ORGANIC ACIDS

An equation correlating the thermodynamic ionization constants of monoprotic (carboxylic) organic acids in a mixed solvent and a reference solvent (water) is derived employing a curve-fitting program. The equation covers the range of bulk dielectric constant represented by that of pure water and that of very concentrated organic component. An equation for interconversion of the ionization constants between two solvents is also described. The form of the equations is similar to that of BORN's equation. Interionic distances between hydrated proton and the hydrated anions were calculated for a large number of acids using the constants of the equations, and these distances are of the right order of magnitude. The bulk dielectric constant of the organic component of the solvent may be computed utilizing the constants of the equation; the computed values of bulk dielectric constants of solvents were less than 7% off from the experimental values.

B. SEN AND L. H. ADCOCK,
Anal. Chim. Acta, 50 (1970) 287–297

STOICHIOMETRY OF THE REACTION BETWEEN METHYLMERCURY(II) IODIDE AND SOLUBLE SULPHIDES

For the specific reaction between methylmercury(II) iodide and sodium sulphide, a strict 2:1 stoichiometry was observed in amperometric titrations at 20° and at pH 9.2. This stoichiometry applies up to at least pH 12.7 and to wide ranges of reagent concentrations. The reaction occurs rapidly and neither of the two steps involved appears to be rate-limiting.

L. C. GRUEN,
Anal. Chim. Acta, 50 (1970) 299–303

SPOT TESTS IN ORGANIC ANALYSIS

Seventh English Edition, completely revised and enlarged

by FRITZ FEIGL in collaboration with VINZENZ ANGER

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.

FROM REVIEWS OF THE NEW EDITION

... As we have come to expect, Professor FEIGL has once more provided an outstanding service to the chemical community ...

Analytica Chimica Acta

... C'est pourquoi le livre du professeur FEIGL est extrêmement précieux pour le chimiste comme le montre la succession des éditions ...

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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THE MICRODETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS IN PRESENCE OF METALS, AND IN ORGANOMETALLIC COMPOUNDS, WITH AUTOMATIC DETERMINATION OF CARBON DIOXIDE

(in German)

The direct determination of oxygen in organic substances in the presence of metals is described. For complete removal of oxygen from metal oxides, the addition of a mixture of ammonium chloride, silver chloride, and hexamethylenetetramine was found to give the best results. The carbon dioxide is finally determined by fully automatic titration with colorimetric end-point detection.

W. MERZ,
Anal. Chim. Acta, 50 (1970) 305–313

POLARITY OF THE GAS CHROMATOGRAPHIC STATIONARY PHASES AND RETENTION INDICES OF ALIPHATIC ESTERS, KETONES AND ALCOHOLS

Retention indices of 71 compounds (aldehydes, ketones, esters and alcohols) were measured on Squalane and Ucon 50LB 1200X at 50° and 70° ,and 12 straight-line relationships were established between retention indices and boiling points. By means of these indices and those obtained by other authors on Apiezon L, Emulphor O, Carbowax 1540 and PEG 400, a comparative study was made of retention index increments caused by the addition of a $-CH_2-$ group in the leading members of some holomogous series, and of mean values of the selectivity of some series in every stationary phase.

J. MARTÍN MIRA AND L. GASCÓ SÁNCHEZ,
Anal. Chim. Acta, 50 (1970) 315–321

THE USE OF AUTOMATIC CALCULATIONS IN THE ESTABLISHMENT OF OPTIMAL EXPERIMENTAL CONDITIONS IN X-RAY FLUORESCENCE SPECTROSCOPY

(in French)

In the case of linear calibration curves for X-ray fluorescence analysis, regression calculation methods make it possible to establish the most appropriate counting time, the influence of the magnitude of the irradiated surface on the accuracy of the determination, and the experimental and theoretical detection limits. Different statistical parameters were calculated for a certain number of typical examples: determination of iron and silicon in aluminum, of chlorine in organics, and of tin in low alloyed steel for various experimental conditions. The results enabled the counting time to be greatly reduced for iron in aluminum, and the excitation X-ray tube to be selected without doubt for silicon in aluminum; the importance of the quality of the standards is emphasized.

G. VOS,
Anal. Chim. Acta, 50 (1970) 323–334

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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SOME PRELIMINARY STUDIES CONCERNING THE ANALYTICAL POTENTIALITIES OF AN AUGMENTED DIFFUSION FLAME

(Short Communication)

K. M. Aldous, R. M. Dagnall, L. C. Ebdon and T. S. West,
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DETERMINATION OF SILICON IN PLUTONIUM METAL BY DIFFERENTIAL LINEAR-SWEEP OSCILLOGRAPHIC POLAROGRAPHY

(Short Communication)

C. E. Plock and J. Vasquez,
Anal. Chim. Acta, 50 (1970) 338–341

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THE DETERMINATION OF PLATINUM BY ATOMIC ABSORPTION SPECTROSCOPY

PART I. AIR-ACETYLENE FLAMES

A. E. PITTS, J. C. VAN LOON AND F. E. BEAMISH
Department of Chemistry, University of Toronto, Toronto 181, Ontario (Canada)

(Received December 2nd, 1969)

Atomic absorption spectroscopy has been a popular analytical method for determining the noble metals, and has permitted the analysis of many different noble metal samples[1-9]. With respect to platinum, no method has yet been developed which completely eliminates all potential interferences. Furthermore, there has been little understanding of the nature of these interferences. Here, a thorough examination of the atomic absorption method for platinum is attempted.

STRASHEIM AND WESSELS[3] determined Pt, Pd, Rh, Ag and Au with a butane–propane–air burner. Contrary to LOCKYER AND HAMES[1], they found serious inter-element interferences for platinum from not only other noble metals, but also from Al, Ca, Co, Cu, Ni, Sr and Zn. Addition of copper sulphate caused an initial sharp decrease in sensitivity for platinum; concentrations of copper sulphate above 20,000 p.p.m. overcame the interference by other noble metals and sodium. For the analysis of platinum in commercial samples, the base metals had to be removed, presumably because of interferences not eliminated by copper sulphate.

A procedure for the determination of Ag, Au, Pt, Pd and Rh with an air–propane flame was described by GINZBURG *et al.*[4]. The effect of base metals and mineral acids was studied; hydrochloric acid (2.9 M) and nitric acid (3.3 M) had no effect. The platinum sensitivity was decreased in the presence of 3.4 M sulphuric acid and the salts of many metals including zinc and copper. It was suggested that a flame with a higher temperature such as air–acetylene might reduce these effects.

VAN LOON[8] described a procedure for the determination of platinum, palladium and gold in silver beads. Serious interferences of palladium, gold and silver on platinum were eliminated by the addition of 1% lanthanum chloride. SCHNEPFE AND GRIMALDI[9] determined platinum and palladium by atomic absorption after fire-assay concentration into a gold bead. Serious depressive inter-element interferences were removed by buffering the solutions with a mixture of cadmium and copper sulphates with the cadmium and copper concentrations each at 0.5%. Substantial amounts of Ag, Al, Au, Bi, Ca, Co, Cr, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, V, Y, Zn and the other platinum metals did not interfere in the determination. The sensitivity of the platinum absorption decreased with increasing concentrations of hydrochloric, nitric and especially perchloric acids. There were other restrictions in the determination method; concentrations of up to 200 p.p.m. of Ir, Os, Pd and Ru were tolerated.

Unless larger quantities of copper and cadmium were used, rhodium had to be restricted to 150 p.p.m. Gold depressed the absorbance of platinum by 1% for each 100 p.p.m. of gold present, hence gold had to be added to standards. At the 10-p.p.m. level of platinum, 1000 p.p.m. each of mercury, lanthanum and yttrium and 400 p.p.m. of chromium did not interfere; at the 100-p.p.m. level of platinum, only half the concentrations noted for each of these elements could be tolerated.

This paper presents information on the parameters affecting the determination of platinum in air–acetylene flames; through detailed studies of various cations and anions, plausible explanations of their interferences on platinum are proposed. A new analytical method for the atomic absorption determination of platinum is described and this is applied to synthetic mixtures and a commercial platinum metal concentrate.

EXPERIMENTAL

Apparatus

The Techtron model AA-4 atomic absorption spectrophotometer with a linear/log Varicord 43 recorder was used for all measurements. Other accessories included a Perkin-Elmer platinum hollow-cathode lamp, a Techtron AB-51 air–acetylene burner and calibrated Gilmont flowmeters for air and acetylene.

Reagents

Standard stock solutions of platinum as chloroplatinic acid were prepared from spectrographically pure platinum sponge obtained from Engelhard Industries. The sponge was dissolved in aqua regia and the nitrous oxides were removed by repeated evaporations with hydrochloric acid; the platinum solution was standardized with thiophenol[10]. Stock solutions of gold were prepared from gold foil and standardized with hydroquinone[11]. Rhodium, ruthenium and iridium were obtained as their ammonium or sodium chloro salts (Johnson, Matthey and Co. Ltd.) and dissolved in 0.1 *M* hydrochloric acid. Each solution was passed through a regenerated Dowex 50 W-X8 (20–50 mesh; hydrogen form) cation-exchange resin in a standard column, in order to eliminate interfering sodium and ammonium cations. The rhodium, ruthenium and iridium solutions were standardized gravimetrically by standard procedures[10,13].

Lanthanum chloride solutions were prepared by dissolving high-purity lanthanum(III) oxide in a minimum amount of hydrochloric acid. All other chemicals were analytical regent grade.

General procedure

To test the atomic absorption method developed in this paper, a precious metal concentrate (Falconbridge Nickel Mines Ltd.) was analyzed for platinum. The fusion procedure was similar to that used by PAYNE[11] and VAN LOON[12].

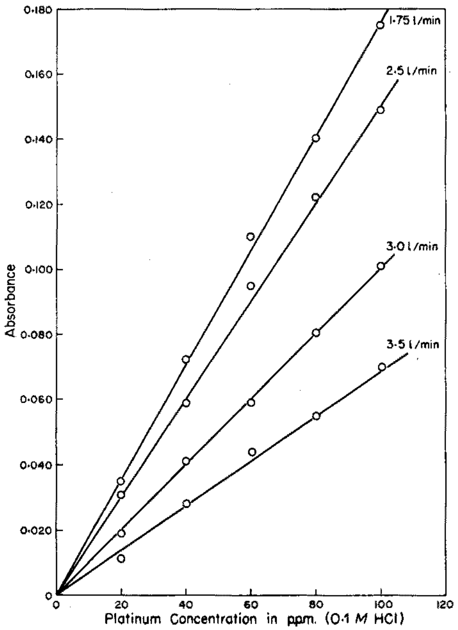
Weigh an appropriately sized sample into a 25-ml nickel crucible (0.2 g with this ore). Add a few drops of water to moisten the sample and follow with 5 ml of hydrofluoric acid. Heat to expel all the silica and hydrofluoric acid. Mix an excess of sodium peroxide (2 g for 0.2 g of sample) intimately with the residue by means of a glass rod and brush the rod clean of the sample. Sinter the material over a flame for 30 min and then fuse at red heat for 5 min. Cool the crucible and contents and place in a 250-ml covered beaker. Add water to fill the crucible and after 5 min, quantitatively transfer the crucible contents to the beaker; finally rinse the crucible with a 50% solution of hydrochloric acid. Slowly acidify the solution in the beaker with 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid, digest on a steam bath and evaporate to 20 ml. Then destroy most of the nitrates by four successive additions of concentrated hydrochloric acid followed by evaporation after each addition. Dilute the sample to 75 ml with doubly distilled water and filter into a 100-ml volumetric flask; silver which is precipitated as silver chloride is thus eliminated from the sample solution. Transfer a 15-ml aliquot of the precious metal solution by pipette into a 50-ml volumetric flask together with 1 ml of 10% lanthanum chloride solution, and dilute to the mark with 0.1 *M* hydrochloric acid.

Determine the platinum content of the ore with the instrument parameters suggested below.

RESULTS AND DISCUSSION

Factors affecting platinum determination

Factors such as burner height, fuel flow, lamp current and slit width have important effects on the atomic absorption determination of platinum in air–acetylene flames. Since limited information has been published for this flame, extensive data are presented here.



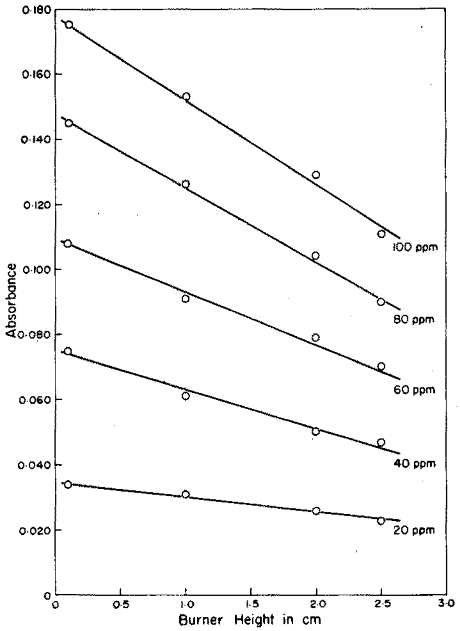


Fig. 1. The effect of various acetylene flow rates on the absorbance of platinum. ×2 Scale expansion, air flow = 7 l/min, slit = 9.9 Å.

Fig. 2. The effect of burner height on the absorbance of platinum. ×2 Scale expansion, air flow = 7 l/min, slit = 9.9 Å.

Figures 1 and 2 show the effect of burner height and fuel flow on the absorbance of various platinum solutions (0.1 *M* hydrochloric acid). Optimum sensitivity was obtained at a height of 0.1 cm above the burner tip and an acetylene-to-air flow ratio of 1:4; Beer's law was obeyed in all instances. Platinum sensitivity was reduced in the higher temperature regions of the flame presumably because of partial ionization; reducing flames having slightly higher temperatures also markedly reduced the sensitivity.

Lamp current and spectral band width had a considerable effect on the response; Table I indicates that low lamp currents and small slit widths give up to 30% better sensitivity.

TABLE I

ABSORBANCE OF PLATINUM WITH DIFFERENT LAMP CURRENTS AND SPECTRAL BAND WIDTHS[a] (50 p.p.m.)

Lamp current (mA)	*Spectral band width (Å)*			
	9.9	*6.6*	*4.9*	*3.3*
6	0.074	0.082	0.087	—
8	0.069	0.083	0.087	0.094
10	0.071	0.083	0.088	0.090
12	0.070	0.080	0.086	0.088
14	0.071	0.083	0.086	0.086

[a] × 2 Scale expansion.

TABLE II

SENSITIVITIES AND DETECTION LIMITS FOR PLATINUM WITH AN AIR–ACETYLENE FLAME

Wavelength (Å)	*Slit width(Å)*	*Sensitivity (p.p.m.)*	*Detection limit[a] (p.p.m.)*	*Solution composition*
2659	3.3	1.4	0.5	Pt
2659	3.3	0.8	0.4	Pt + 2000 p.p.m. La
2659	3.3	1.0	0.5	Pt + 20,000 p.p.m. $CuSO_4$
3065	4.9	2.5	0.8	Pt
2175	9.9	10.0	4.0	Pt
2628	4.9	4.0	2.0	Pt
2830	4.9	4.4	2.0	Pt

[a] Signal equivalent to 2 × background.

The sensitivities (μg/ml/% absorption) and detection limits of platinum at the various absorbing lines are tabulated in Table II; the 2659 Å line was used for all measurements since the sensitivity and background noise were lowest. Platinum solutions having a concentration of 2000 p.p.m. lanthanum chloride (see below) increased the sensitivity by approximately 40% to 0.8 μg/ml/% absorption. This compared very favourably with a value of 1.0 μg/ml/% absorption obtained by current methods[3] in which platinum solutions have a copper sulphate concentration of 20,000 p.p.m.

For normal working conditions in this paper, a spectral band width of 4.9 Å and a lamp current of 10 mA were used to lower the gain and therefore, the background noise level.

TABLE III

EFFECTIVE CATIONIC INTERFERENCES ON THE PLATINUM ABSORBANCE (50 p.p.m.)

Conc. (p.p.m.)	*Fuel flow*	*Burner height (cm)*	*Concomitant*					
			NH₄(I)	*Li(I)*	*Na(I)*	*K(I)*	*Mg(II)*	*Ca(II)*
A[a] Stand	1.75	0.1	0.130	0.130	0.130	0.130	0.130	0.130
25	1.75	0.1	0.138	0.083	0.076	0.079	0.102	0.107
50	1.75	0.1	0.138	0.083	0.076	0.070	0.100	0.107
75	1.75	0.1	0.130	0.081	0.080	0.070	0.098	0.107
100	1.75	0.1	0.130	0.080	0.080	0.072	0.098	0.107
250	1.75	0.1	0.130	0.076	0.081	0.072	0.094	0.106
500	1.75	0.1	0.116	0.074	0.079	0.072	0.091	0.107
750	1.75	0.1	0.116	0.072	0.077	0.072	0.089	0.106
1000	1.75	0.1	0.111	0.072	0.077	0.072	0.090	0.106
2000	1.75	0.1	0.091	0.076	0.070	0.072	0.095	0.096
4000	1.75	0.1	0.069	0.078	0.065	0.067	0.109	0.099
6000	1.75	0.1	0.050	0.085	0.063	0.063	0.121	0.104
8000	1.75	0.1	0.044	0.057	0.055	0.059	0.120	0.093
Stand	1.75	0.5	0.108	0.108	0.108	0.108	0.108	0.108
100	1.75	0.5	0.112	0.086	0.078	0.070	0.093	0.091
1000	1.75	0.5	0.097	0.083	0.072	0.066	0.089	0.093
8000	1.75	0.5	—[c]	—[c]	—[c]	0.060	—[c]	—[c]
Stand	1.75	1.0	0.095	0.095	0.095	0.095	0.095	0.095
100	1.75	1.0	0.092	0.075	0.072	0.065	0.083	0.082
1000	1.75	1.0	0.089	0.070	0.068	0.066	0.082	0.082
8000	1.75	1.0	—	—	—	0.058	—	—
Stand	1.75	1.5	p.077	0.077	0.077	0.077	0.077	0.077
100	1.75	1.5	0.077	0.063	0.061	0.053	0.067	0.068
1000	1.75	1.5	0.069	0.060	0.059	0.051	0.065	0.067
8000	1.75	1.5	—	—	—	0.050	—	—
Stand	3.0	0.1	0.087	0.087	0.087	0.087	0.087	0.087
100	3.0	0.1	0.077	0.017	0.046	0.016	0.025	0.034
1000	3.0	0.1	0.074	0.017	0.038	0.010	0.016	0.027
8000	3.0	0.1	—	—	—	0.013	—	—
B.[b] Stand	1.75	0.1	0.180	0.180	0.180	0.180	0.180	0.180
100	1.75	0.1	0.170	0.180	0.180	0.180	0.188	0.180
1000	1.75	0.1	0.170	0.189	0.179	0.181	0.184	0.179
8000	1.75	0.1	—	—	—	0.185	—	0.180

Conc. (p.p.m.)	*Fuel flow*	*Burner height (cm)*	*Concomitant*					
			Cu(II)	*Zn(II)*	*Hg(II)*	*La(III)*	*Sn(IV)*	*Pb(II)*
A. Stand	1.75	0.1	0.130	0.130	0.130	0.130	0.130	0.130
25	1.75	0.1	0.078	0.131	0.126	0.116	0.130	0.097
50	1.75	0.1	0.066	0.131	0.126	0.127	0.128	0.076
75	1.75	0.1	0.066	0.131	0.124	0.137	0.130	0.065
100	1.75	0.1	0.065	0.129	—	0.146	0.123	0.060
250	1.75	0.1	0.067	0.115	0.091	0.159	0.127	0.052
500	1.75	0.1	0.067	0.103	0.083	0.164	0.125	0.033
750	1.75	0.1	0.065	0.096	0.077	0.165	0.123	0.028
1000	1.75	0.1	0.067	0.093	0.074	0.169	0.121	0.031
2000	1.75	0.1	0.067	0.077	0.068	0.177	0.107	0.032
4000	1.75	0.1	0.066	0.071	0.062	0.178	0.090	0.032
6000	1.75	0.1	0.071	0.066	0.062	0.181	0.080	0.033
8000	1.75	0.1	0.080	0.063	0.063	0.181	0.078	0.033
Stand	1.75	0.5	0.108	0.108	0.108	0.108	0.108	0.108
100	1.75	0.5	0.067	0.109	0.111	0.128	0.102	0.068
1000	1.75	0.5	0.062	0.085	0.081	0.138	0.096	0.047
8000	1.75	0.5	0.075	0.065	0.073	0.139	0.064	0.053
Stand	1.75	1.0	0.095	0.095	0.095	0.095	0.095	0.095
100	1.75	1.0	0.064	0.094	0.091	0.098	0.092	0.064
1000	1.75	1.0	0.067	0.078	0.074	0.122	0.084	0.050

TABLE III *(continued)*

Conc. (p.p.m.)	*Fuel flow*	*Burner height (cm)*	*Concomitant*					
			Cu(II)	*Zn(II)*	*Hg(II)*	*La(III)*	*Sn(IV)*	*Pb(II)*
8000	1.75	1.0	0.071	0.062	0.067	0.114	0.064	0.058
Stand	1.75	1.5	0.077	0.077	0.077	0.077	0.077	0.077
100	1.75	1.5	0.055	0.077	0.083	0.089	0.069	0.057
1000	1.75	1.5	0.055	0.064	0.071	0.090	0.058	0.035
8000	1.75	1.5	0.059	0.053	0.066	0.090	0.047	0.044
Stand	3.0	0.1	0.087	0.087	0.087	0.087	0.087	0.087
100	3.0	0.1	0.014	0.091	0.061	0.046	0.083	0.035
1000	3.0	0.1	0.014	0.057	0.012	0.052	0.068	—
8000	3.0	0.1	0.014	0.022	0.011	0.062	0.045	—
B. Stand	1.75	0.1	0.180	0.180	0.180	—	0.180	0.180
100	1.75	0.1	0.180	0.181	0.180	—	0.182	0.183
1000	1.75	0.1	0.183	0.176	0.177	—	0.156	0.194
8000	1.75	0.1	0.183	0.170	0.180	—	0.157	0.180

Conc. (p.p.m.)	*Fuel flow*	*Burner height (cm)*	*Concomitant*					
			Sr(II)	*Ba(II)*	*Cr(III)*	*Fe(III)*	*Co(II)*	*Ni(II)*
A. Stand	1.75	0.1	0.130	0.130	0.130	0.130	0.130	0.130
25	1.75	0.1	0.101	0.104	0.070	0.122	0.098	0.125
50	1.75	0.1	0.093	0.089	0.060	0.116	0.088	0.121
75	1.75	0.1	0.089	0.086	0.063	0.112	0.083	0.118
100	1.75	0.1	0.089	0.086	0.061	0.117	0.081	0.115
250	1.75	0.1	0.086	0.090	0.070	0.095	0.074	0.081
500	1.75	0.1	0.077	0.086	0.089	0.101	0.066	0.059
750	1.75	0.1	0.074	0.080	0.099	0.108	0.063	0.054
1000	1.75	0.1	0.071	0.075	0.108	0.110	0.059	0.054
2000	1.75	0.1	0.071	0.061	0.131	0.118	0.058	0.053
4000	1.75	0.1	0.067	0.056	0.151	0.125	0.056	0.053
6000	1.75	0.1	0.070	0.052	0.153	0.129	0.056	0.053
8000	1.75	0.1	0.066	0.044	0.151	0.130	0.046	0.054
Stand	1.75	0.5	0.108	0.108	0.108	0.108	0.108	0.108
100	1.75	0.5	0.086	0.080	0.058	0.114	0.081	0.098
1000	1.75	0.5	0.074	0.067	0.089	0.122	0.064	0.060
8000	1.75	0.5	—[c]	—[c]	—[c]	0.143	—[c]	0.062
Stand	1.75	1.0	0.095	0.095	0.095	0.095	0.095	0.095
100	1.75	1.0	0.085	0.078	0.060	0.082	0.072	0.088
1000	1.75	1.0	0.071	0.068	0.085	0.088	0.057	0.062
8000	1.75	1.0	—	—	—	0.099	—	0.059
Stand	1.75	1.5	0.077	0.077	0.077	0.077	0.077	0.077
100	1.75	1.5	0.065	0.073	0.054	0.068	0.062	0.072
1000	1.75	1.5	0.059	0.066	0.071	0.071	0.053	0.049
8000	1.75	1.5	—	—	—	0.071	—	0.051
Stand	3.0	0.1	0.087	0.087	0.087	0.087	0.087	0.087
100	3.0	0.1	0.028	0.020	0.028	0.044	0.028	0.084
1000	3.0	0.1	0.020	0.019	0.045	0.047	0.021	0.014
8000	3.0	0.1	—	—	—	0.074	—	0.013
B. Stand	1.75	0.1	0.180	0.180	0.180	0.180	0.180	0.180
100	1.75	0.1	0.180	0.180	0.178	0.180	0.180	0.184
1000	1.75	0.1	0.184	0.181	0.186	0.177	0.180	0.176
8000	1.75	0.1	—	—	—	0.170	0.172	0.176

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[a] A. Absorbance for 50 p.p.m. platinum solutions in 0.1 *M* HCl (× 2 scale expansion).

[b] B. Absorbance for 50 p.p.m. platinum solutions in 0.1 *M* HCl with a concentration of 2000 p.p.m. $LaCl_3$ (× 2 scale expansion).

[c] Absorbance omitted due to particle scattering in flame.

Cationic interferences

A complete summary of the interference effects of twenty-three cations on standard platinum solutions in air–acetylene flames is given in Tables III and IV; since chloride ions have little effect on the platinum absorbance, all cations were used in their chloride form. In order to get a better insight into the nature of these cationic interferences, measurements were taken for distinctly different concentration ranges of the concomitant (0–100 p.p.m., 250–1000 p.p.m., 2000–8000 p.p.m.), for different burner heights and for different fuel flow rates.

Although the air–acetylene flame is 400° hotter than the air–propane one[14], unsystematic interferences similar to those mentioned by STRASHEIM AND WESSELS[3] occurred; interferences of the various noble metals (0–100 p.p.m.) on the platinum absorbance were similar to those reported by SCHNEPFE AND GRIMALDI[9]. Referring

TABLE IV

EFFECTIVE CATIONIC INTERFERENCES OF GOLD(III) AND OTHER PLATINUM METALS ON THE PLATINUM ABSORBANCES (50 p.p.m.)

Conc. (p.p.m.)	*Fuel flow*	*Burner height (cm)*	*Concomitant*				
			Ru(IV)	*Rh(III)*	*Ir(III)*	*Pd(II)*	*Au(III)*
A.[a] Stand	1.75	0.1	0.130	0.130	0.130	0.130	0.130
25	1.75	0.1	0.078	0.086	0.087	0.123	0.127
50	1.75	0.1	0.062	0.070	0.076	0.114	0.128
75	1.75	0.1	0.062	0.060	0.074	0.107	0.129
100	1.75	0.1	0.058	0.054	0.071	0.095	0.130
250	1.75	0.1	0.053	0.042	0.066	0.069	0.122
500	1.75	0.1	0.051	0.039	0.066	0.059	0.119
750	1.75	0.1	0.050	0.036	0.065	0.053	0.124
1000	1.75	0.1	—[b]	0.034	0.062	0.053	0.127
1250	1.75	0.1	—[b]	—[b]	0.062	0.054	0.120
1500	1.75	0.1	—[b]	—[b]	—[b]	0.052	0.117
Stand	1.75	0.5	0.108	0.108	0.108	0.108	0.108
100	1.75	0.5	0.056	0.045	0.060	0.083	0.109
500	1.75	0.5	0.049	0.038	0.058	0.081	0.101
1000	1.75	0.5	—	0.030	0.057	0.056	0.109
Stand	1.75	1.0	0.095	0.095	0.095	0.095	0.095
100	1.75	1.0	0.052	0.044	0.056	0.077	0.098
500	1.75	1.0	0.046	0.036	0.054	0.062	0.093
1000	1.75	1.0	—	0.028	0.054	0.058	0.096
Stand	1.75	1.5	0.077	0.077	0.077	0.077	0.077
100	1.75	1.5	0.045	0.037	0.045	0.065	0.077
500	1.75	1.5	0.035	0.031	0.045	0.050	0.071
1000	1.75	1.5	—	0.023	0.043	0.050	0.077
Stand	3.0	0.1	0.087	0.087	0.087	0.087	0.087
100	3.0	0.1	0.024	0.017	0.021	0.048	0.084
500	3.0	0.1	0.033	0.017	0.021	0.026	0.080
1000	3.0	0.1	—	0.017	0.021	0.026	0.084
B.[a] Stand	1.75	0.1	0.180	0.180	0.180	0.180	0.180
25	1.75	0.1	0.177	0.183	0.179	0.179	0.181
50	1.75	0.1	0.177	0.181	0.176	0.179	0.182
100	1.75	0.1	0.176	0.177	0.172	0.180	0.179
200	1.75	0.1	0.173	0.170	0.168	0.178	0.180
250	1.75	0.1	—	0.160	0.169	—	—
1000	1.75	0.1	—	0.120	0.153	—	—

[a] A and B as in Table III.

[b] Stock solution insufficiently concentrated to permit preparation of sample.

to the flame and burner parameters in Tables III and IV, the general observations that can be made include: (*a*) there was an initial sharp decrease in absorbance of platinum solutions with 25–250 p.p.m. of concomitant added except for ammonium(I), gold(III), tin(IV), zinc(II), and mercury(II); (*b*) above 250 p.p.m. of concomitant, the absorbance gradually decreased further except for chromium(III), iron(III), magnesium(II) and lanthanum(III) which gradually increased and gold(III) which remained relatively constant; (*c*) in most instances, the interference was slightly reduced at higher burner heights where the temperature is higher; (*d*) interferences were far greater in reducing flames.

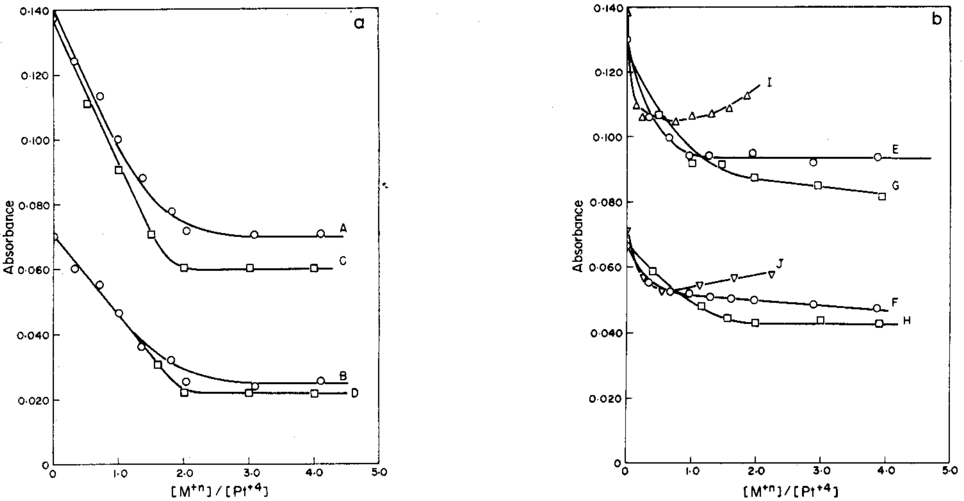

Fig. 3a, b. The depression of platinum absorbance with concomitant added (× 2 scale expansion). (A) 50 p.p.m. platinum with sodium; (B) 25 p.p.m. platinum with sodium; (C) 50 p.p.m. platinum with potassium; (D) 25 p.p.m. platinum with potassium; (E) 50 p.p.m. platinum with magnesium; (F) 25 p.p.m. platinum with magnesium; (G) 50 p.p.m. platinum with calcium; (H) 25 p.p.m. platinum with calcium; (I) 50 p.p.m. platinum with lanthanum; (J) 25 p.p.m. platinum with lanthanum.

Figure 3 provides some insight into the type of interference that may occur. Plots of absorbance *vs.* $[M^{n+}]/[Pt^{4+}]$ where $[M^{n+}]$ is the concentration of concomitant, show distinct breaks in absorbance depression at $[M^{n+}]/[Pt^{4+}] = 2$ for sodium and potassium, and a value of 1 for magnesium and calcium. This suggests a condensed phase chemical interference[15] in which a less volatile platinum salt is formed.

$$(2/n)M^{n+} + H_2[PtCl_6] \rightleftharpoons M_{2/n}[PtCl_6] + 2H^+ \qquad (1)$$

In the case of the alkali metals and alkaline earths, displacement to the right may be almost complete. In general, the interference by a cation would depend on the extent of displacement in eqn. (1), and the volatility of the platinum salt formed as compared to $H_2[PtCl_6]$. This might explain why some cations such as ammonium(I), tin(IV), zinc(II) and mercury(II) behave irregularly; gold(III) which forms an extremely stable chloro anion, does not interfere as would be expected.

As shown in Table III, 1–25 p.p.m. of lanthanum(III) depressed the platinum absorbance; in Fig. 3b, the absorbance of platinum solutions with lanthanum(III) added, reached a minimum at $[La^{3+}]/[Pt^{4+}] \simeq 0.7$. This again could be due to a similar displacement reaction.

$$2\ La^{3+} + 3H_2[PtCl_6] \rightleftarrows La_2[PtCl_6]_3 + 2\ H^+ \qquad (2)$$

With excess concentrations of lanthanum(III), the absorbance of platinum solutions gradually increased and eventually the readings were enhanced up to 38% (8000 p.p.m. lanthanum(III)). This means that lanthanum(III) in large quantities, releases more platinum for the determination. It is not unreasonable to assume that some platinum could exist as the volatile oxide species Pt_xO_2 in air–acetylene flames; volatile platinum oxides are known to exist at high temperatures[16]. Thus, lanthanum could also prevent or inhibit the formation of Pt_xO_2 species by one of the following reactions:

$$4\ La(g) + 3\ O_2(g) \rightleftarrows 2\ La_2O_3(g) \qquad (3)$$

$$La(g) + Pt_xO_2 \rightleftarrows La_2O_3 + x\ Pt(g) \qquad (4)$$

When equimolar quantities of concomitant such as sodium and lanthanum were added together, the depression and enhancement of the platinum absorbance were similar to that of lanthanum(III) rather than sodium(I), which indicated that $La_2\ [PtCl_6]_3$ was preferentially formed. If lanthanum(III) were to displace other interfering cations similarly, it would provide a reproducible means of determining platinum. When 2000 p.p.m. of lanthanum(III) was added to standard platinum solutions containing various concentrations of interfering concomitant, the interferences were indeed eliminated (Table III). Most cationic interferences were eliminated by the addition of lanthanum(III) with the exception of rhodium(III) and iridium(III) which begin to interfere with concentrations in excess of 100–200 p.p.m.; in addition, Beer's law was obeyed for 0–100 p.p.m. of platinum (2000 p.p.m. lanthanum(III)).

Anionic interferences

The study of anionic interferences of platinum was somewhat limited by the interference of most cations; thus, the introduction of anions as soluble salts was not possible. However, since the hydrogen ion itself has little effect on the dissociation of $H_2[PtCl_6]$, the effect of various acids of commonly occurring anions was studied. The results shown in Table V can be divided into two categories; (*a*) acids which had little

TABLE V

THE EFFECT OF VARIOUS ACIDS ON THE ABSORBANCE OF 50-p.p.m. PLATINUM SOLUTIONS[a]

Concentration of acid (N)	*HCl*	*HNO_3*	*H_2SO_4*	*HAc*	*H_3PO_4*	*$HClO_4$*	*HBr*
Stand (H_2O)	0.140	0.140	0.140	0.140	0.140	0.140	0.140
0.1	0.134	0.134	0.104	0.135	0.081	0.119	0.116
0.5	0.133	0.136	0.089	0.134	0.051	0.099	0.114
1.0	0.134	0.121	0.085	0.133	0.040	0.090	0.111
3.0	0.125	0.122	0.069	0.139	0.018	0.079	0.100
6.0	0.097	0.112	0.059	0.137	0.017	0.067	0.076

[a] × 2 Scale expansion.

interference at low concentrations, but a significant physical interference at higher concentrations, and (*b*) acids which interfered at all concentrations.

Hydrochloric acid, nitric acid and acetic acid were included in the first category. The decrease in platinum absorbance with concentrations greater than 1.0 *M* may be attributed to changes in the physical properties of the solutions which effect the efficiency of transportation and atomization of the analyte into the flame. These effects were a result of lower sample flow rates, changes in solution density and viscosity and different particle sizes in the flame when working with concentrated solutions; these factors have been discussed in several papers[17–21].

Sulphuric acid, phosphoric acid, hydrobromic acid and perchlorate acid were included in the second category. Extensive interferences of the platinum absorbance, even at low acid concentrations, indicate a chemical interference in which the species, $H_2[PtCl_6]$, reacts with the respective anions forming less volatile compounds. The explanation of some of these interferences may be as follows.

Evaporation of platinic acid solutions in the presence of sulphuric acid is known to yield platinum sulphate[22] ($H_2[Pt(SO_4)_2 (OH)_2]$). Although the reaction may not occur appreciably in solution, the evaporation of $H_2[PtCl_6]$ in the presence of sulphuric acid in the flame could yield a considerable quantity of non-volatile platinum sulphate. Similarly, the presence of phosphoric acid probably produces a non-volatile platinum polyphosphate in the flame. Although the exact nature of such a reaction is not known, platinum pyrophosphate has been isolated (PtP_2O_7)[23].

Hydrobromic acid reacts with platinic acid in solution to form $H_2 [PtBr_6]$.

$$6\ HBr + H_2[PtCl_6] \rightleftarrows H_2[PtBr_6] + 6\ HCl$$

In solution, the colour of the hexachloroplatinate anion gradually changes to a deep yellow characteristic of the bromide species; this reaction does not go to completion unless the solution is evaporated to dryness with hydrobromic acid. The reaction of perchloric acid is unclear; no information has been recorded in the literature.

TABLE VI

STUDY OF SULPHATE AND PHOSPHATE INTERFERENCES IN THE PRESENCE OF LANTHANUM CHLORIDE

Composition of solution			*Absorbance*
Acid concentration	*Molar ratio La(III) : anion + excess*	*Concentration of Pt (p.p.m.)*	
Standard (H_2O)	2000 p.p.m. La(III)	50	0.180
0.1 *N* H_2SO_4	1:1.5 + 2000 p.p.m. La(III)	50	0.185
0.5 *N* H_2SO_4	1:1.5 + 2000 p.p.m. La(III)	50	0.185
1.0 *N* H_2SO_4	1:1.5 + 2000 p.p.m. La(III)	50	0.180
Standard (0.5 *N* HCl)[a]	2000 p.p.m. La(III)	50	0.172
0.1 *N* H_3PO_4 + 0.5 *N* HCl	1:1	50	0.149
0.1 *N* H_3PO_4 + 0.5 *N* HCl	1:1 + 2000 p.p.m. La(III)	50	0.169
0.1 *N* H_3PO_4 + 0.5 *N* HCl	2:1	50	0.176
0.5 *N* H_3PO_4 + 0.5 *N* HCl	1:1	50	0.174
0.5 *N* H_3PO_4 + 0.5 *N* HCl	1:1 + 2000 p.p.m. La(III)	50	0.176
0.5 *N* H_3PO_4 + 0.5 *N* HCl	2:1	50	0.167

[a] 0.5 *N* HCl was necessary to prevent the precipitation of lanthanum phosphate.

JOFE *et al.*[24] successfully eliminated phosphate interference in the flame photometric determination of strontium and barium; they concluded that both barium and strontium formed relatively non-volatile pyrophosphates with phosphoric acid in air–acetylene flames. By the addition of lanthanum chloride, which forms a stable, less volatile pyrophosphate, they were able to release the barium and strontium for determination.

Since lanthanum forms insoluble phosphates and sulphates, its efficiency in eliminating the above anionic interferences was investigated. As shown in Table VI, lanthanum chloride added in excess of the required molar ratio of lanthanum to anion, completely eliminated interferences caused by sulphuric and phosphoric acid; an excess of 2000 p.p.m. of lanthanum ensured uniform enhancement of the platinum absorbance in order to agree with the standard. These results give credibility to the chemical interferences by anions discussed above. Methods for eliminating the interferences of perchlorate and bromide ions were not developed.

ANALYTICAL APPLICATIONS

Analytically, the addition of lanthanum to platinum solutions provides a very useful atomic absorption method; Tables VII and VIII demonstrate that platinum can be determined in the presence of synthetic solutions of noble metals and base metals with considerable accuracy even at 5 p.p.m. concentrations. In addition, lanthanum is one of the few cations, which does not interfere, that will eliminate the potential interferences of sulphate and phosphate.

TABLE VII

ABSORBANCE OF PLATINUM IN THE PRESENCE OF INTERFERING NOBLE METALS

Concentration of element added in p.p.m.[a] *(v̄ 1 ml × 10% La^{3+} in 50 ml)*						*Absorbance*	*Equivalent p.p.m. Pt*
Pt	*Au*	*Pd*	*Ru*	*Ir*	*Rh*		
A.[b] 50	—	—	—	—	—	0.180	50.0
50	25	—	—	—	—	0.177	49.2
50	25	25	—	—	—	0.180	50.0
50	25	25	25	—	—	0.181	50.3
50	25	25	25	25	—	0.177	49.2
50	25	25	25	25	25	0.174	48.3
B.[c] 5	—	—	—	—	—	0.021	5.0
5	25	—	—	—	—	0.021	5.0
5	25	25	—	—	—	0.021	5.0
5	25	25	25	—	—	0.021	5.0
5	25	25	25	25	—	0.021	5.0
5	25	25	25	25	25	0.019	4.6

[a] 1.0 ml of 10% La^{3+} solution per 50 ml was added.
[b] A. Measurements taken at × 2 scale expansion.
[c] B. Measurements taken at × 5 scale expansion.

This procedure was compared with current atomic absorption methods for platinum. Table IX gives a summary of results obtained by the procedure of STRASHEIM AND WESSELS[3] with the addition of copper sulphate; 20,000 p.p.m. of copper sulphate does effectively eliminate most interferences. However, concentrations of gold(III) and rhodium(III) above 100 p.p.m. cannot be tolerated; large

TABLE VIII

THE ABSORBANCE OF PLATINUM IN CONCENTRATED SOLUTIONS OF BASE METALS WITH LANTHANUM CHLORIDE ADDED

Concentration of element in p.p.m.[a]				*% Absorbance*	*Net*[b] *absorbance*	*Equivalent p.p.m. Pt*
Pt	*Fe*	*Cu*	*Ni*			
A.[c] 50	—	—	—	70.0	0.187	50.0
—	2000	2000	2000	2.0		
50	2000	2000	2000	73.0	0.190	50.8
—	5000	5000	5000	3.5		
50	5000	5000	5000	73.6	0.187	50.0
—	10,000	5000	5000	6.2		
50	10,000	5000	5000	76.2	0.187	50.0
B.[d] 5	—	—	—	29.0	0.026	5.0
—	2000	2000	2000	5.0		
5	2000	2000	2000	32.8	0.025	4.8
—	5000	5000	5000	9.5		
5	5000	5000	5000	35.5	0.023	4.4
—	10,000	5000	5000	14.5		
5	10,000	5000	5000	38.0	0.021	4.0

[a] 1 ml of 10% La^{3+} solution was added per 50 ml.

[b] To obtain the net absorbance, % absorption values for blanks were subtracted from the values of the platinum salted samples, then converted to absorbance.

[c] A. Measurements at × 2 scale expansion.

[d] B. Measurements at × 5 scale expansion.

TABLE IX

ABSORBANCE OF PLATINUM IN THE PRESENCE OF SOME NOBLE METALS AND BASE METALS WITH ADDITION OF 20,000 p.p.m. OF COPPER SULPHATE[a]

Element added	*Conc. (p.p.m.)*	*Net absorbance*	*Effective p.p.m. Pt*
Stand	—	0.148	50.0
Pd	50	0.143	48.3
Pd	100	0.145	49.0
Rh	50	0.146	49.3
Rh	100	0.142	48.0
Ir	50	0.149	50.3
Ir	100	0.149	50.3
Ru	50	0.148	50.0
Ru	100	0.148	50.0
Au	50	0.142	48.0
Au	100	0.134	45.2
Fe	2000	0.137	46.2
Fe	5000	0.127	42.9
Ni	2000	0.148	50.0
Ni	5000	0.148	50.0

[a] All readings were compared against blanks, and the net absorbance taken (× 2 scale expansion).

concentrations of iron, which is a commonly occurring base metal, introduce significant interferences. The similar method presented by SCHNEPFE AND GRIMALDI[9] uses a mixture of cadmium and copper sulphate (0.5% each) to eliminate interferences; again Au(III) and Rh(III) and to a lesser extent Hg(II), La(III), Y(III) and Cr(III)

TABLE X

DETERMINATION OF PLATINUM IN A PRECIOUS METAL CONCENTRATE[a]

Weight of sample (g)	*Mg Pt found*	*% Pt*	*Deviation from mean*
0.1950	2478	1.27	+ 0.2
0.2210	2811	1.27	+ 0.02
0.2208	2591	1.17	– 0.08
0.2349	2928	1.25	0.00
0.2089	2638	1.26	+ 0.01
0.2436	3044	1.25	0.00
Mean value		1.25 ± 0.02	
ZACHARIASEN AND BEAMISH[25]		1.21	
Falconbridge Nickel Mines Ltd.		1.36	

[a] × 5 Scale expansion.

introduce interferences. Neither of the above methods eliminates anionic interferences.

The proposed method of determining platinum with 0.2% lanthanum chloride in air–acetylene flames provides a useful alternative with four distinct advantages. (*a*) It lowers the effective salt concentration necessary, thus eliminating such effects as burner clogging and light scattering. (*b*) It gives a better sensitivity for platinum (see Table II). (*c*) It has been proven effective for determining platinum in the presence of large concentrations of base metals. (*d*) It completely eliminates anionic interferences from sulphates and phosphates.

The general procedure described above, was applied to several samples of a precious metal concentrate obtained from Falconbridge Nickel Mines Ltd. who have reported the following values: 20.01% Ag, 0.25% Au, 1.36% Pt, 1.72% Pd, 4.72% Ru, 5.65% Rh, and 2.80% Ir. The results are shown in Table X. The mean value of 1.25 ± 0.02% is in good agreement with the 1.21% platinum concentration recorded by ZACHARIASEN AND BEAMISH[25] and 1.36% by Falconbridge.

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SUMMARY

The atomic absorption determination of platinum in air–acetylene flames is thoroughly studied and reasons for the cationic and anionic interferences are discussed. A superior analytical method is proposed in which lanthanum is used to suppress interferences; the method has been successfully applied to synthetic mixtures and a commercial platinum metal concentrate.

RÉSUMÉ

Une étude est effectuée sur le dosage du platine par absorption atomique, dans les flammes air–acétylène. On examine en particulier les interférences cationiques et anioniques. Une méthode est proposée, dans laquelle le lanthane est utilisé pour supprimer les interférences. Ce procédé a fourni des résultats tout à fait satisfaisants avec des mélanges synthétiques et un concentré de platine du commerce.

ZUSAMMENFASSUNG

Die Bestimmung von Platin durch Atomabsorption in Luft–Acetylen-Flammen ist gründlich untersucht worden; Ursachen für die kationischen und anionischen Störungen werden diskutiert. Es wird eine bessere analytische Methode vorgeschlagen, bei der Lanthan zur Unterdrückung der Störungen verwendet wird; die Methode ist auf künstliche Gemische und ein kommerzielles Platinmetallkonzentrat mit Erfolg angewendet worden.

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THE DETERMINATION OF PLATINUM BY ATOMIC ABSORPTION SPECTROSCOPY

PART II. NITROUS OXIDE–ACETYLENE FLAMES*

A. E. PITTS, J. C. VAN LOON AND F. E. BEAMISH
Department of Chemistry, University of Toronto, Toronto 181, Ontario (Canada)

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Atomic absorption determinations of platinum, up to the present time, have curiously been limited to the use of low-temperature flames (see Part I*). The most obvious reason for avoiding high-temperature flames such as nitrous oxide–acetylene, has been the reduction of platinum sensitivity owing to ionization interferences. However, the proven advantages of the nitrous oxide flame in overcoming cationic and anionic interferences make this study with platinum extremely important, especially considering the complexity of platinum interference patterns.

The following is a study of the parameters affecting the determination of platinum in nitrous oxide–acetylene flames and the possible cationic and anionic interferences. Platinum is determined in synthetic samples and a precious metal concentrate.

EXPERIMENTAL

Apparatus

The equipment described in Part I*, was used in this research with the inclusion of the 5-cm Techtron AB-50 nitrous oxide–acetylene burner.

Reagents

The standard reagents used were described in Part I*. All other chemicals were analytical-reagent grade.

RESULTS AND DISCUSSION

Factors affecting platinum determination

Table I summarizes the absorbance values obtained when platinum solutions were aspirated into nitrous oxide–acetylene flames and the burner height and acetylene fuel flow rate were varied. Platinum sensitivity was constant and highest at burner heights between 0.5 cm and 2.0 cm, and at an acetylene-to-nitrous oxide ratio of 3:4.5 l/min (oxidizing flame). Lower burner heights and higher acetylene-to-nitrous oxide ratios reduced the sensitivity and in some instances Beer's law was no longer obeyed.

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TABLE I

ABSORBANCE OF PLATINUM SOLUTIONS IN NITROUS OXIDE–ACETYLENE FLAMES (100 p.p.m.)[a]

Conc. of Pt (p.p.m.)	*Acetylene flow rate (l/min)*	*Burner height (cm)*				
		0.1	*0.5*	*1.0*	*1.5*	*2.0*
20	3.0	0.010	0.014	0.012	0.012	0.013
40	3.0	0.021	0.026	0.024	0.025	0.025
60	3.0	0.029	0.037	0.035	0.037	0.037
80	3.0	0.037	0.049	0.046	0.049	0.048
100	3.0	0.047	0.059	0.058	0.060	0.061
20	3.5	0.011	0.013	0.011	0.012	—
40	3.5	0.020	0.025	0.026	0.025	—
60	3.5	0.028	0.035	0.034	0.034	—
80	3.5	0.035	0.042	0.045	0.047	—
100	3.5	0.041	0.052	0.056	0.058	—
20	4.0	0.007	0.010	0.010	0.012	—
40	4.0	0.015	0.017	0.019	0.024	—
60	4.0	0.021	0.027	0.030	0.034	—
80	4.0	0.027	0.035	0.040	0.046	—
100	4.0	0.032	0.046	0.049	0.054	—

[a] × 3 Scale expansion

Recommended parameters from the above are as follows: a lamp current of 10 mA, a spectral band width of 4.9 Å, a burner height of 1.0 cm, an acetylene flow rate of 3 l/min and a nitrous oxide flow rate of 4.5 l/min.

Table II shows the sensitivities (μg/ml/% absorption) and detection limits (signal of platinum equivalent to twice the background) of platinum at different absorbing wavelengths; the line, 2659 Å, has one-fourth the corresponding sensitivity of air–acetylene flames, presumably because of the larger fraction of platinum atoms being ionized in the hotter flame (2700°). In addition, the flow rate with the nitrous oxide burner was 2.40 ml/min as compared to 3.1 ml/min for air–acetylene. Thus, less analyte was aspirated into the flame.

TABLE II

SENSITIVITIES AND DETECTION LIMITS FOR PLATINUM WITH A NITROUS OXIDE–ACETYLENE FLAME

Wavelength (Å)	*Slit width (Å)*	*Sensitivity (p.p.m.)*	*Detection limit (p.p.m.)*
2659	4.9	7.0	2.0
3065	4.9	13.3	6.0
2175	9.9	18.5	20.0
2628	4.9	16.7	8.0
2830	4.9	25.0	20.0

The study of possible cationic and anionic interferences

The main advantage of the nitrous oxide–acetylene flame is that its high temperature dissociates most possible non-volatile compounds of the analyte (condensed phase chemical interference) and eliminates such problems as variable particle size in

TABLE III

ABSORBANCE OF PLATINUM SOLUTIONS IN THE PRESENCE OF VARIOUS CATIONS IN NITROUS OXIDE–ACETYLENE FLAMES[a] (100 p.p.m.)

Concomitant	*Burner height (cm)*	*Concentration of concomitant*		
		100 p.p.m.	*500 p.p.m.*	*1000 p.p.m.*
NH_4	1.0	0.063	0.062	0.062
Li	1.0	0.060	0.062	0.063
Na	1.0	0.062	0.063	0.063
K	1.0	0.062	0.063	0.063
Mg	1.0	0.062	0.064	0.066
Ca	1.0	0.061	0.065	0.065
Sr	1.0	0.064	0.065	0.066
Ba	1.0	0.062	0.063	0.065
Ti	1.0	0.063	0.062	0.063
Fe	1.0	0.062	0.061	0.062
Co	1.0	0.062	0.063	0.064
Ni	1.0	0.061	0.063	0.064
Cu	1.0	0.062	0.064	0.066
Zn	1.0	0.061	0.062	0.063
Hg	1.0	0.062	0.064	0.063
Al	1.0	0.057	0.062	0.064
Sn	1.0	0.062	0.062	0.064
Pb	1.0	0.062	0.062	0.063
La	1.0	0.061	0.063	0.063
Au	1.0	0.061	0.062	0.062
Pd	1.0	0.062	0.062	0.063
Rh	1.0	0.061	0.054	—
Rh	2.0	0.061	0.060	—
Ru	1.0	0.060	0.053	—
Ru	2.0	0.061	0.058	—
Ir	1.0	0.051	0.051	—
Ir	1.5	0.058	0.055	—
Ir	2.0	0.061	0.059	—

[a] Absorbance of 100 p.p.m. Pt standard is 0.062 (× 3 scale expansion).

the flame and non-volatile matrices of the concomitant[1,2]. This would be especially useful for platinum owing to the numerous interferences discussed in Part I.

The absorbances of 100-p.p.m. platinum solutions in the presence of 100 p.p.m., 500 p.p.m. and 1000 p.p.m. concentrations of concomitant are tabulated in Table III. There were no interferences with the exception of rhodium(III), iridium(III) and ruthenium(IV); as with air–acetylene flames (see Part I) these particular metals appear to form extremely non-volatile combinations with platinum. At a higher burner height of 2.0 cm, however, 500 p.p.m. of each can be tolerated.

Anionic interferences have been discussed in Part I. The absorbance readings of standard 100-p.p.m. platinum solutions in 0.1–6.0 *N* acid solutions are presented in Table IV. In all instances, there was negligible interference except in the 6.0 *N* solutions; these were most probably physical effects due to changes in density and viscosity of the solutions which directly affect the transportation properties of the analyte into the flame[3,4]. The solution flow rates were reduced from 2.4 ml/min to 2.0 ml/min with the concentrated acids. The chemical interferences introduced by the sulphate, perchlorate, phosphate and bromide ions were, therefore, completely eliminated at higher temperatures.

TABLE IV

THE EFFECT OF VARIOUS ACIDS ON THE ABSORBANCE OF 100 p.p.m. PLATINUM SOLUTIONS[a]

Concentration of acid	*HCl*	*HNO_3*	*H_2SO_4*	*HAc*	*H_3PO_4*	*$HClO_4$*	*HBr*
Standard (H_2O)	0.062	0.062	0.062	0.062	0.062	0.062	0.062
0.1 *N*	0.061	0.061	0.061	0.060	0.062	0.061	0.059
0.5 *N*	0.062	0.060	0.059	0.061	0.064	0.062	0.061
1.0 *N*	0.062	0.060	0.062	0.065	0.061	0.064	0.060
3.0 *N*	0.062	0.060	0.058	0.064	0.058	0.061	0.059
6.0 *N*	0.057	0.055	0.049	0.055	0.051	0.052	0.052

[a] × 3 Scale expansion.

TABLE V

DETERMINATION OF PLATINUM IN SYNTHETIC MIXTURES

Synthetic mixtures (chlorides)	*Concentration of Pt (p.p.m.)*	*Burner height (cm)*	*% Absorbance (×3)*	*Absorbance*
Standard	25	1.0	10.5	0.016
2000 p.p.m. Fe + 2000 p.p.m. Cu + 2000 p.p.m. Ni	25	1.0	10.9	0.016
Standard	100	1.0	39.5	0.062
2000 p.p.m. Fe + 2000 p.p.m. Cu + 2000 p.p.m. Ni	100	1.0	41.5	0.065
Standard	25	2.0	11.5	0.017
100 p.p.m. Au, Pd, Rh, Ru + Ir	25	2.0	11.4	0.017
Standard	100	2.0	40.8	0.064
100 p.p.m. Au, Pd, Rh, Ru + Ir	100	2.0	40.2	0.063

TABLE VI

DETERMINATION OF PLATINUM IN A PRECIOUS METAL CONCENTRATE[a]

Weight of sample	*Pt found (mg)*	*Pt (%)*	*Deviation from mean*
0.1950	2550	1.31	+ 0.04
0.2210	2530	1.14	− 0.13
0.2208	2715	1.23	− 0.04
0.2349	3175	1.35	+ 0.08
0.2089	2675	1.28	+ 0.01
0.2436	3150	1.29	+ 0.02
Mean value		1.27 ± 0.05	
ZACHARIASEN AND BEAMISH[5]		1.21	
Falconbridge Nickel Mines Ltd.		1.36	

[a] × 5 Scale expansion.

Determination of platinum

The atomic-absorption determination of platinum with nitrous oxide–acetylene flames is very feasible. Admittedly, the method is not as sensitive as the other atomic-absorption procedures (Part I), but it has the distinct advantage of eliminating all potential interferences; other noble metals in high concentrations are also tolerated. Platinum was determined in synthetic samples of noble metals and some base metals

(Table V); with a larger scale expansion (× 5), 5–10-p.p.m. concentrations of platinum could easily be estimated.

With the same precious metal concentrate samples prepared in Part I, the platinum content was estimated with the nitrous oxide flame. Because of the lower sensitivity, determinations were done on the concentrated sample solutions; the mean value of 1.27 ± 0.05% (see Table VI) again agrees favourably with 1.21% obtained by ZACHARIASEN AND BEAMISH[5] and 1.36% by Falconbridge Nickel Mines Ltd.

The special loan of the nitrous oxide burner by the Varian Instrument Division, Malton, Ontario for this research, is appreciated.

SUMMARY

Platinum can be successfully determined by atomic absorption spectroscopy with nitrous oxide–acetylene flames. Although the sensitivity is less than that obtained with air–acetylene flames, all potential interferences are eliminated; high concentrations of precious metals are tolerated.

RÉSUMÉ

Le platine peut être dosé par spectroscopie par absorption atomique, avec des flammes oxyde nitreux–acétylène. Bien que la sensibilité soit inférieure à celle obtenue avec des flammes air–acétylène, toutes les interférences potentielles sont éliminées; de fortes concentrations de métaux précieux sont tolérées.

ZUSAMMENFASSUNG

Platin kann durch Atomabsorptionsspektroskopie mit Distickstoffoxid–Acetylen-Flammen gut bestimmt werden. Obwohl die Empfindlichkeit geringer als die bei Luft–Acetylen-Flammen ist, werden alle potentiellen Störungen ausgeschaltet; es können hohe Konzentrationen an Edelmetallen vorliegen.

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COMPLEX EXTRACTION OF VANADIUM FOR ATOMIC ABSORPTION SPECTROSCOPY

DETERMINATION OF MICROGRAM QUANTITIES OF VANADIUM IN LAKE WATERS

Y. K. CHAU AND K. LUM-SHUE-CHAN
Canada Centre for Inland Waters, Burlington, Ontario (Canada)

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Several methods for the determination of vanadium are available, including spectrophotometric, spectrographic and polarographic techniques. Early atomic absorption methods[1-3] were not sensitive. Application of the nitrous oxide–acetylene flame[4] and of complexing agents[5] provided better sensitivities; 0.8 mg/ml and 1.0 mg/ml of vanadium could be determined by the additions of aluminum ion and diethylene glycol to aqueous solution, and by extraction of vanadium with cupferron in methyl isobutyl ketone (MIBK), respectively. CRUMP-WIESNER AND PURDY[6] evaluated eight chelating agents for extraction of vanadium into MIBK and found cupferron to be most satisfactory.

The biochemical and physiological roles of vanadium in biological systems are not fully understood. In the aquatic environment it is well known that certain ascidians and tunicates concentrate vanadium[7]. A concentration factor of 280,000 times has been found in marine organisms compared to sea water[8]. In recent years there has been an increasing interest in the study of vanadium as a biologically active trace element.

Under normal aerobic conditions, vanadate is the thermodynamically most probable species in natural waters although vanadyl cation has been detected at a level of *ca.* 1% of the total vanadium[9]. Vanadium(III) exists in extremely low concentration in natural waters except for unusual waters with very high acidity.

Vanadium forms a number of complexes extractable into organic solvents, and this allows concentration of vanadium from a very dilute solution. The present paper describes the investigation of 13 chelating agents for atomic absorption spectroscopy of vanadium and the development of a method for the determination of trace amounts of vanadium in lake waters.

EXPERIMENTAL

Apparatus

A Jarrell-Ash atomic absorption spectrophotometer (model 820-528) equipped with a "Triflame" burner (5-cm path) for nitrous oxide was used. The gas supplies were 30 psi for nitrous oxide and 15 psi for acetylene. Slits were 100 μ and 150 μ, respectively, for entrance and exit. The spectral source was a Westinghouse hollow-cathode lamp operated at 12.5 mA. The 3184 Å vanadium line was used. The output was coupled to a Coleman-Hitachi recorder (model 165) operated at 10 × expansion.

A Nuclear-Chicago γ-counting system (model 4454) with a thallium-activated NaI well was used to measure the ^{48}V activity.

Reagents

All chemicals used were analytical grade. Solvents were distilled. Water was double-distilled from an all-glass apparatus.

Vanadium(V) standard solution (100 μg/ml) was prepared by dissolving 0.2296 g of ammonium vanadate in water and diluting to 1 l. A working solution (10 μg/ml) was prepared fresh daily by dilution.

Vanadium(IV) solution (100 μg/ml) was made by warming 0.0177 g of vanadium pentoxide with *ca.* 10 ml of concentrated hydrochloric acid until the solution turned blue. The solution was evaporated almost to dryness and diluted to 100 ml in a volumetric flask.

Vanadium(III) solution (100 μg/ml) was prepared by warming an aliquot of vanadium(V) solution with a piece of mossy zinc until the color changed to green. This solution is oxidizable by air and should be made fresh when required.

A 0.3%(w/v) solution of 5,7-dichloro-oxine in *n*-butyl acetate was used.

^{48}V solution (as dioxovanadium chloride), carrier free, was supplied by Radiochemical Centre, Amersham, England. A solution of 0.1 μC/ml containing 1 μg V/ml as carrier was used for tracer experiments.

Acetate buffer contained 50 ml of 0.2 *M* sodium acetate and 950 ml of 0.2 *M* acetic acid.

Vanadium-free lake water was prepared by passing the filtered lake water which was adjusted to pH 5 through a Chelex-100 column[10]. No vanadium was detected in 1 l of this stripped water when it was used as blank by the present method.

Extraction procedures

Aliquots (1 ml) of vanadium(V) solution containing 10 μg of vanadium and 3 ml of acetate buffer were diluted to *ca.* 15 ml and the pH was adjusted to suitable values by dilute sulfuric acid. The solution was diluted to 20 ml and equilibrated for 15 min with 10 ml of MIBK containing different chelating agents. The organic layer was separated and aspirated into the flame to compare the absorption intensity.

Experiments on pH dependence of extraction were carried out with 100 ml of distilled water, spiked with an appropriate amount of ^{48}V and 10 μg V as carrier. After addition of 5 ml of acetate buffer, the solution was adjusted to various pH values by dilute sulfuric acid or ammonia and equilibrated with 5 ml of 0.3% dichloro-oxine for 15 min in a mechanical shaker. The separated organic phase was made up to 5 ml with pure MIBK in a volumetric flask to compensate for the variation in solubility of the solvent in solutions of different acidity. A 3-ml aliquot was pipetted for scintillation counting of the γ-activity against a suitable aliquot of standard. Similar experiments were carried out with vanadium-free lake water.

Interference studies

Vanadium-free lake water was used in order to provide a uniform ionic concentration for extraction. A 100-ml aliquot of lake water spiked with 5 μg of vanadium(V) and 1000 μg of each of the interfering ions was extracted as detailed above but at pH 2.8–3.2. The absorption signals of the organic extracts were compared with a control spiked with vanadium only.

RESULTS AND DISCUSSION

Extraction of vanadium complexes

Thirteen chelating agents different from those studied by CRUMP-WIESNER AND PURDY[6] were investigated for their extraction efficiency and flame behavior with the nitrous oxide–acetylene mixture. Their relative absorption intensities are listed in Table I; the optimal extraction pH for each reagent as described in the literature was used. For those that have not been reported previously, a pH value of 2–3 was used as the extractable species of vanadium are generally in the cationic form[11].

TABLE I

ABSORPTION INTENSITY OF SOME VANADIUM COMPLEXES

Chelating agent	*Absorption (% A)*	*Concentration of chelating agent*[a]	*pH at extraction*
Cupferron[5]	12	5 ml aq. 1 %	2–2.5
Diaminobenzidine[12]	n.s.[b]	2 ml aq. 0.2 %	1
Acetylacetone[14]	2	3 ml	2
Benzoylphenylhydroxylamine[15]	5	0.2%	2–3
2-Methyl-8-hydroxyquinoline[13]	7	1 %	4–5
1-(2-Pyridylazo)-2-naphthol[16]	5	0.1 % in ethanol	3.5–4.5
Oxine[5]	10	1 %	2–3
APDC[17]	17	5 ml aq. 1 %	1–2
Dichloro-oxine	15	0.3%	3–3.5
Diiodo-oxine	14	0.3%	3–3.5
Dibromo-oxine	14	0.3 %	3–3.5
Thio-oxine	n.s.	0.5 %	3–3.5
Dithizone	n.s.	0.5 %	3–3.5
Dibenzoylmethane	3	1 %	3–3.5
Thenoyltrifluoroacetone	3	0.5 %	2–3
Dimethylglyoxime	n.s.	1%	2–3

[a] All chelating agents were dissolved in MIBK or specified otherwise; 10 ml of MIBK was used for extraction.

[b] No signal obtained.

Of the ligands studied, four gave no signal (Table I) probably because no complex was formed or the complexes formed were not extractable in the solvent used. The APDC complex showed very sensitive absorption, but its rapid precipitation in MIBK[6] seriously limited its application. Attempts to stabilize the APDC complex by changing the solvent to methyl amyl ketone, butyl acetate and isopropyl ether failed; addition of acetic acid or pyridine to the extract also failed.

The dihalo-substituted oxinates of vanadium gave the best extraction efficiency and absorption intensity. However, the low solubility of dibromo-oxine in organic solvents caused clogging of burner once it became hot. Diiodo-oxine was unstable; the reagent decomposed to liberate iodine even when shaken vigorously with solvent.

Dichloro-oxine was the only one that satisfied both extraction efficiency and absorption sensitivity and caused no trouble in the nitrous oxide–acetylene flame when a 0.5% solution was sprayed. The dichloro-oxinate complex was chosen for further studies.

Extraction of vanadium as dichloro-oxinate

The effect of pH on the extraction of vanadium(V) by dichloro-oxine in MIBK indicated that maximum extraction of the complex occurred at pH 2–4.5. The recovery of 10 μg of V from 100 ml of solution was 96±2%. Increasing the concentration of the dichloro-oxine above 0.5% in MIBK did not improve the recovery further. Increase of chelating agent concentration increases the extraction efficiency and hence the absorption until a point is reached when the effect on aspiration rate due to change of viscosity becomes more significant; at this stage, there is a decrease in absorption. This effect was observed for solutions of dichloro-oxine greater than 0.5% in MIBK; at this concentration, an emulsified layer developed. For 5–50 μg of vanadium in 100 ml solution, 5 ml of 0.2–0.3% dichloro-oxine was optimal. A shaking time of 15 min sufficed under these conditions; prolonged shaking did not improve the yield.

The solvent effect was also studied by dissolving the dichloro-oxine in various organic solvents. After extraction, the organic layer was made up with the respective solvent to 5 ml to compensate for the difference in solubility of each solvent. Among MIBK, butyl acetate, *n*-butyl alcohol, methyl amyl ketone, amyl acetate, *n*-amyl alcohol, isopropyl ether, isoamyl alcohol and 1,2-dichloroethane, MIBK and butyl acetate gave the best sensitivity. Butyl acetate was chosen because it gave a steadier base line than MIBK, especially when the burner became hot. Another advantage with butyl acetate was its low solubility in water (0.7 ml/100 ml); the volume change after extraction was thus less pronounced than with MIBK (*ca.* 2 ml/100 ml).

After extraction, the organic phase can be carefully separated into a volumetric flask and adjusted to a definite volume, or the extract can be aspirated directly into the flame. When a large volume of aqueous phase must be extracted with a small organic phase, the latter method is preferable. Provided that the volume and the pH of the solution are well controlled for both samples and standard, the organic phase after extraction is quite reproducible and can be directly aspirated after centrifugation. Quantitative separation of phases can thus be avoided.

Extraction of vanadium(IV) and vanadium(III)

Under the optimal conditions for extraction of vanadium(V), vanadium(IV) at similar concentration level (5 μg V/100 ml) was also extracted completely. The extraction of vanadium(III) was not quantitative under the present conditions; its extraction yield increased from 68% to 90% with increase of shaking times from 10 to 45 min, but times up to 5 h did not then improve the recovery. The vanadium(III), -(IV) and -(V) dichloro-oxinate complexes had the same color and ultraviolet spectra. The extracted complex absorbed strongly at 406 nm and could be used as a spectrophotometric method for vanadium.

Stability of vanadium dichloro-oxinate

The stability of the vanadium dichloro-oxinate complex was investigated. The complex was brownish in color in both MIBK and butyl acetate and was stable in both solvents. No change in color and no deterioration in absorption intensity occurred in a period of up to two weeks.

The cupferrate of vanadium has been the most recommended complex for atomic absorption of vanadium. This complex, however, was found to decompose at different rates depending on the pH of the extraction and solvents used. Vanadium(V) cupferrate extracted at pH 1 into MIBK decomposed rapidly in *ca.* 45 min, probably because of the instability of cupferron itself; at pH 3, the extracted complex was stable for *ca.* 2 h.

Interferences

The behavior of dichloro-oxine is in many ways analogous to oxine, hence several metals would be expected to form complexes and be co-extracted. In the determination of 10 μg of V in 100 ml of spiked lake water samples, no interference in absorption signal was observed in the presence of 1000 μg of each of the following ions: Na, Ca, Cu, Mg, Ni, Pb, Zn, Mn(II), Al, Bi, Cr(III), Mo(VI) and Sb. Cr(VI), Fe(III), Sn(IV) and W(VI) suppressed absorption seriously; several masking agents were tried but only ascorbic acid was satisfactory in eliminating the interferences of iron and chromium. With 5 ml of 2% ascorbic acid, up to 1000 μg of Cr(VI), 100 μg Sn(IV) and 250 μg Fe(III) could be tolerated. No masking agent was found effective for tungsten. In the determination of 10 μg of V in 100 ml solution, up to 50 μg of W(VI) could be tolerated; higher levels are unlikely to occur in natural waters or biological materials.

Calibration curve

Various amounts of vanadium were added to 100 ml of stripped lake water and extracted with 3 ml of dichloro-oxine in butyl acetate. The plots of absorption signals *vs.* concentration were linear up to at least 10 μg of V, hence the extraction yield in this concentration range was constant. The sensitivity of vanadium dichloro-oxinate in butyl acetate was calculated to be 0.13 μg V/ml for a 2% absorption signal. When this extraction is applied to the analysis of vanadium in various materials, the sensitivity can be increased further by using a larger sample and also reducing the volume of the organic phase for extraction.

DETERMINATION OF VANADIUM IN LAKE WATERS

The natural occurrence of vanadium is *ca.* 0.5–5 μg/l in sea water and is quite variable in the lakes. A large sample has to be used to obtain reliable analysis. To test the validity of dichloro-oxine as a complexing agent to concentrate vanadium from a large volume, appropriate aliquots of ^{48}V and 5 μg of V as carrier were spiked to different volumes of stripped lake water. The solutions were processed as described above except that larger amounts of organic solvent were used to compensate for its solubility. The concentration of the extractant was so adjusted that the final concentration of dichloro-oxine did not exceed 0.5%. Shaking time was accordingly prolonged. After separation, the organic layer was carefully drained and the separatory funnel was washed with butyl acetate into a 5-ml volumetric flask. A 3-ml aliquot was counted and compared to a standard to calculate the recovery. For extraction of 5 μg of V from 500 and 1000 ml of lake water, radiometric recoveries of 93% and 92% were obtained.

Spiking of different volumes of stripped lake water showed that excellent agreement could be achieved between different volumes, provided that the calibration graph for atomic absorption measurements was prepared in a similar way (Table II).

TABLE II

RECOVERY OF VANADIUM(V) FROM VARIOUS VOLUMES OF STRIPPED LAKE WATER

Volume of water (ml)	*Vanadium added (μg)*	*Vanadium found (μg)*	*Recovery (%)*
100[a]	3.0	3.07	102
100	5.0	5.00	100
500[b]	3.0	2.95	98
500	5.0	4.90	98
1000[c]	3.0	2.95	98
1000	5.0	4.90	98

[a] 3 ml of 0.3% dichloro-oxine in butyl acetate used; shaking time 15 min.
[b] 5 ml of 0.1% dichloro-oxine in butyl acetate used; shaking time 30 min.
[c] 9 ml of 0.1% dichloro-oxine in butyl acetate used; shaking time 30 min.

Recommended procedure

Filter the sample through a membrane (0.5 μ) immediately after collection. The sample may be acidified if it is intended for other trace element analyses. Measure accurately 1 l of sample into a 1000-ml separatory funnel, and add 5 ml of acetate buffer and 5 ml 2% ascorbic acid. After adjustment of the pH to 2.8–3.2, equilibrate the mixture with 9 ml of 0.1% dichloro-oxine in butyl acetate for 30 min in a mechanical shaker. Leave the solution for 30 min to allow the phases to separate. Drain off the aqueous phase slowly until *ca.* 5–6 ml is left with the organic phase, then drain the mixture into a centrifuge tube, and centrifuge to facilitate separation. Aspirate the organic extract from the centrifuge tube without separation.

Since the stripped lake water contains no detectable vanadium and always shows zero absorption reading, the blank may be conveniently prepared by running the complete procedure with 1 liter of distilled water. Calibrate the method by spiking 2 μg of vanadium to 1 l of vanadium-free lake water and taking it through the entire process.

RESULTS

The precision of the method was tested by four analyses of 500-ml and 1000-ml lake water samples spiked with 5 μg of vanadium. The coefficients of variation were 1.30% and 2.05%, respectively, for 500- and 1000-ml samples. Other analyses (5) on 1-l samples of a surface sample taken from Lake Ontario near Hamilton Bay showed an average vanadium content of 0.50 ± 0.05 μg/l.

The sensitivity of the method applied to lake water analysis was calculated from the calibration control. For a 5-μg spike in 1 l of lake water (5 p.p.b.), the absorbance obtained was 0.164 (31.5%); the sensitivity was 0.27 μg (0.27 p.p.b.) for a signal of 0.0088 (2% absorption).

Storage of samples

Radiometric investigation indicated that there was no appreciable loss of vanadium in filtered lake water samples when stored in pyrex glass, polyethylene and polypropylene containers at its natural pH of *ca.* 8 or at pH 2. Its stability in sea water was reported by CHAN AND RILEY[18].

SUMMARY

Thirteen chelating agents have been investigated for their suitability for extraction of vanadium for atomic absorption spectroscopy. Dichloro-oxine was found to extract vanadium(IV), vanadium(V) and 90% of vanadium(III). The complex formed was very stable and gave high sensitivity for atomic absorption. A method combining extraction and atomic absorption has been developed for the determination of vanadium in lake water with a sensitivity of 0.3 p.p.b.

RÉSUMÉ

Treize réactifs de chélation ont été examinés en vue de l'extraction du vanadium pour spectroscopie par absorption atomique. La dichloro-oxine permet d'extraire vanadium(IV), vanadium(V) et 90% de vanadium(III). Les complexes formés sont très stables et permettent d'arriver à des grandes sensibilités pour l'absorption atomique. Une méthode combinant extraction et absorption atomique est proposée pour le dosage du vanadium dans l'eau des lacs, avec une sensibilité de 0.3 p.p.b.

ZUSAMMENFASSUNG

Dreizehn chelatbildende Angenzien sind auf ihre Anwendbarkeit auf die Extraktion von Vanadin für die Atomabsorptionsspektroskopie untersucht wurden. Dichloroxin extrahiert Vanadin(IV), Vanadin(V) und 90% von Vanadin(III). Der gebildete Komplex ist sehr stabil und ergibt bei der Atomabsorption eine hohe Empfindlichkeit. Es wurde ein kombiniertes Verfahren der Extraktion und Atomabsorption entwickelt für die Bestimmung von Vanadin in Seewasser mit einer Empfindlichkeit von 0.3 p.p.b.

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A COMPARISON OF THE USE OF CUPFERRON AND OXINE IN THE SUBSTOICHIOMETRIC DETERMINATION OF MOLYBDENUM BY NEUTRON ACTIVATION

N. K. BAISHYA AND R. B. HESLOP
Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester 1 (England)

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Molybdenum has been determined by radiochemical methods in various materials such as rocks[1] and alloys[2]. These methods all depend on the isolation of radiochemically pure molybdenum and the determination of its chemical yield. In some of these methods[3] α-benzoinoxime was used to precipitate molybdenum to give a gravimetric finish. Extraction with α-benzoinoxime in chloroform[4], which is claimed to be more reliable than an ion-exchange separation[5], has also been used in the determination of molybdenum-99 in fission products.

The substoichiometric principle was applied by RŮŽIČKA AND STARÝ[6] to simplify the time-consuming separation procedure and eliminate the necessity for determining the chemical yield in activation analysis. Using this substoichiometric principle, STARÝ, ZEMAN AND RŮŽIČKA[7] determined traces of molybdenum by neutron activation analysis in semiconductor-grade germanium dioxide. They used a solution of 8-hydroxyquinoline in chloroform to extract molybdenum substoichiometrically. RŮŽIČKA AND STARÝ[8], in a critical discussion of the conditions for substoichiometric determination of twenty-four metals, drew attention to the possibility of using cupferron for isotope dilution analysis of molybdenum.

In the present work, we have studied the substoichiometric determination of molybdenum, using both 8-hydroxyquinoline and cupferron. In repeating the work of RŮŽIČKA, ZEMAN AND STARÝ, it was found that under their conditions molybdenum oxinate was precipitated from 1 ml of 0.1 M solution when extracted with 3 ml of 0.02 M oxine in chloroform. This was confirmed by radiometric determination of the solubility of molybdenum oxinate in chloroform, which is $3 \cdot 10^{-3}$ mole l^{-1} independent of the pH of the aqueous phase, in agreement with the value given in the literature[9]. Furthermore, the count-rate on the chloroform extract of molybdenum oxinate increased fairly rapidly for several hours, making it impossible to obtain consistent values. A study showed that the count-rate varied least with time after about 24 h, the time required for the ratio ^{99m}Tc/^{99}Mo to reach a constant value. It was found most satisfactory to keep extracts for a full day before the count-rate was measured.

Cupferron extraction of molybdenum with chloroform gave results similar to those with oxine. In both cases a reproducible substoichiometric extraction was possible when the organic extract was counted 24 h after the completion of extraction.

On the basis of this, methods have been developed to determine molybdenum in germanium dioxide, by means of liquid extraction with substoichiometric amounts of either 8-hydroxyquinoline or cupferron; this simplifies radiochemical purification and avoids the need for the determination of chemical yield. The optimum condition of pH has been studied in each case and the extent of interference by other metal ions has been compared.

EXPERIMENTAL

Reagents

Chloroform. A.R. grade chloroform was used as the solvent for extraction.

8-Hydroxyquinoline reagent. A 0.001 *M* solution of 8-hydroxyquinoline was prepared by dissolving 0.145 g of A.R. 8-hydroxyquinoline per litre of chloroform.

Cupferron reagent. A 0.005 *M* solution of cupferron was prepared by dissolving 0.0775 g of A.R. cupferron in 100 ml of distilled water. The reagent was prepared freshly every 2 weeks. A suggested method[10] of preparation by extracting a 0.1 *M* hydrochloric acid solution of cupferron with chloroform was not found to be useful because the solution was too unstable.

Ammonium molybdate solution. A solution of ammonium molybdate about 0.01 *M* with respect to MoO_4^{2-} was prepared by dissolving 1.7657 g of reagent-grade ammonium molybdate per litre of distilled water and was labelled with ^{99}Mo. All molybdate molarities mentioned in this paper refer to the MoO_4^{2-} ion.

Perchloric acid. A 70–72% A.R. perchloric acid was used.

Other inactive metal salts that were used for the study of interference were ammonium iron(III) sulphate, copper(II) sulphate, cobalt sulphate, nickel sulphate, manganese ammonium sulphate, aluminium sulphate, magnesium sulphate, palladium chloride, titanium chloride, zirconium nitrate, ammonium metavanadate and zinc sulphate. Chromium chloride was made by dissolving chromium metal in dilute hydrochloric acid.

Apparatus

A PYE model 79 pH meter was used with a glass electrode and a calomel reference electrode for pH measurement.

The γ-counting of ^{99}Mo was done by means of a Panax scintillation counter and a Panax P7102 scaler. Experiments were designed to give at least 10,000 counts so that the standard deviation did not exceed 1%.

Preliminary study of the decay of ^{99}Mo activity in the chloroform extract of its oxinate and cupferrate

A 0.01 *M* ammonium molybdate solution (1 ml), labelled with ^{99}Mo, was diluted to 5 ml, and the pH of the solution was adjusted to 1.3 with 2 *N* sulphuric acid. The molybdenum was extracted by shaking with 5 ml of 0.001 *M* oxine in chloroform for 10 min. After the two layers were separated, 2 ml of the organic layer was taken and its count-rate was measured. Counting on the same liquid was continued every 5 min. It was observed that count-rates continued to increase during the day and began to decrease slowly only after 24 h. Counting on the same liquid was continued for two weeks. A plot of count-rate against time shows the growth of ^{99}Mo activity until the ratio $^{99m}Tc/^{99}Mo$ reaches a constant value. The activity then decays according to the half-life of ^{99}Mo ($t_{\frac{1}{2}} = 67$ h).

In another experiment, 1 ml of 0.01 *M* ammonium molybdate was taken and diluted to 5 ml. The addition of 1 ml of 70–72% perchloric acid adjusted the pH to about 0.3. Cupferron (1 ml of 0.005 *M* aqueous solution) was added, followed by 5 ml of chloroform. The solution was then shaken for 5 min, 2 ml of the organic layer was taken and the count-rate was measured, in the same way as above, for several days.

The time of attainment of maximum activity given, according to theory, by

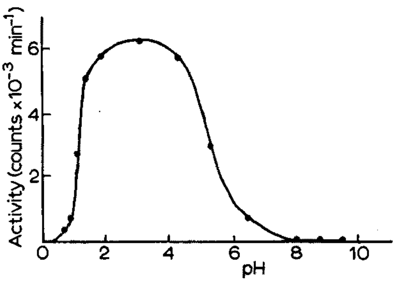
$$t_{max}=2.303/(\lambda_2-\lambda_1)\log\lambda_2/\lambda_1,$$

where λ_1 and λ_2 are the decay constants for the long- and short-lived radioactive isotopes (in this case ^{99}Mo and ^{99m}Tc respectively), gave a value of 22.95 h which agreed closely with the experimentally observed time.

Experiments were therefore designed so that the count-rate of the organic extract was measured 24 h after extraction.

Effect of pH on the substoichiometric extraction of molybdenum with (a) oxine and (b) cupferron in chloroform

(*a*) In a series of solutions containing 1 ml of 0.01 *M* ammonium molybdate, labelled with ^{99}Mo, and diluted to 5 ml, the pH was adjusted within the range 0.5–10 with sulphuric acid or ammonia. Each solution was then shaken for 10 min with 5 ml of 0.001 *M* oxine in chloroform. After allowing the two layers to separate, 2 ml of the organic layer was taken and the count-rate was measured after 24 h. A plot of count-rate against pH is shown in Fig. 1.



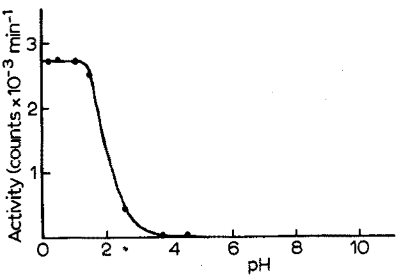


Fig. 1. Substoichiometric extraction of molybdenum with oxine in chloroform: dependence on pH.

Fig. 2. Substoichiometric extraction of molybdenum with cupferron in chloroform: dependence on pH.

(*b*) In a similar set of experiments, a series of solutions at different pH were treated with 1 ml of 0.005 *M* cupferron and then shaken with 5 ml of chloroform for 5 min; the count-rate on 2 ml of the organic layer in each case was measured after 24 h. Figure 2 shows the variation of count-rate with pH.

In subsequent experiments the extraction of molybdenum as oxinate was carried out at pH 1.3. Although a more efficient extraction was achieved at rather higher pH (Fig. 1) it was found that interference of other metals was less at pH 1.3. The pH used in the extractions with cupferron was about 0.3. Again the low pH reduced the interference of other metals.

Reproducibility of substoichiometric extraction

Reproducibility of substoichiometric separation was tested by adjusting to

1.3 the pH of a series of 0.002 *M* ammonium molybdate solutions, labelled with ^{99}Mo, and extracting each for 10 min with 5 ml of 0.001 *M* oxine in chloroform. In each case the count-rate on 2 ml of the organic layer was measured after 24 h. The reproducibility curve obtained by plotting count-rate against volume of 0.002 *M* molybdate is shown in Fig. 3a.

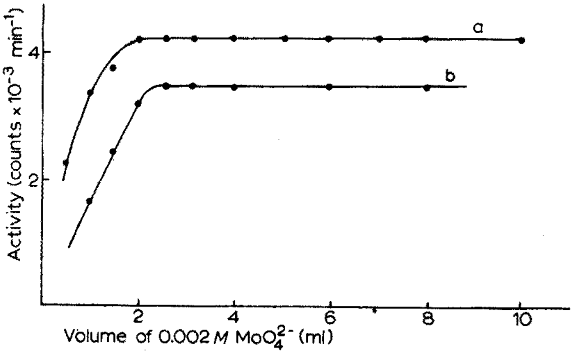


Fig. 3. Reproducibility of substoichiometric extraction of molybdenum (a) with cupferron and chloroform at pH 0.3, (b) with oxine and chloroform at pH 1.3.

A similar series of solutions of 0.002 *M* molybdate, labelled with ^{99}Mo were adjusted to pH 0.3 with perchloric acid. Each solution was treated with 1 ml of 0.005 *M* aqueous cupferron and was then shaken for 5 min with 5 ml of chloroform; the count-rate on 2 ml of the organic layer was measured after 24 h. A plot of count-rate against volume of 0.002 *M* molybdate gave the reproducibility curve shown in Fig. 3b.

Selectivity of substoichiometric separation

The selectivity of substoichiometric separation by solvent extraction with oxine and cupferron was studied with the same radioactive isotope, ^{99}Mo.

A solution of 0.01 *M* molybdate (1 ml), labelled with ^{99}Mo, was substoichiometrically extracted with 8-hydroxyquinoline at pH 1.3 or with cupferron at pH 0.3 in the absence and in the presence of iron, copper, cobalt, nickel, manganese, aluminium, chromium, magnesium, titanium, zirconium, vanadium, palladium and zinc, in a number of different concentration ratios to the test metal (Table I). Triplicate experiments were carried out in each case.

The interference of iron(III) was removed by reducing to iron(II). To 1 ml of 0.01 *M* molybdate, labelled with ^{99}Mo, was added sufficient iron(III) to make the ratio $[Fe^{3+}]/[Mo]=5$. The pH of the solution was adjusted to 1.3 for the extraction with oxine or to 0.3 for the extraction with cupferrate. The solution was then treated with ammonium iodide (*ca.* 30 mg) or sodium thiosulphate (*ca.* 35 mg); for the cupferron extraction, ascorbic acid (*ca.* 50 mg) was also examined. The resulting solution was then extracted in the usual way with oxine or cupferron and chloroform. The results are shown in Table II.

Determination of molybdenum in germanium dioxide

Silica tubing of 4 mm internal diameter was used for sealing the sample and

TABLE I

THE EFFECT OF OTHER METAL IONS ON THE EXTRACTION OF MOLYBDENUM BY A SUBSTOICHIOMETRIC AMOUNT OF OXINE AND CUPFERRON IN CHLOROFORM[b]

Interfering element	*Oxine extraction*			*Cupferron extraction*		
	Activity isolated in absence of diverse ion (counts min^{-1})	*Activity[a] isolated in presence of diverse ion (counts min^{-1})*	*% Interference*	*Activity isolated in absence of diverse ion (counts min^{-1})*	*Activity isolated in presence of diverse ion (counts min^{-1})*	*% Interference*
Fe(III)	3451	a 2809	18	3281	a 2337	29
	3041	b 2780	8	4197	b 3628	14
	2988	c 2995	—	3943	c 3896	—
Cu(II)	3451	a 3181	8	3281	a 3183	—
	3041	b 2737	10	4197	b 4244	—
	2988	c 2949	—	3943	c 3921	—
Co(II)	3959	a 3876	—	3281	a 3275	—
	4314	b 4337	—	4197	b 4271	—
	4199	c 4212	—	3943	c 3959	—
Ni(II)	3451	a 3410	—	3281	a 3189	—
	4314	b 4263	—	4197	b 4206	—
	4199	c 4114	—	3054	c 3050	—
Mn(II)	3951	a 3805	—	3281	a 3275	—
	3557	b 3626	—	4197	b 4074	—
	4199	c 4071	—	3943	c 3915	—
Al(III)	3951	a 4028	—	2646	a 2576	—
	1921	b 1944	—	4197	b 4236	—
	4199	c 4090	—	3943	c 3841	—
Cr(III)	2268	a 1698	25	2264	a 2262	—
	2268	b 1958	14	2264	b 2360	—
	2268	c 2003	12	2264	c 2270	—
Mg(II)	3451	a 3487	—	2937	a 2888	—
	3557	b 3551	—	2937	b 2971	—
	4199	c 4083	—	2937	c 3001	—
Pd(II)	10,524	d 6890	34	2478	d 2421	—
	10,524	e 9489	10	2478	e 2464	—
Ti(IV)	6617	a 2549	62	2211	a 513	77
	6617	b 5360	19	2211	b 923	58
	6617	c 6388	—	2211	c 1290	42
Zr(IV)	6617	a 5520	16	2211	a 0	100
	6617	b 6411	—	2211	b 17	100
	6617	c 6463	—	2211	c 24	100
V(V)	6617	a 6611	—	4000	a 2980	28
	6617	b 6560	—	4000	b 3892	—
	6617	c 6644	—	4000	c 3948	—
Zn(II)	2629	a 2600	—	3281	a 3243	—
	2629	b 2689	—	4197	b 4136	—
	2629	c 2685	—	3943	c 3873	—

[a] a = [M]/[M$_0$] ratio = 5, b = [M]/[M$_0$] ratio = 1, c = [M]/[M$_0$] ratio = 0.2, d = [M]/[M$_0$] ratio = 0.5, e = [M]/[M$_0$] ratio = 0.1.

[b] The absence of a figure in the 4th or the last column indicates that the two activities were within the range of statistical error.

TABLE II

THE REMOVAL OF THE INTERFERENCE OF IRON(III) IN THE EXTRACTION OF MOLYBDENUM AS OXINATE OR CUPFERRATE

Activity in absence of Fe^{3+} *(counts* min^{-1}*)*	*Activity in presence of* Fe^{3+} *(counts* min^{-1}*)*	*Activity after reduction with* NH_4I *(counts* min^{-1}*)*	*Activity after reduction with* $Na_2S_2O_3$ *(counts* min^{-1}*)*	*Activity after reduction with ascorbic acid (counts* min^{-1}*)*
Extraction as oxinate				
3935	3770	4007	4009	—
3097	2901	3166	3131	—
Extraction as cupferrate				
3532	2194	3609	3519	—
1948	1347	1957	2030	—
3278	1937			3243
2206	1493			2284

the standard for irradiation. The tubes were cleaned thoroughly by rinsing with concentrated nitric acid, distilled water and alcohol, and then dried and cooled in a desiccator. Samples of germanium dioxide (400–500 mg) and ammonium molybdate standard (20–40 mg) were carefully weighed and sealed in silica tubes and irradiated together for 30 h in a neutron flux of $3 \cdot 10^{12}$ n cm^{-1} sec^{-1}. Earlier experiments with a smaller weight of the sample (100–200 mg) and a shorter time of irradiation (8 h in a neutron flux of $3 \cdot 10^{12}$ n cm^{-1} sec^{-1}) did not give satisfactory results.

Irradiated samples were allowed to decay for 2 days to avoid counting ^{93}Mo ($t_{\frac{1}{2}} = 6.9$ h) and to ensure equilibration of ^{99}Mo with its daughter ^{99m}Tc.

For the standard active solution, a weighed amount of irradiated ammonium molybdate was dissolved in water and made up to 500 ml. A 10-ml aliquot of this solution was transferred to a 1-l flask containing 1.765 g of inactive ammonium molybdate as carrier. The solution so prepared was 0.01 *M* with respect to molybdenum.

Oxinate method. The irradiated germanium dioxide sample was weighed and dissolved in 3 ml of 8 *M* sodium hydroxide. The solution was neutralized by the dropwise addition of *M* sulphuric acid until a white precipitate appeared which was dissolved by the addition of few drops more acid. Standard active solution (1 ml) was then added and the pH was adjusted to 1.3. The resulting solution was shaken with 5 ml of 0.0013 *M* oxine in chloroform for 10 min; 2 ml of the organic layer was taken and its count-rate (a_1) was measured after 24 h. The standard solution (1 ml) was treated in exactly the same way and the count-rate given by 2 ml of extract (a_s) was measured after 24 h.

Cupferrate method. Standard active molybdate solution (1 ml) was added to the germanium dioxide sample after dissolving and neutralising as described for the oxinate method. The solution was adjusted to pH 0.3 with 70–72% perchloric acid, treated with 1.5 ml of aqueous 0.005 *M* solution of cupferron and then shaken for 5 min with 5 ml of chloroform. The count-rate (a_1) on 2 ml of the organic extract was measured after 24 h. The standard solution (1 ml) was treated similarly and the count-rate (a_s) was measured in exactly the same way.

The quantity of molybdenum in both cases was calculated as follows. Since a_s is the count-rate obtained from the extraction of 1 ml of the standard + carrier, and

TABLE III

SUBSTOICHIOMETRIC DETERMINATION OF MOLYBDENUM IN GeO_2 BY ACTIVATION ANALYSIS, WITH OXINE AND CUPFERRON

	Weight of sample (g)	*Weight of Mo standard added (μg)*	*Activity a_1*[a] *(counts min⁻¹)*	*Activity a_s*[b] *(counts min⁻¹)*	*Activity of sample $a_1 - a_s$ (counts min⁻¹)*	*Amount of Mo found*	
						(ng)	*$(\cdot 10^{-5}\%)$*
Oxine method	0.4941	0.3184	293	243	50	65.6	1.327
	0.5224	0.3184	316	243	73	95.7	1.832
Cupferron method	0.4846	0.3184	277	221	56	80.7	1.665
	0.4949	0.3184	275	221	54	77.8	1.572

[a] a_1 is activity from sample with standard + carrier.
[b] a_s is activity from standard + carrier.

a_1 the count-rate obtained from the extraction of the sample together with 1 ml of the standard + carrier, the count-rate due to the sample is given by $a = a_1 - a_s$.

The weight of molybdenum in the sample is given by $y = y_s \cdot a/a_s$, where y_s is the weight of standard in 1 ml of prepared solution. The results obtained are shown in Table III. It was necessary to count the activity for 30 min. All activities are expressed in counts/min, corrected for the background.

Preliminary study on isotope dilution analysis of molybdenum using cupferron

The substoichiometric determination of molybdenum by isotope dilution based on the cupferron method was also studied. Preliminary experiments were found to be promising.

Thus, to a series of 1-ml samples of 0.01 *M* molybdate, labelled with ^{99}Mo, was added, respectively, 0.5, 1.0, 1.5, 2.0 or 3 ml of 0.01 *M* inactive molybdate. The total volume was made up to 5 ml in each case and the pH was adjusted to 0.3 with perchloric acid. Each of the resulting solutions was then extracted with cupferron and chloroform, and the count-rate was measured, as described above. The standard 0.01 *M* molybdate (1 ml) was treated in exactly the same way in the absence of inactive molybdate. The amount of molybdenum in the inactive sample is given by $w = w_s (a_s/a - 1)$, where w_s is the weight in the standard and a_s and a are the activity of the extract of the standard and the sample, respectively (Table IV).

However, traces of molybdenum, of the order of $10^{-5}\%$, in germanium dioxide could not be determined because the cupferron reagent at such dilution was found to be very unstable.

TABLE IV

SUBSTOICHIOMETRIC DETERMINATION OF MOLYBDENUM BY ISOTOPE DILUTION

Amount of Mo in standard (mg)	*Activity of standard (counts min⁻¹)*	*Amount of Mo used for dilution (mg)*	*Activity after dilution (counts min⁻¹)*	*Amount of Mo found (mg)*
0.9560	5522	0.4798	3890	0.4021
0.9560	5522	0.9596	2761	0.9560
0.9560	5522	1.4394	2188	1.4560
0.9681	9727	1.9192	3299	1.8860
0.9681	9727	2.8788	2331	3.0720

DISCUSSION

Extraction into chloroform with oxine was carried out at pH 1.3. Although more efficient extraction is possible at higher pH up to 4, it was found that many other metals interfere even below pH 2. The pH of 1.3, being critical, has to be maintained in all experiments with oxine to obtain a reasonable count-rate in the extract and at the same time to minimise interference. Iron, copper, chromium, titanium and zirconium in five-fold excess interfere in the extraction. These metals when present in only one-fifth the concentration of molybdenum do not interfere. Zirconium even in equal concentrations does not interfere.

In the extraction with cupferron, reproducible substoichiometric extraction was possible in the pH range 0–1.5 but a pH of 0.3 is to be preferred to reduce interference by other metals. Iron, titanium and zirconium interfere to a greater extent than in the oxinate method; vanadium also interferes but only when present in five-fold excess. The other metals studied, including copper, do not interfere even in five-fold excess. Because the pH for the extraction is less critical and there are fewer interferences, cupferron is, in general, to be preferred to oxine.

Iron(III) is extracted both by oxine and cupferron in chloroform. Reduction of iron(III) to iron(II), with ammonium iodide or sodium thiosulphate in the oxine method, and with one of these or ascorbic acid in the cupferron method, removes the interference.

The amount of molybdenum in germanium dioxide being very small, an activity only a little above the background is produced when a sample weighing 100 mg is irradiated for 8 h at a neutron flux of $3 \cdot 10^{12}$ n cm^{-1} sec^{-1}. A larger sample and a greater time of irradiation gave better results. For high-purity substances like germanium dioxide, the irradiation of a sample weighing 400–500 mg for 30 h at a neutron flux of $3 \cdot 10^{12}$ n cm^{-1} sec^{-1} is necessary to give reasonable precision.

Cupferron can also be used for the substoichiometric isotope dilution analysis of molybdenum when present in milligram quantities. But in such small concentrations as those present in germanium dioxide, isotope dilution is not satisfactory because of the instability of cupferron in very dilute solution.

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

SUMMARY

Extraction into chloroform with substoichiometric amounts of 8-hydroxyquinoline and cupferron has been used for the determination of molybdenum in germanium dioxide. The effect of interfering metal ions on both methods of extraction has been studied. A substoichiometric isotope dilution method with cupferron is feasible for milligram quantities of molybdenum but not for microgram quantities.

RÉSUMÉ

Une extraction dans le chloroforme, en présence de quantités substoechiométriques d'hydroxy-8-quinoléine et de cupferron, est utilisée pour le dosage du molybdène dans le dioxyde de germanium. On examine l'influence d'ions métalliques sur l'extraction. Une méthode substoechiométrique par dilution isotopique est possible pour le dosage de quantités de molybdène de l'ordre du milligramme, mais pas pour celles de l'ordre du microgramme.

ZUSAMMENFASSUNG

Die Extraktion mit Chloroform und unterstöchiometrischen Mengen an 8-Hydroxychinolin und Cupferron wurde auf die Bestimmung von Molybdän in Germaniumdioxid angewendet. Der Einfluss störender Metallionen auf beide Extraktionsmethoden wurde untersucht. Eine unterstöchiometrische Isotopenverdünnungsmethode mit Cupferron ist auf Milligram-Mengen von Molybdän anwendbar, nicht aber auf Mikrogramm-Mengen.

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DETERMINATION OF TRACES OF CHLORINE IN ORGANIC LIQUIDS A COMBUSTION-MICROCOULOMETRIC METHOD

W. LÄDRACH, F. VAN DE CRAATS AND (THE LATE) P. GOUVERNEUR*
Koninklijke/Shell-Laboratorium, Shell Research N.V., Amsterdam, (The Netherlands)

(Received January 31st, 1970)

Trace amounts of chlorine in organic compounds are often determined according to the Wickbold oxyhydrogen combustion method. After combustion of the sample the condensate is analysed for chloride ion, *e.g.* by potentiometric titration with silver nitrate solution or spectrophotometrically[1]. This method, though yielding satisfactory results, is rather time-consuming.

In view of the favourable experience previously gained with the Dohrmann microcoulometric system in determining trace amounts of nitrogen in organic products[2], it was thought worthwhile to study the applicability of this new and fast technique to the determination of chlorine. That a microcoulometric method is suitable for this type of analysis after combustion of an organic sample was demonstrated in 1960 by COULSON AND CAVANAGH[3]. BURCHFIELD *et al.*[4] used the microcoulometer as a (chloride, sulfur and phosphorus) detector in gas chromatographic studies of pesticide residues when the emerging fractions were subjected to hydrogenation. After the investigation described in the present paper had been completed, DRUSHEL[5] also reported on this subject.

GENERAL PRINCIPLE

The Dohrmann procedure is a microcoulometric method which enables the automatic performance of, for example, argentometric titrations, acid–base titrations and iodimetric titrations of nanogram quantities of titrand.

The argentometric titration cell discussed here contains a 70% acetic acid solution and has four electrodes, a sensing pair (silver *vs.* silver acetate) and a generating pair (silver *vs.* platinum). The concentration of silver ions in the cell can be adjusted by applying a bias potential across the sensing electrode pair. Any change in concentration (in this case caused by incoming hydrochloric acid) is detected by the sensing electrode pair as a potential difference which leads through the coulometer–amplifier to the generation of titrant ions (silver ions) at the generator electrode. The current required is recorded via a precision series resistance on a potentiometric recorder. The peak area, which is the current integral with the chart speed as the time

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* The Editors of *Analytica Chimica Acta* take this opportunity to express their deep sense of loss at the sudden and untimely death of PIET GOUVERNEUR on December 21st, 1969.

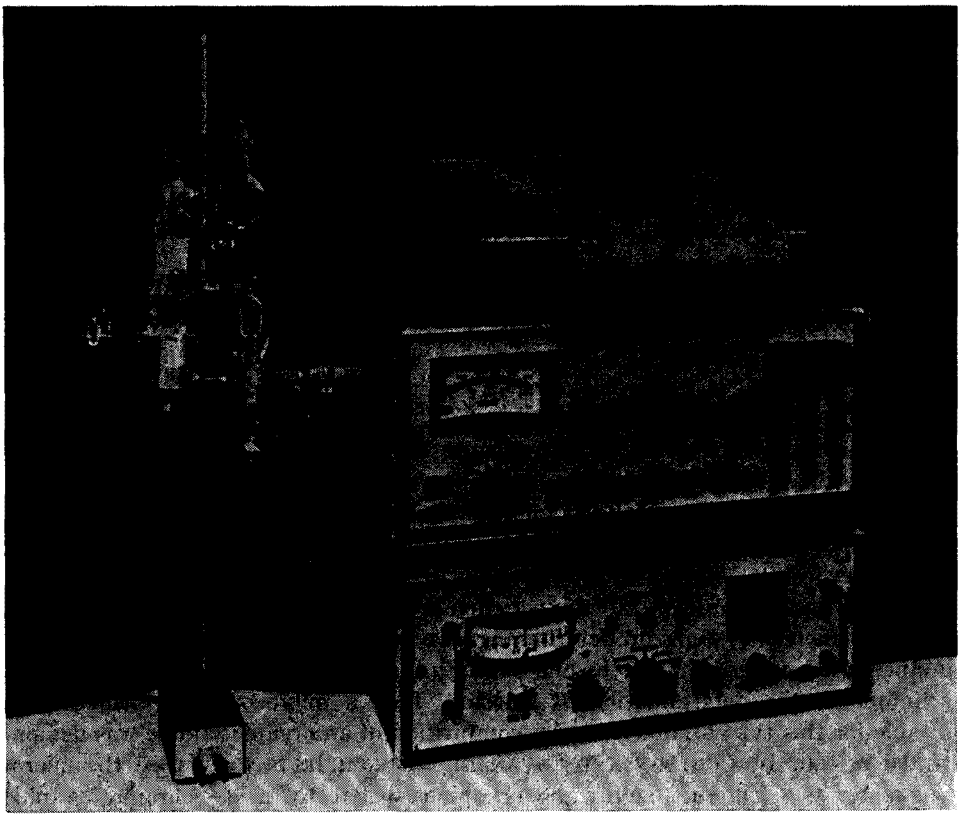

Fig. 1. Arrangement for the determination of trace amounts of chlorine.

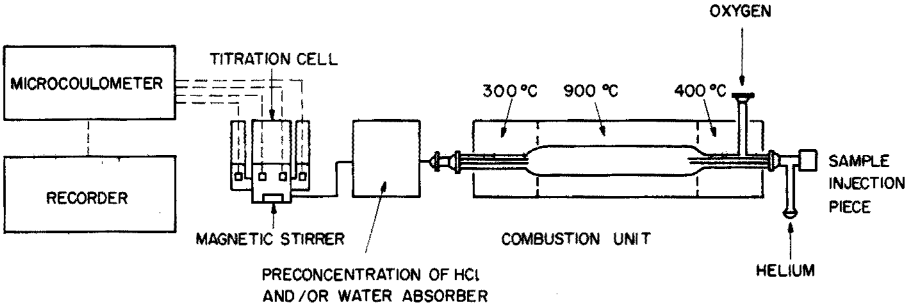

Fig. 2. Apparatus for microcoulometric chlorine determination.

basis, provides the quantity of electricity, in coulombs, required for the reaction. Combination with a suitable method of decomposing the organic sample makes it possible to obtain very rapid information; a qualitative result is produced almost at once whereas a quantitative calculation takes some more time. The apparatus is shown in Figs. 1 and 2.

DEVELOPMENT OF THE METHOD

Choice of decomposition method

Before the titration can be made the organic sample must be decomposed in such a way that the combined chlorine is converted into hydrochloric acid. This may in principle be effected by either hydrogenation or combustion of the sample. The latter method was chosen because the hydrochloric acid can then be titrated without interference from sulfur. (The disadvantage of hydrogenation is that sulfur is converted into hydrogen sulfide, which is also titrated in the silver cell.) Sulfur dioxide and sulfur trioxide resulting from the combustion do not interfere in the silver cell.

Combustion system

For the determination of the total chlorine content of a sample, the combustion must proceed uniformly and evenly, so that the combustion products are introduced into the titration cell neither discontinuously, nor as a "plug". Initially, an attempt was made to effect this by injecting the sample slowly into a stream of oxygen at 900°. This method, however, had the drawback that the needle of the syringe was damaged by the hot flame burning at its tip. The best results were obtained by vaporizing the sample in a stream of an inert gas (helium) and subsequently passing the resulting mixture of sample vapour and helium into a stream of oxygen, where it burnt with a fierce flame. The presence of a roll of platinum wire gauze was found not to be essential. For uniform combustion it is important that the sample is vaporized in a narrow capillary (diameter 1 mm). The combustion tube, shown in Fig. 3, gave a better performance than tubes provided by the manufacturer. A special advantage is that the inlet and outlet capillaries can easily be disconnected for inspection and cleaning.

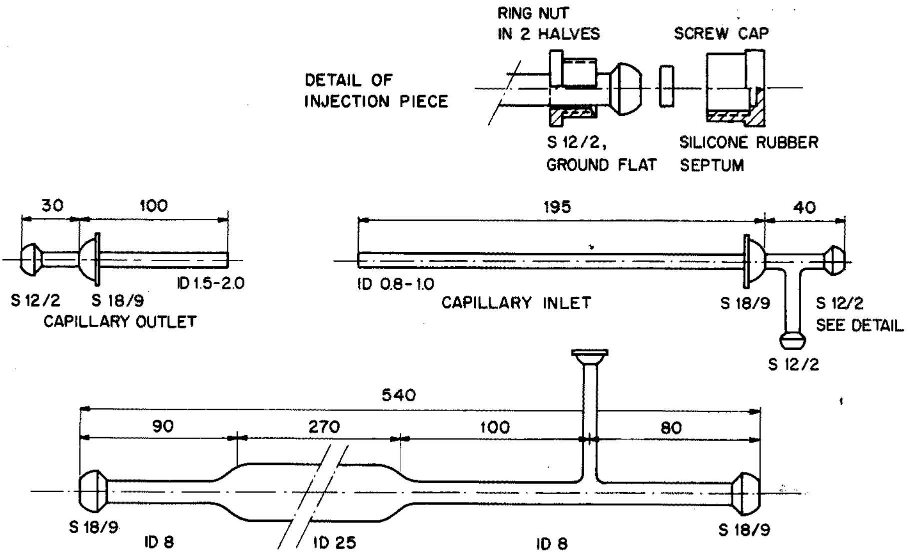

Fig. 3. Quartz combustion tube.

Transport of hydrochloric acid formed; cell stability

The quantity of hydrochloric acid formed is of nanogram order. To sweep these small amounts quantitatively from the combustion tube a gas velocity of about 400 ml/min is required. This high gas velocity is not exactly beneficial to cell stability; especially in the beginning quite a few problems regarding the cell stability were encountered. These problems were solved by selecting optimum conditions (bias and gain). According to the Dohrmann manual[6] the bias, which is representative of the silver ion concentration in the titration cell, can have any value between 240 and 280 mV. However, it was found that a bias of from 235 to 240 mV gave the best results. It is also important that the gain of the coulometer amplifier is correctly adjusted: too high gain will give rise to "overshoot" or even oscillation; too low a value will result in peak tailing.

Effect of combustion water and its elimination

One of the combustion products of organic material is water, and 4–6 mg will be produced from 5 μl of a hydrocarbon sample. In two respects water has an adverse influence: first, the conditions must be chosen so that the water cannot form a condensate, because even a minute drop left in the connecting tube between the combustion tube and the titration cell will absorb nearly all the hydrochloric acid. Admittedly, the water will be gradually evaporated by the stream of oxygen, during which process the hydrochloric acid will be released, but this results in quite appreciable tailing. Secondly, the dilution effect of the water causes the silver potential to change, and for the equilibrium to be restored additional silver ions must be generated. Thus, the water causes an apparent chlorine content; its order of magnitude is given in Table I. To obtain these figures, products with a known, low, chlorine content were subjected to combustion. The effect was found to correspond to an apparent chlorine

TABLE I

APPARENT CHLORINE EFFECT ON COMBUSTION OF ORGANIC SAMPLES

(5 μl isooctane gives about 6 mg water; 5 μl odourless kerosine gives about 5 mg water)

Sample	*Apparent chlorine*[a] *(ng/mg)*	
	Calculated on sample weight	*Calculated on combustion water formed*
Isooctane		
(Cl content acc. to Wickbold	3.2	2.7
method 0.2 p.p.m.)	3.2	2.7
	3.0	2.5
	3.9	3.2
	4.1	3.4
	Mean value 3.5	Mean value 2.9
Odourless kerosine		
(Cl content acc. to Wickbold	2.9	2.9
method < 0.3 p.p.m.)	2.7	2.7
	2.7	2.7
	3.2	3.2
	3.5	3.5
	Mean value 3.0	Mean value 3.0

[a] Allowance made for real chlorine contents.

content of from 3 to 4 p.p.m. calculated on sample or of about 3 p.p.m. calculated on combustion water. To check these results some experiments were also made by carrying water through the procedure. The results, which have been collected in Table II, show that water injected as such causes the same blank as combustion water. If the hydrogen content of a sample is known, the blank value can be subtracted from the measured value.

TABLE II

APPARENT CHLORINE EFFECT OF WATER CARRIED THROUGH THE PROCEDURE

Water (µl)	*Peak area (cm²)*	*Apparent chlorine found (ng)*	*Apparent chlorine in water (p.p.m.)*
5[a]	1.9	12.3	2.5
5[b]	2.6	15.7	3.1
10[a]	3.6	25.0	2.5
10[b]	4.0	28.0	2.8
20[a]	6.5	45.0	2.3
20[b]	8.6	59.0	3.0
30[a]	10.0	66.0	2.2
30[b]	12.7	84.0	2.8

[a] Twice distilled water.
[b] Demineralized water.

TABLE III

ANALYSIS OF ODOURLESS KEROSINE WITH ADDED MYRICYL CHLORIDE ($C_{30}H_{61}Cl$)

(Sample injected in He (400°); combusted in O_2 (900°).
Combustion water removed by scrubbing through 80% sulfuric acid)

Added chlorine (p.p.m.)	*p.p.m. Cl found (nett)*	*Recovery (%)*
1.0	1.0	
	1.2	
	0.9	
	Mean 1.0	100
2.0	1.8	
	2.1	
	2.2	
	Mean 2.0	100
6.0	5.3	
	5.6	
	5.2	
	Mean 5.4	90
20.0	18.7	
	20.0	
	20.1	
	20.0	
	Mean 19.7	98
43	40	
	42	
	39	
	43	
	41	
	Mean 41	93

A further refinement of the method, however, was obtained by trapping the water between the combustion tube and the titration cell. Initially, an attempt was made to attain this end by using various drying agents, such as anhydrous barium chloride, calcium chloride, calcium sulfate and copper(II) sulfate. Attempts to bring about a gas-chromatographic separation between water and hydrochloric acid with the aid of KEL-F oil both on various supports and in a capillary GLC column failed. All these aids were unsatisfactory, because they bound the hydrochloric acid either for a prolonged period or even permanently. The best results were obtained with 80% sulfuric acid in a scrubber as depicted in Fig. 4. (Sulfuric acid stronger than 80% led to disturbance of the cell stability; with more dilute sulfuric acid drying was unsatisfactory). Still, a blank remained of a few tenths of a p.p.m. apparent chlorine; its nature was not systematically investigated. Moreover, it was observed that application of a scrubber with sulfuric acid resulted in a more nearly ideal chlorine peak, probably owing to slight retention of the hydrochloric acid brought about by the

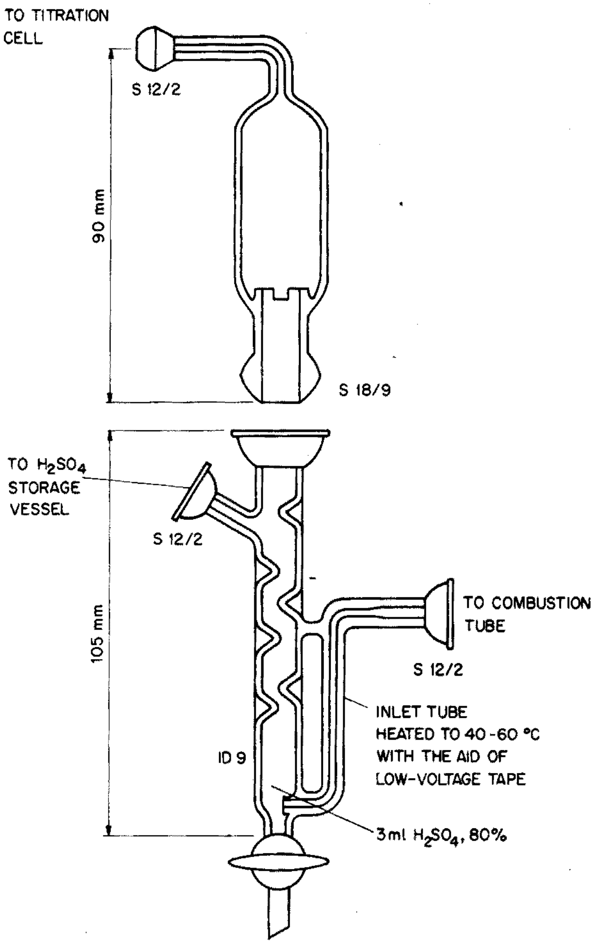

Fig. 4. Water absorber with foam breaker.

sulfuric acid. Results obtained with synthetic samples (myricyl chloride in odourless kerosine) are shown in Table III.

Brief summary of method eventually applied

For samples having chlorine contents of over 1 p.p.m. a 5-μl portion is injected (at a rate of 0.5 μl/sec) into a capillary zone of the reaction tube (400°) where it is vaporized in a stream of helium (20 ml/min). The vapours are passed to an atmosphere of oxygen (400 ml/min) where complete combustion is effected (900°). Subsequently, the combustion products are passed, through a scrubber with 80% sulfuric acid, into the titration cell. The part of the tube between the combustion furnace and the scrubber must be kept at a temperature of 40° to prevent water vapour from condensing.

In the present case, the Dohrmann microcoulometer C 200 A, the Dohrmann pyrolysis furnace S 200 with "total inlet" heater and the Dohrmann titration cell T 300 were used. The arrangement used is shown in Fig. 2. The following conditions were applied:

Electrolyte. 70% acetic acid; bias, 235 mV; gain, adjusted according to the Dohrmann manual[6]; range, 150 Ω or less.

Recorder. A multi-range Goerz-Servogor recorder, model R 512 with ball and disc integrator was used. The most sensitive range is 2 mV.

For optimum use the cell electrodes must be cleaned daily. For this purpose a glass fibre brush was found to be very effective and preferable to other treatments suggested in the Dohrmann manual[6]. A typical example of a recorded peak is given in Fig. 5.

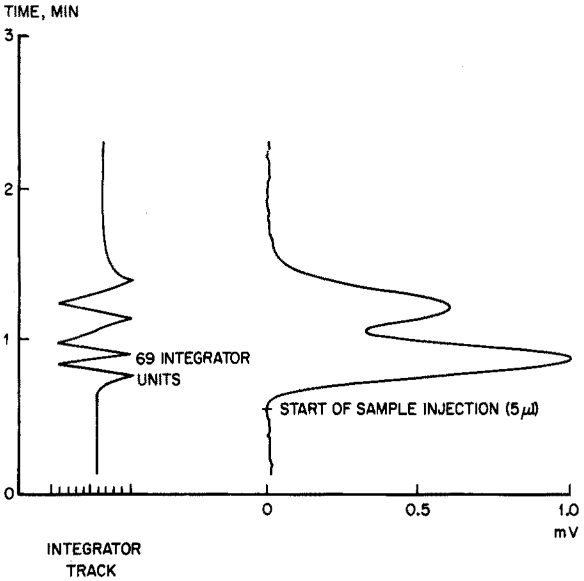

Fig. 5. Analysis of sample containing 22 p.p.m. of chlorine. Measuring range: 2 mV over 100 Ω resistance. Chart speed: 4 cm/min. 1 integrator unit = 0.2 cm^2 = 1.38 mg Cl.

$$\text{p.p.m. Cl} = \frac{\text{int. units} \times \text{factor}}{\mu\text{l sample} \times \text{sp. gr}} = \frac{69 \times 1.38}{5.0 \times 0.85} = 22.4.$$

For samples having chlorine contents below 1 p.p.m., larger portions (*e.g.* 100 µl) can be injected from an automatic syringe and the hydrochloric acid formed is preconcentrated in a cold trap at −80°. Subsequent heating of the trap enables sharp titration of the liberated chloride. The arrangement used is shown in Fig. 6; a double sulfuric acid scrubbing system proved advantageous.

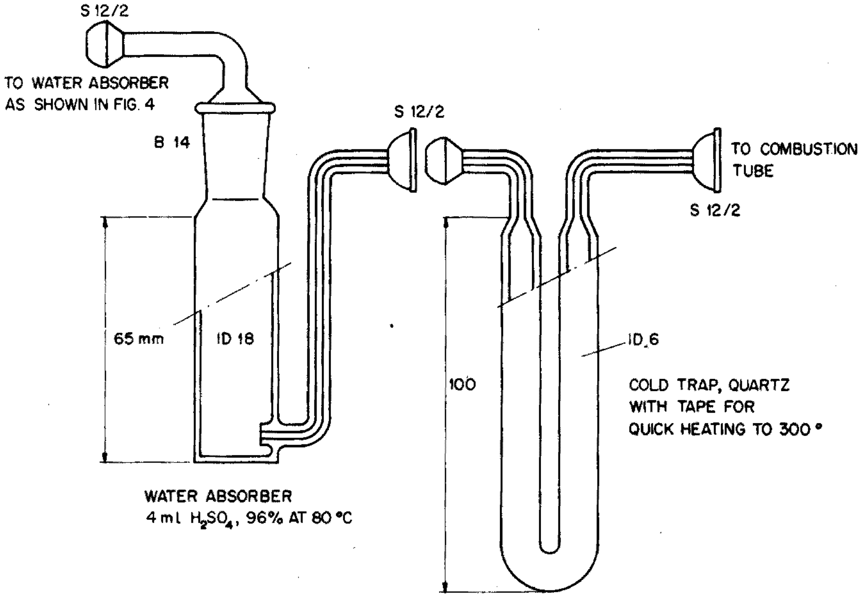

Fig. 6. Arrangement of preconcentration.

The fate of inorganic chlorides

To investigate what happens to inorganic chlorides, test solutions were made by dissolving various chlorides in suitable media. Good possibilities were found to be offered by odourless kerosine to which 5–10% isopropanol had been added. The results are presented in Table IV.

The results demonstrate that chlorides which volatilize or decompose at 400°,

TABLE IV

ANALYSIS OF INORGANIC CHLORIDES ADDED TO ODOURLESS KEROSINE CONTAINING 5–10% ISOPROPANOL

(Chlorine level 20 p.p.m.)

Salt	*Boiling point (°)*	*Result*
NaCl	1413	No chlorine recovered
KCl	1500	No chlorine recovered
$MgCl_2$	1412	No chlorine recovered
$SnCl_2$	623	No chlorine recovered
$AlCl_3$	–	[a]
$CuCl_2$	993	No chlorine recovered
NH_4Cl	Subl. 335	20 p.p.m. recovered
$FeCl_3$	280	20 p.p.m. recovered
$PdCl_2$	500 (decomp.)	20 p.p.m. recovered

[a] Analysis of $AlCl_3$ in a clean tube gave a positive result (20 p.p.m. Cl recovered). With a used tube containing some deposited KCl or NaCl, no chlorine was recovered.

such as ammonium chloride, iron(III) chloride and palladium chloride are recovered completely. More stable chlorides, such as sodium chloride, potassium chloride, magnesium chloride and tin(II) chloride are not recovered. Apparently, aluminium chloride is a border-line case: in a clean tube all chlorine was recovered; in a much-used tube, however, it was not. The latter is probably due to the formation of a double salt ($KAlCl_4$) from the sodium or potassium chloride already present in the tube and the aluminium chloride; this double salt is stable at 400°.

RESULTS AND DISCUSSION

A series of samples from actual practice were analysed according to the method described here. Results obtained on 5-μl samples are collected in Table V; they are in fair agreement with those obtained by other methods. One of the samples of processed oil (B) showed a distinct turbidity. This was ascribed to the presence of inorganic chlorine in the sample, which was confirmed upon extraction of the sample with water: nearly all the chlorine could be recovered from the aqueous extract. This also

TABLE V

RESULTS OBTAINED ON SAMPLES FROM PRACTICE

Sample injected (5 μl)	*Chlorine (p.p.m. found)*		
	Current standard method	*Suggested method*	*Mean*
Processed flashed distillate (350–480°)			
A	5.4[a]	5.3; 4.5; 4.9	4.9
B	25.8[a]	21.2; 27.7; 27.6	25.5
C	3.8[a]	2.4; 1.7; 2.0	2.0
Benzene	1.0[a]	0.7; 0.8; 1.2; 0.7	0.8
White oil	1.5[a]	1.7; 1.2; 1.6; 1.0; 1.0	1.3
Gasoline containing phosphorus[c]	1800[b]	2200; 2080; 2310; 2160; 2100; 2100	2190
Isopropanol A	$<$1[a]	0.1; 0.3; 0.6; 0.6; 0.3;	0.4
Isopropanol B		0.6; 0.6; 0.6; 0.8; 1.0	0.7

[a] Wickbold oxyhydrogen combustion method.
[b] Schöniger flask combustion.
[c] Diluted (1:50) in odourless kerosine.

TABLE VI

RESULTS OBTAINED AFTER PRECONCENTRATION OF THE HYDROGEN CHLORIDE BEFORE TITRATION

Sample	*p.p.m. of chlorine*			*Recovery (%)*
	Expected	*Found*	*Mean*	
Odourless kerosine with added myricyl chloride	0.42	0.43; 0.40; 0.42;0.40	0.41	98
Odourless kerosine with added myricyl chloride	0.22	0.22; 0.25; 0.20; 0.19	0.22	100
Odourless kerosine with added myricyl chloride	0.15	0.14; 0.19; 0.15	0.16	107
Isopropanol C	–	0.21; 0.17; 0.16; 0.16	0.17	–
Processed oil A	–	0.81; 0.83; 0.80	0.81	–
Processed oil B	–	0.55; 0.55; 0.50	0.53	–

demonstrated that the chlorides present in this sample belong to the class of chlorides that decompose when the described method is followed (*cf.* Table IV). The best precision is approximately 0.5 p.p.m. Although this is often satisfactory, it may sometimes be necessary to analyse samples below 1 p.p.m. more precisely. Results collected in Table VI show that this can be attained by means of the preconcentration method using 100-μl samples. In that case, the best precision is *ca.* 0.05 p.p.m.

Finally, it should be remarked that the method is specific for halogen, and not for chlorine only. Any bromine or iodine contained in the samples will—at least partly—be titrated along with chlorine. The quantitative determination of bromine or iodine will require the use of a reducing agent in the titration cell. No interference from fluorine, sulfur or nitrogen present in the samples was observed.

SUMMARY

The Dohrmann microcoulometric titration technique has made it possible to develop a method for the rapid determination of trace amounts of chlorine in organic liquids. The sample (1–100 μl) is vaporized in a stream of helium and then fed to an oxygen atmosphere where it undergoes combustion. The hydrochloric acid formed is titrated with the aid of a silver coulometer cell. In its most sensitive form the method has a precision (repeatability) of *ca.* 0.05 p.p.m. of chlorine.

ZUSAMMENFASSUNG

Die mikrocoulometrische Titriermethode nach Dohrmann hat es gestattet, ein Verfahren zur schnellen Bestimmung von Spurenmengen Chlor in organischen Flüssigkeiten zu entwickeln. Die Probe (1–100 μl) wird in einem Heliumstrom verdampft und dann einer Sauerstoffatmosphäre zugeleitet, worin sie verbrennt. Der so gebildete Chlorwasserstoff wird mit Hilfe einer argentometrischen Coulometerzelle titriert. In ihrer empfindlichsten Verfahrensweise hat die Methode eine Genauigkeit (Wiederholbarkeit) von etwa 0.05 p.p.m. Chlor.

RÉSUMÉ

La titration microcoulométrique selon Dohrmann a permis de mettre au point une méthode pour le dosage rapide de traces de chlore dans les liquides organiques. L'échantillon (1–100 μl) est vaporisé dans un courant d'hélium et est ensuite envoyé à une atmosphère d'oxygène où la combustion est effectuée. L'acide chlorhydrique qui en résulte est titré à l'aide d'une cellule coulométrique argentométrique. La version la plus sensible de la méthode a une précision (répétabilité) voisine de 0.05 p.p.m. de chlore.

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CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF THE OXYGEN–METAL RATIO IN MIXED URANIUM–PLUTONIUM OXIDES

N. E. BÄRRING AND GÜNTHER JÖNSSON
AB Atomenergi, Studsvik-Nykoping 1 (Sweden)

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One method often used for determining the ratio of oxygen to uranium in pure uranium oxides consists of dissolving the sample in phosphoric acid, after which the uranium(VI) present in the sample is determined by a controlled-potential technique. If the total uranium present is known, the stoichiometry of the oxide can be calculated from the relationship $O/U = 2.000 + U(VI)/U_{total}$[1,2]. In a survey of potential methods for the measurement of oxygen/metal ratio in solid solutions of uranium and plutonium dioxides, LYON[3] states that a method similar to that mentioned above does not appear promising because the mixed oxides cannot be dissolved in a non-oxidizing acid. Other complications encountered in the present work are the reduction of plutonium(IV) by uranium(IV) and the re-oxidation of plutonium(III) by dissolved oxygen. These reactions increase the amount of uranium(VI) present.

By introducing the additional determinations of plutonium(IV) and total plutonium in the procedure and by giving careful attention to the removal of dissolved oxygen in the sample solution, it has proved possible, however, to make proper corrections for the interferences mentioned. In the dissolution method developed, the oxygen–metal ratio in mixed oxides of uranium and plutonium is determined by controlled-potential coulometric procedures which are routinely used for determining uranium and plutonium. The method which is described makes use of mg-quantities of the mixed oxide sample, thus permitting analysis also of irradiated fuel material in fume hoods without massive shielding.

OUTLINE OF THE METHOD

The mixed uranium–plutonium oxide may be written $(U_aPu_{1-a})O_x = y\ UO_3 + (a-y)\ UO_2 + z\ PuO_{1.5} + \{(1-a)-z\}\ PuO_2$, where a, y and z are the atomic ratios for uranium, uranium(VI) and plutonium(III).

The oxygen-to-metal ratio may then be expressed as

$$\frac{O}{M} = x = \frac{3y+2a-2y+1.5z+2-2a-2z}{y+a-y+z+1-a-z}$$

$$\text{Hence } x = 2+y-\tfrac{1}{2}z \qquad (1)$$

$$\text{where } y = \frac{[U(VI)]}{[U]+[Pu]} \text{ and } z = \frac{[Pu(III)]}{[U]+[Pu]}$$

Substitution in eqn. (1) yields

$$x = 2 + \frac{[U(VI)] - 0.5[Pu(III)]}{[U] + [Pu]} \qquad (2)$$

Equation (2) forms the basis of the present method. The quantities to be inserted are determined by controlled-potential coulometric procedures.

The mixed oxide sample for analysis is treated with phosphoric acid, which does not alter the oxidation states of uranium and plutonium. Uranium(IV) ions, however, reduce plutonium(IV) according to the net reaction

$$U^{4+} + 2Pu^{4+} + 2H_2O \rightarrow UO_2^{2+} + 2Pu^{3+} + 4H^+.$$

RYDBERG[4] and JENKINS[5] have studied this reaction in nitric acid. Although it has not been studied in the 0.5 *M* sulfuric acid–0.3 *M* phosphoric acid mixture used in the present procedure, it is clear from Fig. 1 that the reaction occurs in this medium. This reaction does not, however, interfere with the results calculated from eqn. (2), because equivalent amounts of uranium(VI) and plutonium(III) are formed.

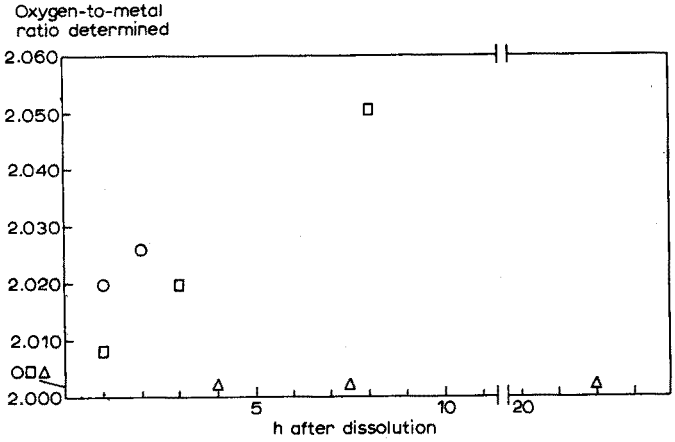

Fig. 1. Effect of standing time on the oxygen-to-metal ratio determined. The diagram shows that dissolved oxygen in the presence of uranium(IV) causes re-oxidation of plutonium(III) to plutonium(IV) which in turn is reduced by uranium(IV). No precautions were taken to exclude air. (△) $UO_{2.0018}$ mixed with 0% PuO_2, (□) $UO_{2.0018}$ mixed with 3% PuO_2, (○) $UO_{2.0018}$ mixed with 6.5% PuO_2.

In the presence of dissolved oxygen plutonium(III) is re-oxidized to plutonium(IV), which in turn is reduced by uranium(IV) ions, and there will be a steadily increasing amount of uranium(VI) as indicated in Fig. 1. This re-oxidation reaction is avoided by carefully excluding air from the sample solution.

The mixed oxide samples may vary in physical appearance from fine powders to hard pellets and cannot conveniently be completely dissolved in phosphoric acid. Sufficient material for performing the analysis is, however, always brought into solution when the sample is treated with hot concentrated phosphoric acid for about 1 h. In all investigated samples about the same plutonium-to-uranium ratio was found in solution as in the solid sample, but this may not be true for all types of sample, particularly where the plutonium is not in solid solution in the UO_2 matrix. Table I shows some results from previous experiments with pure uranium oxide samples. Each sample was first treated with phosphoric acid until the surface layer was judged to be dissolved. This fraction was separated and the sample was then treated with a new portion of phosphoric acid. Both fractions were analysed for the oxygen-to-uranium ratio. Higher oxygen contents were due to adsorbed oxygen always found in the fraction containing the surface layer. This "descaling" fraction is discarded in the procedure to be described.

TABLE I

OXYGEN-TO-URANIUM RATIO DETERMINED IN URANIUM OXIDE SAMPLES

$UO_{2.0}$ sample	*O/U ratio*	
	In the surface layer	*Without surface layer ("descaled" sample)*
SF 21, pellet	2.0028 ± 0.0002	2.0015 ± 0.0002
K 1060, powder	2.066 ± 0.001	2.055 ± 0.001
K 1063, powder	2.059 ± 0.001	2.045 ± 0.001
K 1078, powder	2.071 ± 0.001	2.061 ± 0.001

EXPERIMENTAL

Apparatus

The coulometric measurements were made with locally constructed instruments similar to the ORNL Model Q-2005[6] with provision for graphical readout of the integrated current as a function of titration time. Readout voltages from the inte-

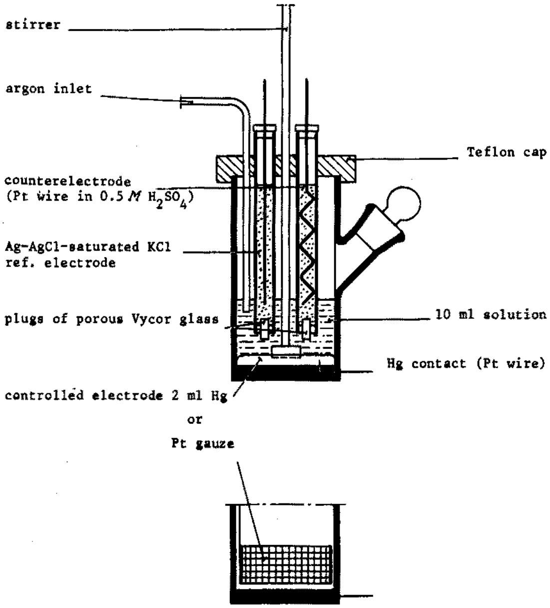

Fig. 2. Electrolysis cell.

grator were measured with a Solartron Digital Voltmeter LM 1420. The integrator was calibrated electrically.

The titration cell assembly used is shown schematically in Fig. 2. The cell can be so arranged that titrations can be made at either a mercury pool or at a platinum gauze electrode shaped to fit the inside of the cell. The counterelectrode was a platinum wire in a small tube filled with 0.5 *M* sulfuric acid. All potentials cited in this work were measured with respect to the Ag–AgCl reference electrode which has a potential of about − 45 mV *vs.* S.C.E. in 0.5 *M* sulfuric acid. Both the counterelectrode and the reference electrode were isolated from the solution to be titrated by pieces of porous Vycor (type 7930) glass rods plugged into the ends of the glass-tubes containing the electrodes. These porous glass plugs have proved to be low-resistance junctions which, when stored wet, have performed satisfactorily for over a year. A side-arm provides access for introducing the electrolyte and sample and for rinsing the cell. During the titration this arm is closed with a stopper. A tube passes through the Teflon cap to permit sparging the sample continuously during the titration. Pure argon (< 3 p.p.m. oxygen) was used as sparge gas. The solution (about 10 ml in volume) was stirred mechanically with a propeller stirrer. All operations were carried out in fume hoods.

Dissolution of sample

The oxide sample (20–200 mg) which has been previously crushed if necessary, is placed in a 50-ml conical flask fitted with a reflux condenser and a gas inlet tube. Sparge argon continuously through the solution to remove oxygen during all steps of the analytical procedure. Add 10 ml of deoxygenated phosphoric acid and heat on a hot plate until the solution is coloured slightly green owing to dissolved uranium. Discard the solution and add a new portion of 10 ml of phosphoric acid. Boil gently until a suitably large fraction of the sample is brought into solution. (This is the case when the operator estimates by the colour of the solution that the uranium concentration is 10–15 mg U/ml.) Allow to cool and make up the solution volume to 30 ml by adding a deoxygenated solution of 0.3 *M* phosphoric acid–0.5 *M* sulfuric acid. The coulometric titrations are made as soon as possible after the dissolution.

Titration of plutonium(IV) and uranium(VI)

Make the titration cell ready. Add 2 ml of mercury and 3 ml of 0.3 *M* phosphoric acid–0.5 *M* sulfuric acid solution. Start the stirrer and sparge argon continuously through the solution. Adjust the potential of the mercury electrode to −0.30 V (all potentials cited below refer to the Ag–AgCl electrode). Prepare the instrument for current integration and reduce the solution (blank) until the current drops to a constant value (*ca.* 3 μA in our case). Adjust the controlled potential to 0.10 V and add rapidly an aliquot (1 ml) of the sample solution. Integrate the current as plutonium(IV) is reduced to plutonium(III) until constant background current is attained. Adjust the potential to −0.30 V and reduce in the same way uranium(VI) to uranium(IV). A typical recording of readout voltage, which is proportional to the total quantity of charge transferred, *versus* time for the above titration is shown in Fig. 3.

Titration of total uranium and total plutonium

Add two sample portions (1 ml) to small beakers. Oxidize all uranium to uranium(VI) by treating the sample portions with small amounts of fuming nitric acid under a heating lamp. To remove the nitric acid add 0.5 ml of sulfuric acid to each sample and evaporate the solutions to fumes of sulfur trioxide. Allow the samples to cool and dilute them to 5 ml with 0.1 *M* sulfuric acid. Transfer one sample portion to a clean titration cell. Adjust the potential of the mercury electrode to 0.10 V and prereduce the sample until a low and constant background current is attained. Then shift the potential to −0.30 V, zero the integrator and reduce uranium(VI). Sparge with argon continuously.

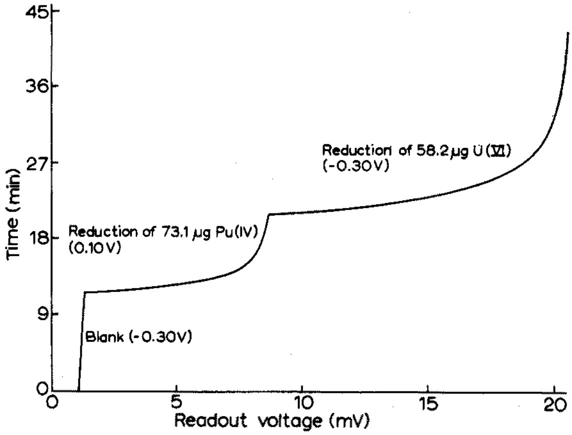

Fig. 3. Reduction of plutonium(IV) and uranium(VI) at the mercury electrode in 0.3 *M* phosphoric acid–0.5 *M* sulfuric acid media.

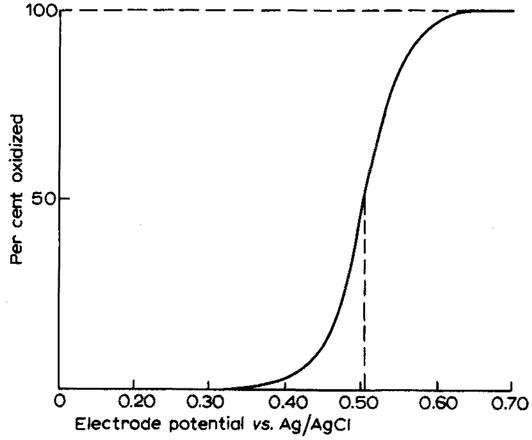

Fig. 4. Percentage of plutonium(IV) as a function of the electrode potential for the redox system $Pu^{4+} + e^- = Pu^{3+}$ (in 0.5 *M* H_2SO_4–0.3 *M* H_3PO_4). U(VI) was present in excess.

Transfer the other sample portion to a clean cell fitted with a platinum working electrode. Prereduce at 0.15 V. Shift the potential to 0.73 V, zero the integrator and integrate the current as plutonium(III) is oxidized to plutonium(IV) until the current drops to a constant value (*ca.* 3 µA), sparging continuously with argon.

The potentials for the prereduction and for coulometric oxidation are based on the curve in Fig. 4. (This curve was obtained experimentally by coulometric oxidation of a solution of plutonium(III) and uranium(VI) in 0.5 *M* sulfuric acid–0.3 *M* phosphoric acid at different potentials.)

Calculate the oxygen-to-metal ratio by inserting the obtained values of [U(VI)], [U], [Pu] and {[Pu]–[Pu(IV]}, corrected for blank and residual currents if necessary, in eqn. (2).

RESULTS

The method was tested with mixtures of uranium and plutonium oxides of known composition. In one series of experiments test portions of a solution of a uranium dioxide pellet, the stoichiometry of which had previously been determined many times, were mixed with aliquots of solution containing known amounts of plutonium(III) and plutonium(IV). The latter solutions were carefully prepared by controlled-potential coulometric reduction of solutions of pure plutonium in 0.5 *M* sulfuric acid–0.3 *M* phosphoric acid until all plutonium was reduced to plutonium(III) and then partial oxidation to known Pu(IV)/Pu(III) ratios. In some other experiments, weighed amounts of the $UO_{2.0018}$ pellet were mixed with weighed amounts of a plutonium dioxide powder. This powder had been heated in air at 900° until constant weight, when the composition could reasonably be assumed to be $PuO_{2.000}$.

The samples of known composition thus prepared were treated as described above; the results obtained are given in Table II.

TABLE II

OXYGEN–METAL RATIOS AS DETERMINED IN MIXED OXIDE SAMPLES OF KNOWN COMPOSITION

(Argon was sparged continuously through the sample solution)

	$UO_{2.0018}$ + solutions with known Pu(IV)/Pu(III) ratios			*88% $UO_{2.0018}$ 12% $PuO_{2.000}$*		*92% $UO_{2.0018}$ 8% $PuO_{2.000}$*	
	6	*7*	*8*	*A1*[a]	*A2*[b]	*B1*[a]	*B2*[b]
U mg	1.96	0.975	7.69	4.60	4.63	2.98	3.03
± σ%	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Pu mg	0.111	0.111	0.124	0.244	0.244	0.148	0.148
± σ%	3	3	3	2	2	3	3
U(VI) mg added	0.0035	0.0018	0.0134	0.0083	0.0083	0.0054	0.0055
U(VI) mg found	0.0318	0.0059	0.0254	0.0524	0.0540	0.0074	0.0085
± σ%	3	7	3	2	2	7	7
Pu(IV) mg added	0.111	—	0.067	0.244	0.244	0.148	0.148
Pu(IV) mg found	0.053	0.011	0.013	0.154	0.164	0.139	0.142
± σ%	4	10	10	3	3	3	3
Pu(III) mg added	—	0.111	0.057	—	—	—	—
Pu(III) mg found	0.058	0.100	0.111	0.090	0.080	0.009	0.006
σQ/Q (eqn. (5))	0.8	0.04	0.07	0.6	0.7	1.1	1.3
O/M expected	2.0017	1.952	1.998	2.0017	2.0017	2.0017	2.0017
O/M found	2.0014	1.959	1.996	2.0014	2.0029	2.0010	2.0017
± σQ	0.001	0.002	0.001	0.0008	0.002	0.001	0.002

[a] A1, B1 were analysed immediately after completion of dissolution.

[b] A2, B2 were analysed about 2 h after completion of dissolution.

Evidently the precision indices of the calculated quotient, Q, (eqn. (2); $O/M = 2 + Q$) depend on the indices of the measured quantities. The standard deviations of these quantities at different concentration levels are known or may be estimated from previous experience. Then by applying the principle of the propagation of error[7], the best precision with which the O/M measurements can be made was calculated from the equations:

$$\bar{Q} = \frac{\bar{x}}{\bar{y}} \quad \frac{[\bar{U}(VI)] - 0.5[\overline{Pu}(III)]}{[\bar{U}] + [\overline{Pu}]} \tag{3}$$

$$\sigma\bar{x}^2 = \sigma[\bar{U}(VI)]^2 + 0.25\sigma[\overline{Pu}(III)]^2 \tag{4}$$

$$\sigma\bar{y}^2 = \sigma[\bar{U}]^2 + \sigma[\overline{Pu}]^2$$

and

$$\frac{\sigma\bar{Q}^2}{\bar{Q}^2} = \frac{\sigma\bar{x}^2}{\bar{x}^2} + \frac{\sigma\bar{y}^2}{\bar{y}^2} \tag{5}$$

Every determination was repeated several times and the mean values and their standard deviations are presented in Table II.

TABLE III

OXYGEN–METAL RATIOS AS DETERMINED IN VARIOUS UNIRRADIATED MIXED OXIDE SAMPLES

Sample	*Composition*	*Sintered in H_2 for 4 h at temp. (°)*	*Average $O/M \pm \sigma\bar{Q}$*
L3, L6	UO_2, 1.5% PuO_2	1680	1.998 ± 0.002
C2, F2	UO_2, 1.5% PuO_2	1680	1.994 ± 0.001
N3, F5	UO_2, 1.5% PuO_2	1700	2.000 ± 0.001
1040	UO_2, 4% PuO_2	1550	2.003 ± 0.001
1042	UO_2, 4% PuO_2	1700	2.002 ± 0.001
1048	UO_2, 8% PuO_2	Powder, calcined at 1000°	2.034 ± 0.002

The results in Table II compare well with those expected from the data of the known mixtures except for sample 7, for which a too high ratio was found. This was not unexpected in this very unfavourable case where all plutonium was added as plutonium(III). A small leakage of oxygen into the system is difficult to avoid; by using a more elaborate technique for transferring the sample portion to the cell the oxygen interference should be further minimized.

Table III shows typical results from the analyses of various mixed oxide pellets and of mixed powder before sintering.

The new method described entails four coulometric titrations and is consequently rather lengthy. With the routine used and instruments available in this laboratory, it is possible for an experienced operator to perform three complete analyses during a working day. By working at the mg level, safety and handling problems in the analyses of irradiated samples are reduced. Experience has as yet been gained only on uranium dioxide materials irradiated in thermal reactors up to 10 MW·day per kg

UO_2. All operations during these analyses could be safely performed in fume hoods provided with temporarily arranged shields of lead bricks.

SUMMARY

A method has been developed for the determination of the oxygen–metal ratio in mixed oxides of uranium and plutonium. The sample is treated with hot concentrated phosphoric acid. Plutonium(IV), uranium(VI), total plutonium and total uranium are then determined by controlled-potential coulometric procedures. The ratio is calculated from the equation:

$$\frac{O}{M} = 2 + \frac{[U(VI)] - 0.5[Pu(III)]}{[U] + [Pu]}$$

RÉSUMÉ

Une méthode est proposée pour la détermination du rapport oxygène–métal dans des oxydes mixtes d'uranium et de plutonium. L'échantillon est traité par de l'acide phosphorique concentré, chaud. Plutonium(IV), uranium(VI), plutonium total et uranium total sont ensuite dosés par coulométrie à potentiel contrôlé. Le rapport est calculé à partir de l'équation suivante:

$$\frac{O}{M} = 2 + \frac{[U(VI)] - 0.5[Pu(III)]}{[U] + [Pu]}$$

ZUSAMMENFASSUNG

Es ist eine Methode für die Bestimmung des Sauerstoff–Metall-Verhältnisses in gemischten Oxiden von Uran und Plutonium entwickelt worden. Die Probe wird mit heisser konzentrierter Phosphorsäure behandelt. Plutonium(IV), Uran(VI), Gesamt-Plutonium und Gesamt-Uran werden dann durch potential-regulierte coulometrische Verfahren ermittelt. Das Verhältnis wird berechnet nach der Gleichung:

$$\frac{O}{M} = 2 + \frac{[U(VI)] - 0.5[Pu(III)]}{[U] + [Pu]}$$

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SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF RARE EARTHS IN PLUTONIUM—USE OF TRILAURYLAMINE

R. K. DHUMWAD, M. V. JOSHI AND A. B. PATWARDHAN
Fuel Reprocessing Division, Bhabha Atomic Research Centre, Trombay, Bombay 85 (India)

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The spectrochemical determination of impurities in plutonium presents a number of problems more serious than those encountered in the analysis of uranium, thorium or other elements having complex line spectra, mainly because plutonium is highly toxic in nature and has to be handled in glove boxes, at reduced pressures, with elaborate safeguards during the sample preparation and arcing processes. Secondly, as in uranium or thorium, the hundreds of spectral lines of plutonium superimpose on or interfere with the sensitive analysis lines of the impurities, rendering their identification and quantitative photometric measurement inaccurate. To overcome these difficulties, extraction[1-3] and ion-exchange[4,5] methods of isolation of rare earths have been commonly employed.

This paper describes a spectrographic method based on the preseparation of rare earths by extracting plutonium into trilaurylamine in Shell-Sol.T and photographing the spectra on a large quartz prism spectrograph by arcing the aqueous phase containing rare earths. The solvent extraction method was preferred since it was found to be quicker than the ion-exchange method of separation of rare earths from plutonium.

EXPERIMENTAL

Preparation of standards

Spec-pure chemicals (Johnson & Matthey) were used for the preparation of standard solutions of Gd, Sm, Dy, Er and Ce and the scandium solution for internal standard. A concentrated composite solution was prepared which contained 1.5 mg of Gd, 3 mg each of Sm, Dy and Er, and 6 mg of Ce in 1 ml. By suitable dilutions, the lower standards were prepared. All the standard solutions were subjected to extraction in the same way as the samples in order to avoid discrepancies from the probable losses of rare earths during the extraction of plutonium. Each standard solution contained 1 μg of scandium per 200 μl.

Internal standard

A number of experiments on the volatilization of rare earths and other elements were carried out and scandium was found to be quite satisfactory as an internal standard. The Sc 3359.679 Å line was selected as the control line since it was found to be free from line interferences and was in the neighbourhood of the analysis lines of rare earths. Scandium stock solution was prepared by dissolving pure scandium oxide in nitric acid with a few drops of hydrofluoric acid.

Preparation of plutonium samples

The plutonium samples were handled as mentioned earlier[6]. An appropriate aliquot (containing 100 mg of plutonium) of the plutonium nitrate sample was evaporated to near dryness and made up to 20 ml by adding 4 M nitric acid. A few drops of hydrogen peroxide were added to keep plutonium in the tetravalent state. The excess of peroxide was removed by heating under an infrared lamp. The solution was then extracted for 5 min with a 20-ml aliquot of pre-equilibrated 20% (v/v) TLA in Shell-Sol.T. (Trilaurylamine was supplied by Ashland Chemical Co., U.S.A. under their trade name Adogen-363 and Shell-Sol.T by Shell International Petroleum Co., Holland.) A second extraction was done to ensure that the extraction of plutonium into the organic phase was complete. Plutonium in the aqueous phase was estimated by α-counting and was found to be less than 0.05%. After the addition of 5 μg of scandium to the aqueous phase, the volume was reduced to 1 ml; 200 μl of this solution was transferred and dried in the water-repellant shallow cavity of a 6.35-mm diam.

TABLE I

PARAMETERS FOR SPECTROGRAPHIC EXCITATION, RECORDING AND PHOTOMETRIC ANALYSIS

Spectrograph	Hilger large quartz and glass prism spectrograph fully automatic E 478-304.
Slit width	0.020 mm.
Slit illumination	The intermediate real image was formed 38 cm from the arc by means of a spherical lens (Hilger F. 958) 8 cm from the arc. This was focussed on the collimating lens by keeping a spherical lens (Hilger F. 1025) 2 cm from the slit.
Emulsion	Kodak B-10.
Wavelength range	2850–5000 Å.
Excitation unit	Hilger and Watts BNF source unit F.S. 131.
Type of excitation	D.c. arc; 220 V; 10 A.
Electrodes	Anode: 6.35 mm diameter U.C.P. graphite rod (grade UF 4S) with a cavity 1.5 ± 0.5 mm deep and wall thickness of 0.5 mm.
	Cathode: 3.05 mm diameter U.C.P. graphite rod tapered.
Analytical gap	3 mm.
Internal standard	Sc, 1 μg on the electrode.
Exposure	15 sec.
Plate calibration	Rotating seven-step sector with a step ratio of 2:1 with iron arc at 3 A, exposure 15 sec.
Processing	Kodak D-19 b for 4 min at 20°; Kodak F-5 for 10 min.
Densitometer	Hilger non-recording microphotometer L. 451.

graphite electrode. (The electrode was made water-repellant by evaporating two drops of a thinner containing 5% (w/v) "Durofix".) The electrode was then arced and the rare earths estimated by the spectrographic method. Each sample was analysed in triplicate and the average of the three results was reported. Plutonium oxide was dissolved in nitric acid containing a few drops of hydrofluoric acid in a platinum dish and analysed similarly. The data for the measurement process are given in Table I.

RESULTS AND DISCUSSION

Table II gives the details of the line pairs and the range of determinations with the standard deviations. The standard deviations were calculated from at least 15 values of intensity ratios of each standard. The overall standard deviation of the method is 14% at the 67% confidence level.

TABLE II

LINE PAIRS, CONCENTRATION RANGE AND REPRODUCIBILITY

Line pair rare earth (Å)[a]	*Concentration range*		*S.D. at 67% confidence level (%)*
	μg on electrode[b]	*p.p.m. on 100 mg Pu*[c]	
Gd 3350.482	0.2–2.0	10–100	14
Sm 3382.407	1.0–4.0	50–300	11
Dy 3385.027	0.1–2.0	5–100	11
Dy 3388.863	0.4–4.0	20–200	15
Er 3264.781	0.1–4.0	5–200	14
Ce 3201.714	2.0–8.0	100–600	18

[a] Internal standard Sc 3359.679 Å.
[b] The amount of rare earth in 200 μl deposited on the electrode for spectrographic analysis.
[c] For a 200-μl aliquot of effluent from 100-mg Pu sample concentrated to 1 ml.

Losses of rare earths during plutonium extraction

Experiments were carried out to estimate the losses, *i.e.* extraction of rare earths along with plutonium into the organic phase. The losses of gadolinium, cerium and samarium were estimated to be less than 4% by using ^{153}Gd, ^{141}Ce and ^{153}Sm tracers and gross γ-counting.

Effects of impurities

Since some of the plutonium samples were found to contain appreciable amounts of calcium and iron, it was thought necessary to study the effect of these impurities on the estimation of the rare earths.

Four samples RE-STD 3-1, 3-2, 3-3 and 3-4 were prepared by adding calculated amounts of 26 impurities to rare earth standard 3 which contained 0.5 μg Gd, 1.0 μg Sm, Dy and Er each and 2.0 μg Ce in an aliquot of 200 μl. The concentrations of impurities added to the standard are given in Table III. These samples were analysed by the proposed method and the intensity ratios for rare earth: scandium were plotted as shown in Fig. 1. The % deviations of the intensity ratios from the values obtained for rare earth standard 3 are also indicated. It can be seen that there is no appreciable effect of the various impurities on the intensity ratios for samples RE-STD 3-1 and RE-STD 3-2, in which the deviations are within 20%. In the case of samples RE-STD 3-3 and RE-STD 3-4, there are significant deviations in the ratios which indicate that for such samples (Ca and Fe each ⩾2000 p.p.m.) the major impurities may have to be further separated chemically before the estimation of rare earths.

TABLE III

CONCENTRATION OF IMPURITIES ADDED TO RARE EARTH STANDARD 3

(All values in p.p.m. on Pu, on the basis of a 100-mg Pu sample)

Element	*RE-STD*				
	3	*3-1*	*3-2*	*3-3*	*3-4*
Gd	25	25	25	25	25
Sm, Dy, Er	50	50	50	50	50
Ce	100	100	100	100	100
Ca		500	1000	2000	5000
Fe		500	1000	2000	5000
Zn		50	100	200	500
Al, Sb, Ag, Ba, Be, Bi, B, Cd, Cr, Co, Cu, In, La, Mg, Mn, Mo, Ni, Sr, Th, Ti, U, V, Zr		5	10	20	50

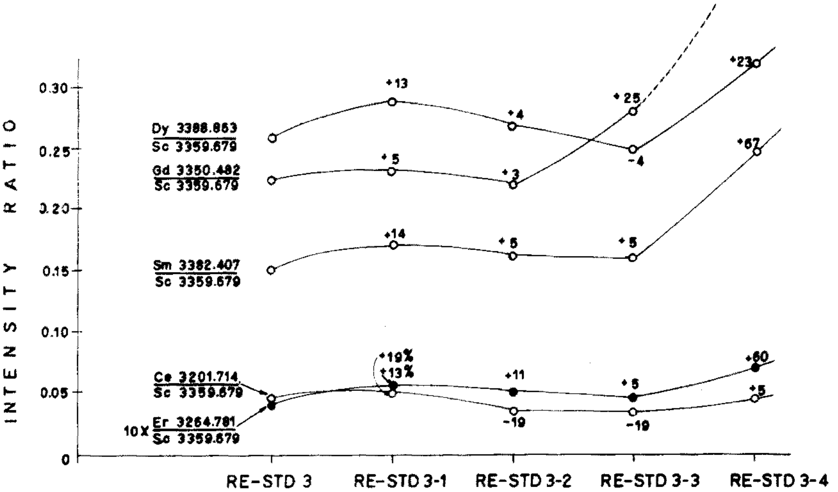

Fig. 1. The effect of calcium and iron on the line intensity ratios rare earth/scandium.

Line interferences and resolving power of the spectrograph

Since the resolving power of the spectrograph used in the present work was about 30,000 (in the region of 3350 Å), two spectral lines of comparable intensity and 0.11 Å apart could be just resolved.

The spectral region of ±0.11 Å in the vicinity of each rare earth analysis line and the 3350.679 Å Sc line on the photographic plate was examined to study the possible line interferences. Reference was made to the table of wavelengths published by HARRISON[7]. Table IV gives the wavelengths and other details of the lines which, if present, could not have been resolved from the respective analysis lines. The Table,

TABLE IV

LINE INTERFERENCES

Element	*Wavelength*[7] *(Å)*	*Intensity in arc*	*Interfering line*		
			Element	*Wavelength (Å)*	*Intensity in arc*
Gd	3350.482	150	Ca I	3350.360	15
			Eu	3350.43	30
			Ti I	3350.548	10
Sm(II)	3382.407	100	Ti I	3382.312	30
			Fe I	3382.409	50
Dy	3385.027	25	Ho	3385.05	10
			Er	3385.087	25[a] double line
Dy	3388.863	20	Fe I	3388.964	3
Er	3264.781	25	Fe I	3264.710	4
			Mn	3264.711	75
			Fe	3265.048	200
Ce	3201.714	50	Ti I	3201.594	12
			Sm	3201.792	30 double line
Sc(II)	3359.679	50	The background intensity due to the maxima of Q branch (0,0) of NH at 3360 Å does not affect the intensity ratios rare earth:scandium.		

[a] In the present investigation, Er 3385.087 Å was found to be much weaker than Er 3264.781 Å though they were reported to be of equal intensity (*i.e.* 25) by HARRISON[7].

however, does not include elements such as Os, Se, Ir, etc. which are not likely to be present in the plutonium samples. Very weak interfering lines are also not included. From the Table, it can be seen that the estimations of gadolinium (with 3350.482 Å), dysprosium (3388.863 Å) and erbium (3264.781 Å) will be affected if the plutonium samples contain calcium and iron (in excess of 1000 p.p.m.) as discussed above.

These studies indicate that the present method is applicable to the routine analysis of plutonium samples. The estimations of rare earths are not affected by the presence of impurities such as calcium and iron even when 1000 p.p.m. or less is present. The overall standard deviation of the method is 14%.

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SUMMARY

A spectrographic method for the estimation of some rare earths (Gd, Sm, Dy, Er and Ce) in plutonium samples is described. The rare earths were separated from 100 mg of plutonium by extracting plutonium with trilaurylamine. After concentration of the solution, the spectrum was photographed on a Hilger large quartz spectrograph, with scandium as internal standard. The estimation ranges are Gd 10–100 p.p.m., Sm 50–300 p.p.m., Dy 5–100 p.p.m., Er 5–200 p.p.m. and Ce 100–600 p.p.m. The overall standard deviation is 14%. The method is applicable to samples containing calcium and iron upto 1000 p.p.m. The resolving power and line interferences are discussed.

RÉSUMÉ

On décrit une méthode spectrographique pour le dosage de quelques terres rares (Gd, Sm, Dy, Er et Ce) dans des échantillons de plutonium. Les terres rares sont séparées d'avec 100 mg de plutonium par extraction du plutonium à l'aide de trilaurylamine. Après concentration de la solution, le spectre est photographié; on utilise le scandium comme étalon interne. Les domaines de concentrations sont: Gd 10–100 p.p.m., Sm 50–300 p.p.m., Dy 5–100 p.p.m., Er 5–200 p.p.m. et Ce 100–600 p.p.m. Cette méthode peut s'appliquer à des échantillons contenant jusqu'à 1000 p.p.m. de calcium et de fer.

ZUSAMMENFASSUNG

Es wird ein spektrographisches Verfahren für die Bestimmung einiger Seltener Erden (Gd, Sm, Dy, Er, und Ce) in Plutonium-Proben beschrieben. Die Seltenen Erden wurden von 100 mg Plutonium durch Extraktion des Plutoniums mit Trilaurylamin abgetrennt. Nach Konzentrierung der Lösung wurde das Spektrum mit einem Hilger-Quarz-Spektrographen mit Scandium als innerem Standard photographisch aufgenommen. Die Bestimmungsbereiche sind Gd 10–100 p.p.m., Sm 50–300 p.p.m., Dy 5–100 p.p.m., Er 5–200 p.p.m. und Ce 100–600 p.p.m. Die Gesamt-Standardabweichung beträgt 14%. Das Verfahren ist auf Proben anwendbar, die Calcium und Eisen bis zu 1000 p.p.m. enthalten. Auflösungsvermögen und Linieninterferenzen werden diskutiert.

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N-BENZOYL-*o*-TOLYLHYDROXYLAMINE AS A GRAVIMETRIC REAGENT FOR URANIUM(VI)

MRINAL K. DAS* AND A. K. MAJUMDAR
Department of Chemistry, Jadavpur University, Calcutta 32 (India)

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Only a few organic reagents, salicylhydroxamic acid[1], cacodylic acid[2], N-benzoyl-N-phenylhydroxylamine[3], carboxypyridine-N-oxide[4] and combined *m*-aminobenzoic acid and 1,10-phenanthroline[5] have been used in recent years for the gravimetric determination of uranium(VI) by direct weighing of the complex. However, there is no report whether these reagents could be used for the separation of uranium from a large number of foreign metal ions, and with N-benzoyl-N-phenylhydroxylamine (BPHA) the pH range for complete precipitation of uranium(VI) is very narrow (pH 5.2 to 5.6). In order to improve the rather limited success of BPHA and to effect separation and determination of uranium from various other metal ions, three derivatives of BPHA, namely N-benzoyl-*o*-tolylhydroxylamine, N-benzoyl-*p*-tolylhydroxylamine and N-benzoyl-*p*-chlorophenylhydroxylamine were examined. It was found that N-benzoyl-*o*-tolylhydroxylamine was the most suitable for the purpose. This reagent has also been used in our laboratory for the separation of niobium and tantalum[6] and for the spectrophotometric determination of vanadium[7]. This paper reports the separation and determination of uranium(VI) from a large number of other metal ions, with an improved pH range for precipitation of uranium. Uranium and the reagent were found to combine in the ratio 1:3, similar to that of uranium–oxinate.

Although uranium(VI) does not form a complex with EDTA[8-10], in practice it has been found to interfere in the precipitation of uranium. On the other hand, magnesium chloride–EDTA mixture does not interfere with the precipitation of uranium. Aluminum had a tendency to be coprecipitated with uranium even in presence of magnesium chloride–EDTA, but it could be removed completely by precipitating uranium twice in presence of the masking agent.

EXPERIMENTAL

Apparatus and reagents

The pH measurements were made by a Cambridge pH indicator. The n.m.r. spectrum was recorded in $CDCl_3$ (99.8%) by a Varian A-60A spectrometer. The i.r. spectra were recorded with a Beckman IR-10 spectrometer as nujol-mulls. The mass

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* Present address: Chemistry Department, State University of New York at Albany, Albany, N. Y. 12203 (U.S.A.).

spectrum was recorded with an AEI M-S 902. A Chevenard thermobalance (Type 3 Adamel, Paris) was used for thermogravimetry.

N-Benzoyl-*o*-tolylhydroxylamine was prepared by the method described earlier[7]. Reagent solutions were made by dissolving it in 10–15 ml of 95% ethanol before use.

Standard uranium(VI) solution was prepared from reagent-grade uranyl nitrate and standardized by oxine[11].

Diverse ion solutions were prepared from the chlorides, nitrates or sulfates of the metals. For vanadium, molybdenum and tungsten, ammonium metavanadate, ammonium molybdate and sodium tungstate, respectively, were used.

Magnesium–EDTA complex solutions were made, when necessary, by mixing equal volumes of 0.25 *M* magnesium chloride and 0.25 *M* EDTA solutions.

All chemicals used were reagent grade quality.

Procedure

Dilute an aliquot of standard uranium(VI) solution to 250 ml with distilled water and then heat to 45–55°. Add an ethanolic solution of the reagent (3–4 times the theoretical amount) slowly with constant stirring. Adjust the pH of the solution to 5.0–7.5 by adding dilute (1:6) ammonia with constant stirring. A flocculent orange-red precipitate appears. Digest the mixture on a water-bath at 45–55° with occasional stirring for 1.5 h; the precipitate is converted to a granular brick-red form. Filter through a fine sintered-glass crucible, wash with warm (45–55°) water and then dry at 110° to constant weight. Typical results are shown in Table I.

TABLE I

DETERMINATION OF URANIUM(VI)

U taken (mg)	*U complex (mg)*		*U found (mg)*	*Error (mg)*
	Found	*Calcd.*		
5.00	20.1	19.94	5.04	+ 0.04
10.01	40.0	39.92	10.03	+ 0.02
11.54	45.9	46.01	11.52	− 0.02
20.02	80.0	79.84	20.06	+ 0.04
23.08	92.0	92.00	23.08	0

RESULTS AND DISCUSSION

Characteristics and composition of the complex

An orange-red flocculent precipitate appeared at pH 3.0 and came down completely at pH 5.0. On digestion the precipitate became brick-red and granular. Both forms of the precipitate were soluble in many organic solvents including amyl alcohol, amyl acetate, methyl isobutyl ketone, chloroform, carbon tetrachloride, ether, benzene, acetone, ethanol and tetrahydrofuran. The granular complex melted at 200–202° and decomposed at 219°. The n.m.r. spectrum of the complex showed a complex pattern in the aromatic region and a sharp single peak at 7.7 τ in the ratio 3:1. The i.r. spectrum of the complex showed a 45 cm^{-1} shift to lower energy of the carbonyl stretching frequency, indicating coordination to uranium through oxygen.

The mass spectrum showed a complete decomposition to fragments with mass lower than 400 together with a faint peak around the parent at 950. Elemental analysis was consistent with the formulation $UO_2(C_{14}H_{12}O_2N)_2 \cdot C_{14}H_{13}O_2N$ (found U 25.07%, N 4.50%; calcd. U 25.09%, N 4.44%). The conversion factor from the complex to the metal is 0.2509.

Effect of reagent concentration

By using different amounts of reagent with other conditions constant, it was found that at least three times the theoretical quantity of reagent was necessary for complete precipitation.

Effect of pH

Solutions containing uranium(VI) and appropriate amounts of reagent were adjusted to different pH by dilute ammonia (pH meter), then digested, filtered, dried and weighed. Precipitation of uranium was found to be complete between pH 5.0 and 7.5.

Separation of uranium(VI) from foreign ions by using $MgCl_2$–EDTA as masking agent

To a mixture of known amounts of uranium and foreign ions, an appropriate quantity of magnesium chloride–EDTA solution was added so that the total EDTA content was about ten times the total metal ions present. The solution was diluted to 300 ml, boiled for 15 min where necessary and cooled to 45–55°. Uranium was then precipitated and the precipitate was digested, filtered, dried and weighed. Typical results are given in Table II.

TABLE II

DETERMINATION OF URANIUM(VI) BY MASKING FOREIGN IONS WITH $MgCl_2$–EDTA

(11.54 mg U (≡ 46.01 mg U complex) and 50 mg of the foreign ion were taken)

Foreign ion added (mg)	*U complex found (mg)*	*Foreign ion added (mg)*	*U complex found (mg)*
$Mg_2{}^{+}$ [a]	46.0	Hg^{2+}	46.0
Ca^{2+}	45.9	Mn^{2+}	46.1
Sr^{2+}	46.0	Cr^{3+} [b]	46.1
Ba^{2+}	46.0	As^{3+}	46.2
Cu^{2+}	46.1	Sb^{3+}	46.2
Co^{2+}	46.0	Bi^{3+}	46.1
Ni^{2+}	45.9	$R.E^{3+}$ [c]	45.9
Cd^{2+}	46.1	Al^{3+} [d]	45.8
Zn^{2+}	46.1	Th^{4+}	46.1
Pb^{2+}	46.0		

[a] No interference in absence of EDTA.
[b] Boiling for 15 min was necessary.
[c] A mixture of rare earth metal ions.
[d] Precipitation of uranium twice was necessary for complete removal of aluminum.

Separation of uranium(VI) by adjustment of acidity

A mixture of known quantities of uranium and foreign ions was diluted to 250 ml and an ethanolic solution of the reagent (ten times the total amount of metal ions present) was added slowly with stirring. The pH of the solution was adjusted between 2.0 and 2.5 for iron(III), 0 and 2.5 for titanium(IV) and zirconium(IV), and 0 and 1.0 for molybdenum(VI), tungsten(VI) and vanadium(V) by moderately concentrated hydrochloric acid. The precipitate was allowed to stand for 1 h with occasional stirring, filtered and washed with a wash liquid. The wash liquids had the same pH as that of precipitation and contained 1% reagent. The filtrate and washings collected together were concentrated to 200 ml and filtered again to remove any organic matter that might have appeared from excess reagent. From the filtrate uranium was determined as described previously. Table III records the results of one of several determinations.

TABLE III

SEPARATION OF URANIUM(VI) BY ADJUSTMENT OF ACIDITY

(11.54 mg U (≡ 46.01 mg U complex) and 50 mg of the foreign ion were taken)

Foreign ion added (mg)	*U complex found (mg)*
Ti^{4+}	45.9
Zr^{4+}	45.9
Fe^{3+}	46.0
WO_4^{2-}	46.0
MoO_4^{2-}	46.0
VO_3^-	46.8[a]

[a] Slightly high results were obtained with vanadium at all acidities over a wide range of pH values.

Interferences

Beryllium was precipitated under similar conditions and was not masked by magnesium–EDTA complex. Aluminum had a tendency to be coprecipitated with uranium, but could be removed by precipitating uranium twice in presence of the masking agent. Carbonate, fluoride, phosphate and organic acids interfered.

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SUMMARY

N-Benzoyl-*o*-tolylhydroxylamine has been used for the gravimetric determination of uranium(VI) by direct weighing of the complex. Uranium(VI) is precipitated quantitatively in the pH range 5.0–7.5 and its separation from a large number of metal ions is described. The composition of the complex has been formulated as $UO_2(C_{14}H_{12}O_2N)_2 \cdot C_{14}H_{13}O_2N$ in conformity with analysis, n.m.r. and mass spectra. The gravimetric factor for the conversion of the metal-complex to the metal is 0.2509, smaller than that for other reagents for uranium.

RÉSUMÉ

La N-benzoyl-*o*-tolylhydroxylamine est utilisée pour le dosage gravimétrique l'uranium(VI) par pesée directe du complexe. L'uranium(VI) est précipité quantitativement au pH 5.0–7.5; on décrit sa séparation d'avec de nombreux ions métalliques. On peut admettre la formule suivante pour le complexe formé: $UO_2(C_{14}H_{12}O_2N)_2 \cdot C_{14}H_{13}O_2N$. Le facteur gravimétrique pour convertir le complexe-métal en métal est 0.2509, plus petit que celui d'autre réactifs de l'uranium.

ZUSAMMENFASSUNG

N-Benzoyl-*o*-tolylhydroxylamin wurde für die gravimetrische Bestimmung von Uran(VI) verwendet, wobei der Komplex direkt ausgewogen wurde. Uran(VI) wird im pH-Bereich 5.0–7.5 quantitativ gefällt; seine Trennung von einer grossen Anzahl von Metallionen wird beschrieben. Die Zusammensetzung des Komplexes wird in Übereinstimmung mit Analyse, N.M.R.- und Massen-Spektren als $UO_2(C_{14}H_{12}O_2N)_2 \cdot C_{14}H_{13}O_2N$ formuliert. Der gravimetrische Faktor für die Umrechnung von Metallkomplex auf Metall beträgt 0.2509 und ist damit kleiner als der von anderen Reagenzien für Uran.

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THE DETERMINATION OF TERBIUM(III) IN BORATE GLASSES*

RENATA REISFELD, Z. GUR-ARIEH AND E. GREENBERG
Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem (Israel)

(Received December 19th, 1969)

The development of lasers has greatly increased interest both in the luminescence of rare earths in glasses, and in the analytical determination of their composition. Moreover, the increasing use of inorganic glasses as matrices for trapped radicals and ions of unusual valencies[1] requires the development of non-destructive analytical methods for the determination of impurities. While excitation and emission of rare earths is similar in glasses and crystals[2], much higher concentrations of rare earths can be introduced into glasses. The cathode-ray-excited emission method for the determination of terbium[3] was ineffective in the detection of terbium in glasses, probably because of dissipation of the energy of the exciting electrons by the traps in glass[4]. Therefore, a method based on optical excitation was developed.

Initially, the optical conditions for the analysis were established. This study included measurements of excitation spectra, emission spectra and decay times of fluorescence. The concentration dependence of fluorescence was then measured.

This technique of measurement can be adapted as a general procedure for the estimation of rare earths in various glasses.

EXPERIMENTAL

Apparatus

The spectrofluorimeter used for the measurement of excitation and fluorescence emission spectra and decay times was constructed in this laboratory[5]. Briefly, it consists of a 500-W xenon arc (Mazda) lamp, interchangeable with a mercury medium-pressure 100-W lamp, an excitation monochromator (Bausch & Lomb, 250 mm focal length), a sample compartment, an analysing monochromator (Bausch & Lomb, 500 mm focal length), an EMI 9558 Q/B photomultiplier connected through a 16 MΩ resistor to an EIL Vibron electrometer, and a Kipp & Zenon recorder. Slow drifts in light intensity were corrected by frequent measurements of a reference glass which contained 1% (w/w) of terbium(III). Fast fluctuations were filtered out. The fluorescence was viewed from the front (illuminated) side of the glass at an angle of 35°, which was found to be the optimum position for signal-to-noise ratio. The photomultiplier was cooled to 20° for all measurements, thus decreasing the dark current by about two orders of magnitude.

The decay times were measured by the technique described earlier[5].

The absorbance of the glasses in the visible and UV regions was measured with a Perkin & Elmer 137 UV spectrophotometer *versus* pure borax.

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* This work was performed under NBS contract (G) 83.

Reagents

Sodium tetraborate (borax) and boric acid (99.5% purity, Baker Analyzed Reagents) and terbium chloride (Research Chemical Nuclear Corporation of America, 99.5% purity) were used.

Preparation of glasses

The glasses were prepared in a similar way to the europium-containing glasses[6]. Dry terbium chloride, borax and boric acid (123 g:62 g) were mixed in an electric vibrator in plastic vials with glass balls. The mixture contained terbium in concentrations ranging from 10 to 50,000 p.p.m. It was established that homogeneous mixtures were obtained after 10 min. These mixtures were found to melt at temperatures lower than 1000°, but clear transparent solutions resulted only after heating at 1100° for at least 15 min. The melts were made in platinum crucibles. Drops of the hot melt were allowed to fall directly on to a clean white glazed ceramic surface. The drop was placed inside the circumference of a 1-mm thick ring and pressed with a second ceramic tile so as to obtain glasses of constant 1 mm thickness.

The glasses were inserted into a glass holder with a circular opening of 12 mm diameter and their excitation and fluorescence spectra were measured at room temperature.

EXCITATION AND EMISSION SPECTRA

The excitation spectrum of 543-nm fluorescence of terbium(III) with xenon excitation is presented in Fig. 1. It consists of bands peaking at 232, 285, 307, 320, 351, 370, 378 and 485 nm. The excitation spectrum of the 487-nm fluorescence with xenon excitation is identical with that of 543-nm fluorescence, except for the 485-nm band which is obscured by the reflection of the 487-nm excitation line. In both cases, the 232-nm and 378-nm bands are the strongest. The excitation peaks of the 487-nm fluorescence are lower by a factor of about 1.5 than those of the 543-nm fluorescence.

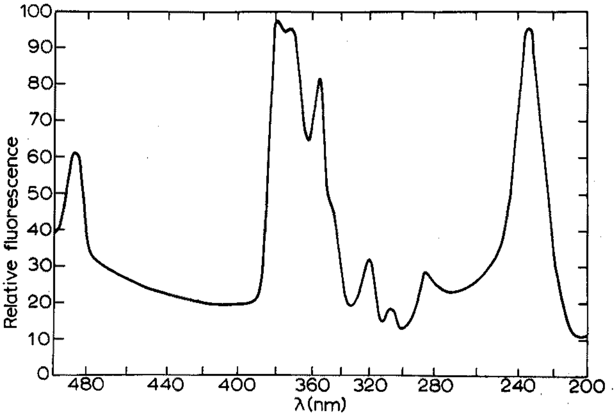

Fig. 1. Excitation spectrum at 543-nm fluorescence with xenon excitation.

This spectrum is similar to the excitation spectrum of the 545-nm fluorescence of terbium(III) in borosilicate glass obtained by CABEZAS AND DESHAZER[7].

Table I shows the relative fluorescence and the experimental lines compared to the centres of gravity of terbium(III) energy levels. The assignments of the levels were taken from the work of CARNALL *et al.*[9] who correlated the experimentally determined band intensities with the theoretical expression in the S′L′J′ coupling scheme derived by JUDD. The short waveband at 232 nm can be attributed to a $4f$–$5d$ transition, consistent with studies of JØRGENSEN AND BRINEN[8] who observed this type of transition in terbium(III) perchlorates. The 232-nm band could be detected in absorption measurements of a glass containing 2% and 5% of terbium(III). The other lines are due to internal f–f transitions and can be detected only in the excitation spectrum, because of their low extinction.

TABLE I

EXCITATION SPECTRUM AT 543-nm FLUORESCENCE AND THE ENERGY LEVELS OF TERBIUM(III)[a]

Assignment of the levels	*Wave no. (cm^{-1})*		*Wavelength (nm)*	*Relative fluorescence*
	Lit. value[9]	*This work*		
$4f^8 \rightarrow 4f^7 5d$[8]	45871[8]	43104	232	2850
$^7F_6 \rightarrow \left.\begin{matrix}{}^5H_4\\ {}^5F_5\\ {}^5H_3\\ {}^5I_8\\ {}^5F_4\end{matrix}\right\}$[9]	34400–35800	35087	285	855
$^7F_6 \rightarrow {}^5H_6$[9]	32500–33500	32573	307	555
$^7F_6 \rightarrow \left.\begin{matrix}{}^5D_0\\ {}^5H_7\end{matrix}\right\}$[9]	30950–32000	31250	320	960
$^7F_6 \rightarrow \left.\begin{matrix}{}^5G_5\\ {}^5D_2\\ {}^5G_4\\ {}^5L_9\end{matrix}\right\}$[9]	27600–28950	28490	351	2445
$^7F_6 \rightarrow \left.\begin{matrix}{}^5D_3\\ {}^5G_6\\ {}^5L_{10}\end{matrix}\right\}$[9]	25900–27600	27027	370	2850
$^7F_6 \rightarrow \left.\begin{matrix}{}^5D_3\\ {}^5G_6\\ {}^5L_{10}\end{matrix}\right\}$[9]	25900–27600	26455	378	2925
$^7F_6 \rightarrow {}^5D_4$[9]	20000–21200	20619	485	1830

[a] Monochromator slits. The entrance/exit slits were 1.0 and 1.0 mm for excitation and 1.0 and 0.8 mm for emission. The applied voltage was 1400 V.

The emission spectrum of terbium(III) measured with xenon source excitation at 378 nm, is presented in Fig. 2. Excitation with mercury lines at 255 nm (the tail of the 232-nm peak) and 365 nm gave a spectrum consisting of the same lines, with intensity lower by a factor of about 2.5. The most intense lines appeared at 543 nm and at 487 nm. Table II shows the relative fluorescence of the emission spectrum measured at 378 nm (xenon source). The assignments of the transitions in this Table are taken from DIEKE AND CROSSWHITE[10] and are expressed formally in the LS coupling.

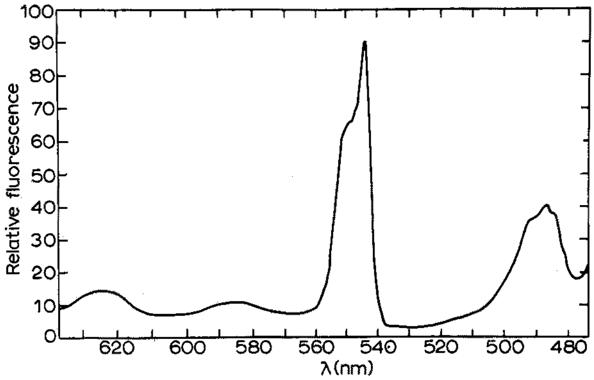

Fig. 2. Emission spectrum at 378-nm (xenon source) excitation.

TABLE II

EMISSION SPECTRUM MEASURED AT 378 nm (XENON SOURCE)[a]

Wavelength (nm)	*Wave no. found (cm^{-1})*	*r.f.*	*Assignment*[10]
485	20619	1140	$^5D_4$–$^7F_6$
487	20534	1215	
491	20367	1095	
543	18416	2730	$^5D_4$–$^7F_5$
548	18248	1980	
585	17094	330	$^5D_4$–$^7F_4$
624	16026	420	$^5D_4$–$^7F_3$

[a] Monochromator slits. The entrance/exit slits were 0.8 and 0.8 mm for excitation and 1.0 and 0.9 mm for emission. The applied voltage was 1400 V.

DETERMINATION OF TERBIUM

Fluorescence measurements as a function of terbium concentration were performed at the excitations of 378 nm (xenon source) and 255 nm (mercury source) with emission measurements at 487 and 543 nm. Linear dependence was observed for both the 543-nm and the 487-nm excitation lines, the fluorescence at 543 nm being stronger by a factor of *ca.* 2 than that at 487 nm. The results are presented in Tables III (543 nm) and IV (487 nm).

A linear concentration dependence was observed over the range 0.001%–1% (w/w). The concentration range 1–5% could also be represented by a straight line with a somewhat larger slope. The scattering of the experimental points with mercury excitation was much lower than that found with xenon excitation, probably because of fluctuations of the xenon source.

TABLE III

CONCENTRATION AND RELATIVE FLUORESCENCE MEASURED AT 543 nm[a]

Excitation at 378 nm (xenon source)		*Excitation at 255 nm (mercury source)*	
Concentration (%)	*r.f.*	*Concentration (%)*	*r.f.*
0.05	10	0.001	3
0.1	18	0.005	15
0.2	39	0.01	27
0.4	56	0.05	140
0.8	159	0.1	310
1.0	180	0.2	585
1.3	570	0.4	1150
2.0	750	1.0	3250
5.0	2490		

[a] Monochromator slits. For measurements at 255-nm excitation the entrance/exit slits were 0.4 and 0.8 mm for excitation and 1.0 and 0.4 mm for emission. For measurements at 378-nm excitation, the respective values were 0.5 and 0.4 mm and 1.0 and 0.16 mm. The applied voltage was 1400 V.

TABLE IV

CONCENTRATION AND RELATIVE FLUORESCENCE MEASURED AT 487 nm[a]

Excitation at 378 nm (xenon source)		*Excitation at 255 nm (mercury source)*	
Concentration (%)	*r.f.*	*Concentration (%)*	*r.f.*
0.2	90	0.1	240
0.4	180	0.2	540
0.8	420	0.4	900
1.0	480	1.0	2150
1.3	800		
2.0	1800		
5.0	4400		

[a] Monochromator slits. For measurements at 255-nm excitation, the entrance/exit slits were 0.8 and 0.8 mm for excitation and 1.0 and 0.4 mm for emission. For measurements at 378-nm excitation, the respective values were 1.0 and 1.0 mm and 1.0 and 1.0 mm. The applied voltage was 1400 V.

The decay curves of terbium(III) were simple exponentials, indicating that the internal energy transfer between the terbium(III) ions is ineffective in the borate glasses. This result is consistent with the absence of concentration quenching in the studied range. The measured decay time for a glass containing 1% of terbium(III) was 2.80 msec. It seems that this decay time is independent of the concentration within the range of the present measurements.

In conclusion, the best procedure for the determination of terbium(III) in glasses, in the absence of other interfering rare earths having emission in the vicinity of 543 nm, is the measurement of the emission at 543 nm with excitation at 255 nm (mercury source). If interfering ions are present, the emission at 487 nm is preferable for the analysis.

SUMMARY

A procedure for the determination of terbium(III) in sodium borate–boric acid glasses is described. The emission and excitation spectra and the decay times are measured. The concentration dependence of the terbium(III) fluorescence can be described by two straight lines intersecting at 1% concentration. Concentrations in the ranges 0.001–1%(w/w) and 1–5%(w/w) can be determined.

RÉSUMÉ

On décrit une méthode pour le dosage du terbium(III) dans des verres borate de sodium–acide borique. On mesure les spectres d'émission et d'excitation. On peut ainsi déterminer des concentrations de l'ordre de 0.001–1% (w/w) et 1–5% (w/w).

ZUSAMMENFASSUNG

Es wird ein Verfahren für die Bestimmung von Terbium(III) in Natriumborat–Borsäure-Gläsern beschrieben. Die Emissions- und Anregungsspektren sowie die Abklingzeiten werden gemessen. Die Konzentrationsabhängigkeit der Terbium(III)-Fluoreszenz kann durch zwei Geraden beschrieben werden, die sich bei einer Konzentration von 1% schneiden. Es können Konzentrationen in den Bereichen 0.001–1 Gew.-% und 1–5 Gew.-% bestimmt werden.

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A DIRECT SPECTROPOLARIMETRIC DETERMINATION OF MAGNESIUM(II), CALCIUM(II), STRONTIUM(II), AND BARIUM(II) WITH D-(−)-*trans*-1,2-CYCLOHEXANEDIAMINETETRAACETIC ACID

J. R. BAKER AND K. H. PEARSON
Department of Chemistry, Texas A &M University, College Station, Texas 77843 (U.S.A.)

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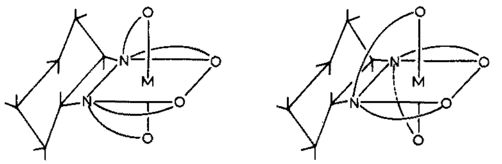
Spectropolarimetric titrimetry is a relatively new analytical technique first described by KIRSCHNER AND BHATNAGAR[1]. The optical rotation of the system is constantly monitored with a photoelectric polarimeter while the titration proceeds. The conditions of the analysis must be chosen so that an inflection in the optical rotation occurs at the titration end-point. Spectropolarimetric titrimetry has been applied to acid–base titrations, as well as to different metal systems[2]. Stereospecific titrants have enabled the scope of this new analytical technique to be extensively increased. In particular, the successful analyses of the 3*d* transition metals, the heavy metals, and the lanthanide metals have been accomplished with the stereospecific ligand D-(−)-1,2-propylenediaminetetraacetic acid (D(−)PDTA) as the titrant[3–7].

The spectropolarimetric method of analysis offers several advantages over other chelometric methods; especially advantageous is the choice of pH range for quantitative titrations, because this pH range is not limited by the need to ensure a sharp indicator color transition. The optically active ligand and the stereospecifically formed complexes serve as self-indicators. Since the observed rotation is essentially linear over large concentration ranges, the end-points are determined by graphical extrapolation. The titrimetric procedures suggested in this paper for the Group IIA metals are rapid and simple, and require no external indicator. A strong stereospecific chelating agent, D-(−)-*trans*-1,2-cyclohexanediaminetetraacetic acid (D(−)CDTA), was selected as the titrant. CDTA forms more stable complexes (generally 1–2 p*K* units for most metal complexes) with most of the metal ions than does EDTA or PDTA[8]. The greater stability of the CDTA metal complexes compared to the EDTA and PDTA metal complexes has been attributed to the fact that during chelation, the carbon chain between the nitrogen atoms on both EDTA and PDTA has to be rotated for the nitrogen atoms to be in the same plane as the metal ion for chelation to occur; the thermodynamically preferred chair configuration of the *trans*-CDTA, with the nitrogen atoms in equatorial positions, requires very little reorientation of the nitrogen atoms for chelation with the metal ion to occur.

DWYER AND GARVAN[9] have shown that only two of the possible four isomers of octahedral metal-chelates can be obtained, thereby proving that either one of the two optical isomers of *trans*-CDTA is completely stereospecific in its reaction with octahedral coordinated metal ions. The stereospecificity of this ligand has been attributed to the stereochemistry of the cyclohexane ring and its inability to accommo-



L^*-[M(D(-)CDTA)]$^{n-}$ D^*-[M(D(-)CDTA)]$^{n-}$

Fig. 1. Stereospecificity of D(−)CDTA in forming L^*–[M(D(−)CDTA)]$^{n-}$ complexes.

date certain chirality because of the steric hindrance between the methylene groups of the ring and the acetato groups (Fig. 1).

EXPERIMENTAL

Apparatus

A Perkin Elmer Model 141 Photoelectric Polarimeter was used to monitor continuously the optical rotation of the solution during the titration. A 1-dm flow-through polarimeter cell with optically inactive end plates was used in all the titrations. The titration vessel and titrimetric apparatus have been described previously[3].

Reagents

With the exception of the solution of D(−)CDTA, all solutions were prepared from reagent-grade chemicals. Optically active D(−) CDTA was prepared by condensation of the resolved D-(−)-*trans*-1,2-cyclohexanediamine with sodium chloroacetate in a strongly basic medium, followed by treatment with strong cation-exchanger to obtain the acid form[10]. An aqueous 0.5% solution of the D-(−)-*trans*-1,2-cyclohexanediaminetetraacetic acid had a specific rotation of −53.5° at 589 nm. *Ca.* 0.15 moles of the anhydrous acid and 0.30 moles of sodium hydroxide pellets were dissolved in 250 ml of deionized water. The Na_2D(−)CDTA was standardized by titration against a standard lead solution at pH 5.0 (10% hexamethylenetetramine buffer) with xylenol orange as the indicator. The pH 10.0 buffer was prepared by dissolving 280 g of ammonium chloride in water, adding 568 ml of concentrated ammonia solution, and diluting to a final volume of 1 l. The standard magnesium(II), calcium(II), strontium(II), and barium(II) solutions were prepared from the perchlorate salts and standardized by EDTA titrimetry[11,12]. The molar concentration ratio of Na_2D(−)CDTA titrant to metal ion solution was *ca.* 60:1, in order to minimize the dilution effects.

Spectropolarimetric titrimetric procedure

An aliquot of the appropriate metal ion solution to be determined was placed in the titration vessel. Ammonia–ammonium chloride buffer (10 ml) was added and the solution was diluted to 100 ml with deionized water. The optical digital readout of the polarimeter was set at zero with the metal ion–buffer solution serving as the blank.

After the addition of each increment of titrant, the digital readout of the polarimeter was allowed to stabilize, which required 10–15 sec, and the observed rotation and volume of titrant were recorded manually. For greatest accuracy the rotational readings were corrected for change in volume. It was necessary to obtain only five points before and five points after the end-point for each determination. Readings near the end-point were not desirable since the equilibrium was attained slowly. The end-point was determined graphically by plotting the corrected optical rotation *versus* the volume of titrant, and extrapolating the two straight lines to the end-point.

RESULTS

The optical rotatory dispersion and absorption spectra for the metal complexes and D(−)CDTA were examined to determine the wavelength giving the maximum optical rotational difference with suitable transmittance. The absorption of D(−)-CDTA and the metal complexes was never the limiting factor in the selection of a suitable wavelength. The molecular rotations for the metal complexes and D(−)CDTA were obtained for 0.010 *M* solutions at pH 10.0. Measurements were made at ambient temperature in a 1-dm polarimeter cell (Table I). All of the metal complexes exhibited their maximum positive rotation at 365 nm for the wavelengths available, while D(−)CDTA had a relatively large negative rotation at this wavelength. Consequently, 365 nm was chosen as the wavelength of analyses for all determinations. Table II gives the change in molecular rotations of D(−)CDTA as a function of pH for a solution with an ionic strength of 0.5 *M* potassium nitrate[13]. In the pH range 8–11 the molecular rotation of D(−)CDTA is nearly constant; therefore, it is not necessary to use large quantities of buffer.

TABLE I

MOLECULAR ROTATIONS OF THE Mg^{2+}, Ca^{2+}, Sr^{2+}, AND Ba^{2+} COMPLEXES OF D(−)CDTA AND D(−)CDTA

Metal complexed	*589 nm*	*578 nm*	*546 nm*	*436 nm*	*365 nm*
Mg^{2+}	+118	+125	+144	+274	+490
Ca^{2+}	+ 29	+ 30	+ 32	+ 76	+167
Sr^{2+}	+ 17	+ 18	+ 24	+ 62	+136
Ba^{2+}	+ 42	+ 45	+ 49	+112	+214
D(−)CDTA	−156	−169	−191	−309	−450

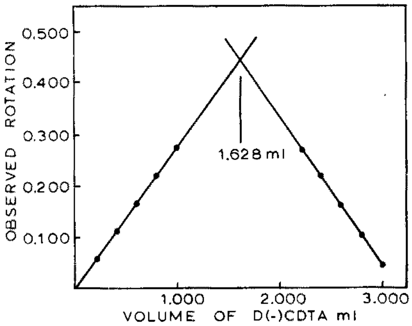
TABLE II

MOLECULAR ROTATIONS OF D(−)CDTA AT DIFFERENT pH VALUES

pH	$[M]^{25°}_{365}$	*pH*	$[M]^{25°}_{365}$	*pH*	$[M]^{25°}_{365}$	*pH*	$[M]^{25°}_{365}$
1.0	−688	2.4	−520	5.9	−354	11.0	−554
1.3	−668	2.7	−458	6.3	−407	11.4	−579
1.4	−655	3.0	−385	6.6	−457	11.7	−611
1.6	−637	3.3	−332	7.3	−509	12.0	−667
1.8	−617	3.5	−324	8.6	−526	12.3	−745
2.0	−577	3.8	−274	10.2	−532	12.5	−795
2.3	−536	4.0	−268	10.8	−537	13.0	−920

Figure 2 shows a typical titration graph for the determination of magnesium-(II). The first straight-line portion of the curve corresponds to the formation of the metal complex of D(−)CDTA which has a positive molecular rotation; the second straight line corresponds to an excess of D(−)CDTA which has a negative molecular rotation. The end-point of the titration is the intersection of these two straight lines. Figure 3 is a typical plot for the spectropolarimetric titration of strontium(II) with D(−)CDTA. All the graphical end-points were very sharp. The sharpness of the barium(II) and calcium(II) titration plots was intermediate between the magnesium(II) and strontium(II), as can be seen from Table I.

Table III gives the results of the titrations for the metal ions. The range of the average deviations from visual chelometry for the four metals determined was 0.00–0.17%.



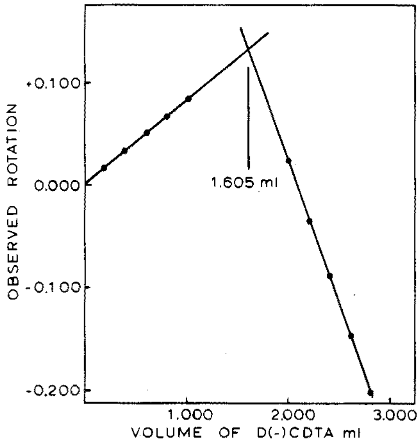


Fig. 2. Titration of 0.09654 *M* magnesium(II) at pH 10.0 and 365 nm.

Fig. 3. Titration of 0.09705 *M* strontium(II) at pH 10.0 and 365 nm.

TABLE III

RESULTS OF SPECTROPOLARIMETRIC TITRATIONS

Metal	*Taken (mg)*	*Found (mg)*	*Deviations*	
			(mg)	*(%)*
Mg	23.42	23.46 ± 0.01	+0.04	+0.17
Ca	36.39	36.43 ± 0.05	+0.04	+0.11
Sr	84.81	84.81 ± 0.00	0.00	0.00
Ba	131.4	131.5 ± 0.1	+0.1	+ 0.08

CONCLUSION

PEARSON *et al.*[6] were unable to titrate magnesium(II) by spectropolarimetric titrimetry with D(−)PDTA, because the molecular rotations of the metal complex and D(−)PDTA were too similar to obtain a good end-point break. When D(−)CDTA is utilized as the stereospecific titrant for the spectropolarimetric titration of magnesium(II), there is a very sharp end-point and magnesium(II) can readily be determined. PEARSON *et al.*[6] also reported that the molecular rotation of D(−)PDTA has its most rapid change between pH 8 and 11; therefore, large quantities of buffer were required in titrating the Group IIA metals by spectropolarimetric titrimetry with

D(−)PDTA. Because the molecular rotation of D(−)CDTA is nearly constant between pH 8 and 11, it is possible to titrate the Group IIA metals with D(−)CDTA without heavy buffering.

Thus, this spectropolarimetric titration with D(−)CDTA offers several advantages over other chelometric methods, especially in choice of pH range for quantitative work. The pH range is not limited by the need to ensure a sharp indicator color transition because the optically active ligand and stereospecifically formed complexes serve as self-indicators. Other advantages of spectropolarimetric titrimetry are its versatility, simplicity, rapidity of analysis, and applicability in solutions of high electrolyte concentration. Since the end-point determination is obtained through relative measurements of optical activity, the spectropolarimetric method yields greater precision than visual methods. Because the best straight line is drawn through a number of experimental points in the construction of titration plots, it is possible to minimize the spectropolarimetric error associated with each point. The extrapolated end-point is not adversely influenced by high electrolyte concentration; whereas chelometry based on indicators, whether visually or spectrophotometrically monitored, can give erroneous results in certain solutions of high electrolyte concentration.

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SUMMARY

A rapid titrimetric method was developed for magnesium(II), calcium(II), strontium(II), and barium(II), with the stereospecific ligand, D-(−)-*trans*-1,2-cyclohexanediaminetetraacetic acid (D(−)CDTA), as titrant. A photoelectric polarimeter was used to monitor continuously the optical rotation of the solution during titration; the titrant and metal complexes formed are optically active and serve as self-indicators. The observed rotation is linear with respect to concentration of the metal complexes and D(−)CDTA, hence the end-point can be established by straight-line extrapolation. The most sensitive wavelength for spectropolarimetric analysis (365 nm) was determined from the optical rotatory dispersion curves. The range of average deviation from visual chelometry for the four metals titrated was 0.00−0.17%.

RÉSUMÉ

Une méthode titrimétrique rapide est proposée pour le dosage du magnésium, du calcium, du strontium et du baryum, en utilisant le ligand: acide D-(−)-*trans*-1,2-cyclohexanediaminotétracétique (D(−)CDTA) comme réactif de titrage. Un polarimètre photoélectrique est employé pour suivre la rotation optique de la solution au cours du titrage. Le titrant et les complexes métalliques formés sont optiquement actifs et servent de self-indicateurs. La rotation observée est linéaire par rapport à la concentration des complexes métalliques et de D(−)CDTA; le point final peut être déterminé par extrapolation. La longueur d'onde la plus sensible pour l'analyse spectropolarimétrique (365 nm) est déterminée à partir des courbes de dispersion optique rotatoire. La déviation moyenne par rapport à la chélométrie visuelle des quatre métaux titrés est de 0.00–0.17%.

ZUSAMMENFASSUNG

Es wurde eine schnelle titrimetrische Methode für Magnesium(II), Calcium(II), Strontium(II) und Barium(II) unter Verwendung des stereospezifischen Liganden D-(−)-*trans*-1,2-Cyclohexandiamintetraessigssäure (D(−)CDTA) als Titrationsmittel entwickelt. Ein photoelektrisches Polarimeter wurde benutzt, um die optische Rotation der Lösung während der Titration kontinuierlich zu verfolgen. Das Titrationsmittel und die gebildeten Metallkomplexe sind optisch aktiv und dienen als Selbstindikatoren. Die beobachtete Rotation verläuft linear mit der Metallkomplex- und mit der D(−)CDTA-Konzentration; daher kann der Endpunkt durch geradlinige Extrapolation bestimmt werden. Die empfindlichste Wellenlänge für die spektropolarimetrische Analyse (365 mn) wurde mit Hilfe der Dispersionskurven der optischen Rotation ermittelt. Die mittleren Abweichungen von der visuellen Chelatometrie lagen bei den vier titrierten Metallen im Bereich 0.00–0.17%.

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A COMPARATIVE STUDY OF VARIOUS COMPLEXING AGENTS (POLYOLS) USED IN THE TITRATION OF BORIC ACID

R. BELCHER
Department of Chemistry, The University, Birmingham 15 (England)
G. W. TULLY AND G. SVEHLA
Department of Analytical Chemistry, The Queen's University, Belfast (N. Ireland)

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Boric acid is too weak an acid to be titrated directly with alkali hydroxides. However, in the presence of polyols having electrophilic character, boric acid forms complexes which have monobasic acid properties. Though still weak, these acids are stronger than boric acid itself, and, if a suitable method of end-point detection is used, they can be titrated with an improved accuracy. Among the complexing agents that have been used, mannitol is by far the most popular, yet only a few comparative studies have reported that this polyol gives the greatest acidity and the best pH jump at the end-point[1-4]. Alternative polyols have, at various times, been claimed to be equal or superior to mannitol, *e.g.* glucose[5], fructose[6,7], sorbitol[8], and ethylene glycol[9]. Moreover, some of the earlier investigators who found mannitol to be best recommended the use of glycerol[1,3] or invert sugar[2] on the grounds of cheapness and/or solubility.

In the present study, the performance of the more common complexing agents has been compared at various concentrations of both boric acid and the polyol, and several criteria have been applied in the assessment of the resulting titration curves. Because the accuracy of a titration depends on the stoichiometry of the reaction, the volume of titrant added at the end-point was recorded for each titration curve. The precision, on the other hand, depends on the sharpness index[10] (η) at the end-point, while the pH range and position of the linear portion at the end-point determine the choice of indicator for visual titrations.

EXPERIMENTAL

Chemicals and equipment

All reagents (B.D.H. Limited) were used as received without further purification. Solutions of boric acid ($5 \cdot 10^{-2}$ *M* and $5 \cdot 10^{-3}$ *M*) were titrated potentiometrically by means of a Metrohm Combi-Titrator 3D fitted with a 20-ml piston burette. A Radiometer Titration Assembly (TTT1c/SBR2C/SBU1a) fitted with a 0.5-ml syringe burette was used to titrate $5 \cdot 10^{-4}$ *M* solutions of boric acid. A Radiometer dual glass/calomel electrode (GK 202 1B) was used with both instruments.

Titration methods

Boric acid solutions of concentration 10^{-1} *M*, 10^{-2} *M*, and 10^{-3} *M* were obtained by successive dilutions of a standard stock solution prepared from AnalaR boric acid. Various volumes of polyol solution were pipetted into 10-ml aliquots of boric acid solution contained in 50-ml titration vessels, and the total volume was adjusted to 20 ml with distilled water. These solutions were titrated with sodium hydroxide solution of concentration 10^{-1} N, 10^{-2} N, and $4 \cdot 10^{-2}$ N respectively, prepared fresh daily by appropriate dilution of B.D.H. concentrated volumetric solution, and standardised just before use by potentiometric titration against standard hydrochloric acid solution. All titrations were performed in duplicate, and in every instance the replicate titration curves were virtually identical in shape.

The titrations were conducted at room temperature, and no provision was made for the removal of dissolved carbon dioxide. The reagent blank titre was determined by titrating a series of solutions at constant polyol concentration, but with varying boric acid concentration. As the plots of volume of titrant consumed *versus* boric acid concentration proved to be straight lines through the origin for all the polyols examined, no corrections for reagent blanks were necessary.

RESULTS AND DISCUSSION

The results obtained for the complexing agents, ethylene glycol, glycerol, mannitol, sorbitol, fructose, and invert sugar, are shown in Table I. Results for glucose and sucrose are not included, for the titration curves obtained with these polyols were indistinguishable from those of boric acid alone, even at a sugar concentration of 12.5% (w/v). Similarly, no data are included for the titration of $5 \cdot 10^{-4}$ M boric acid–ethylene glycol solutions, because no pH jump was observed, even at a glycol concentration of 50.0% (w/v).

Examination of the data in Table I shows that of the various complexing agents studied, the polyalcohols, mannitol and sorbitol, give the largest sharpness index, and the longest linear range at the end-point. For the titration of $5 \cdot 10^{-4}$ M boric acid solution, satisfactory titration curves are obtained when these polyalcohols are used at a concentration of 5.0% (w/v), although considerably smaller amounts of these complexing agents suffice for the titration of more concentrated boric acid solutions. A close examination of the potentiometric data reveals that sorbitol gives marginally better results than mannitol, and in view of its greater solubility and comparable cost, it is recommended in preference to the more popular mannitol.

Fructose also gives reasonably good results at a concentration of 5.0% (w/v) for the titration of $5 \cdot 10^{-3}$ M boric acid solution. However, it is not suitable for the titration of boric acid solutions more dilute than this, and in view of its added expense its use is not justifiable. Although glycerol and invert sugar are cheaper than fructose, they only give satisfactory titration curves when used in high concentrations, *i.e.* $\geqq$25.0% (w/v), and, like fructose, they are both unsuitable for the titration of boric acid solutions more dilute than $5 \cdot 10^{-3}$ M. Ethylene glycol is only of limited use at a concentration in excess of 50.0% (w/v) for the titration of boric acid solutions not less than $5 \cdot 10^{-2}$ M, while glucose and sucrose are of no practical use at all.

In addition to improving the sharpness index and the length of the linear range at the end-point, it is apparent from Table I that the polyols exhibit buffering effects which cause the pH jump to occur at lower pH values than would be expected. This effect is greater for larger amounts of polyol, and it is particularly pronounced in the case of fructose and invert sugar. Hence, if a visual indicator is to be used, it must be chosen according to the nature and amount of polyol to be used. In general, phenolphthalein can be recommended, with the possible exceptions of fructose and invert sugar, where it may be necessary to use phenol red, neutral red, or α-naphtholphthalein.

With regard to the question of comparative stoichiometric accuracy, it can be seen from the data on the volume of titrant added at the end-point that, in general, there is little to choose between any of the polyols tested. However, some difficulties may occasionally be encountered in the titration of very dilute boric acid solutions. In that event, it is advisable to adjust the polyol solution to neutrality before use, and to remove dissolved carbon dioxide by passing a continuous stream of carbon dioxide-free air or nitrogen through the solution to be titrated.

COMPOSITION AND ACID STRENGTH OF THE POLYOL COMPLEXES

The composition and strength of the various hypothetical complex acids formed during the titration of boric acid–polyol solutions can be determined from values of the pH of the solution at the point of half neutralization ($\mathrm{pH}_{\frac{1}{2}}$), measured at different polyol concentrations. An expression relating $\mathrm{pH}_{\frac{1}{2}}$, the association number of the polyol with respect to the borate anion (n), and the pK value of the complex acid can be derived from a consideration of the general equation of the titration curve of boric acid–polyol solutions with $C_P \gg C_B$:

$$i.e.\ [\mathrm{H}^+] = \frac{C_B V_B}{V_S + V_B}\left(\frac{K^*}{[\mathrm{H}^+] + K^*}\right) + \frac{K_W}{[\mathrm{H}^+]} - \frac{C_S V_S}{V_S + V_B} \qquad (1)$$

where

$$K^* = K_a \left\{1 + K_n C_P{}^n \left(\frac{V_B}{V_S + V_B}\right)^n\right\} \qquad (2)$$

The symbols V_S and V_B denote the volume of titrant added during the course of the titration and the initial volume of boric acid–polyol solution respectively. C_S, C_B and C_P represent the molar concentration of the titrant, and the initial molar concentrations of boric acid and polyol respectively. K_W denotes the ionic product for water (10^{-14}), K_a is the ionization constant for boric acid ($6.4 \cdot 10^{-10}$) and K_n is the complex formation constant of the complex anion ($\mathrm{BP}_n{}^-$) formed between one borate anion (B^-) and n molecules of polyol (P):

$$i.e.\ K_n = \frac{K}{K_a} = \frac{[\mathrm{BP}_n{}^-]}{[\mathrm{B}^-]\,[\mathrm{P}]^n} \qquad (3)$$

In the region of the titration curve before the equivalence point one can apply the approximation $[\mathrm{H}^+] - K_W/[\mathrm{H}^+] = 0$ to eqn. (1) to give on rearranging:

$$[\mathrm{H}^+] = K^*\left(\frac{1}{\phi} - 1\right) \qquad (4)$$

where ϕ is the fraction titrated ($\phi = C_S V_S / C_B V_B$), and K^* is as defined by eqn. (2). At the point of half neutralization ($\phi = \frac{1}{2}$), eqns. (2) and (4) can be combined to give:

TABLE I

DATA OBTAINED FROM THE POTENTIOMETRIC TITRATION OF BORIC ACID–POLYOL SOLUTIONS WITH SODIUM HYDROXIDE SOLUTIONS

Concentration of polyol in the boric acid solution (mg/ml)	*End-point* pH			*Volume of titrant added at end-point (ml)*		
	$C_B=5.0\cdot10^{-2}$	$C_B=5.0\cdot10^{-3}$	$C_B=5.0\cdot10^{-4}$	$C_B=5.0\cdot10^{-2}$	$C_B=5.0\cdot10^{-3}$	$C_B=5.0\cdot10^{-4}$
0	10.9	—	—	10.0	—	—
Ethylene glycol						
25	10.9	—	—	10.0	—	—
50	10.8	—	—	10.0	—	—
250	10.3	9.7	—	10.0	10.0	—
500	10.0	9.3	—	9.9	9.9	—
Glycerol						
50	10.4	—	—	10.1	—	—
100	9.9	—	—	10.0	—	—
125	—	9.2	9.0	—	10.0	0.254
150	9.8	—	—	10.0	—	—
200	9.5	—	—	10.0	—	—
250	9.4	8.9	8.5	10.0	10.0	0.249
500	8.9	8.2	8.0	10.0	10.0	0.247
Mannitol						
5	10.7	9.6	9.1	10.0	10.0	0.257
10	10.6	9.1	—	10.0	10.0	—
15	10.2	—	—	10.0	—	—
20	9.9	8.8	—	9.9	10.0	—
25	9.6	—	8.5	10.3	—	0.247
30	9.5	8.5	—	9.9	10.0	—
35	9.5	—	—	9.9	—	—
40	9.2	8.6	—	10.0	10.0	—
45	9.3	—	—	9.9	—	—
50	9.2	8.6	8.4	10.0	10.0	0.249
100	—	—	8.2	—	—	0.247
Sorbitol						
5	10.8	9.5	9.1	10.1	10.1	0.257
10	10.6	9.2	—	9.9	10.0	—
15	10.4	9.0	—	9.9	10.0	—
20	10.1	8.8	—	10.0	10.0	—
25	9.8	8.8	8.5	9.9	10.1	0.250
50	9.1	8.5	8.2	10.0	10.1	0.242
Fructose						
5	10.7	—	—	10.0	—	—
10	10.5	—	—	10.0	—	—
15	10.1	—	—	10.0	—	—
20	9.8	—	—	10.0	—	—
25	9.6	8.3	7.8	10.0	9.7	0.245
30	9.3	—	—	10.0	—	—
35	9.1	—	—	10.0	—	—
40	9.2	—	—	10.0	—	—
45	9.0	—	—	10.0	—	—
50	8.8	7.9	7.8	10.1	9.8	0.253
125	—	7.4	7.2	—	10.1	0.295
250	—	6.9	6.5	—	10.3	0.205
Invert sugar						
25	10.0	8.9	—	10.0	9.9	—
50	9.4	8.4	—	10.0	10.0	—
125	8.6	7.7	7.4	10.0	10.0	0.248
250	8.0	7.3	6.8	10.0	10.1	0.251

[a] pH At the point of half neutralization.

Sharpness index at end-point (η)			*Length of linear range at end-point* (Δ*pH*)			pH_i[a]		
$C_B=5.0 \cdot 10^{-2}$	$C_B=5.0 \cdot 10^{-3}$	$C_B=5.0 \cdot 10^{-4}$	$C_B=5.0 \cdot 10^{-2}$	$C_B=5.0 \cdot 10^{-3}$	$C_B=5.0 \cdot 10^{-4}$	$C_B=5.0 \cdot 10^{-2}$	$C_B=5.0 \cdot 10^{-3}$	$C_B=5.0 \cdot 10^{-4}$
9.7	—	—	0.7	—	—	9.2	—	—
12.4	—	—	0.8	—	—	9.1	—	—
14.3	—	—	0.8	—	—	8.9	—	—
19.7	6.5	—	0.9	0.6	—	8.2	8.2	—
24.9	7.9	—	1.0	0.8	—	7.8	7.7	—
27.7	—	—	1.1	—	—	8.1	—	—
40.6	—	—	1.3	—	—	7.3	—	—
—	19.1	7.2	—	1.1	0.8	—	7.2	7.3
46.9	—	—	1.6	—	—	7.1	—	—
61.8	—	—	1.5	—	—	6.8	—	—
74.7	26.7	10.7	1.7	1.3	0.9	6.6	6.6	6.7
104	33.9	15.0	2.0	1.4	1.1	5.9	5.8	6.0
14.4	19.7	11.1	0.9	0.9	1.0	8.5	7.4	7.3
22.9	32.4	—	1.0	1.2	—	7.6	6.7	—
35.9	—	—	1.4	—	—	6.9	—	—
63.3	48.1	—	1.6	1.8	—	6.4	6.2	—
73.7	—	30.6	1.6	—	1.5	6.2	—	6.2
104	59.6	—	1.7	2.0	—	6.0	5.8	—
>100	—	—	2.2	—	—	5.8	—	—
>100	71.4	—	2.3	2.0	—	5.8	5.6	—
>100	—	—	2.3	—	—	5.6	—	—
>100	77.7	31.3	2.5	2.0	1.6	5.7	5.5	5.6
—	—	35.8	—	—	1.7	—	—	5.1
14.5	24.2	14.2	0.7	1.1	1.0	8.4	7.0	7.1
26.0	45.0	—	1.0	1.3	—	7.5	6.5	—
43.7	54.2	—	1.5	1.6	—	6.8	6.2	—
81.7	63.5	—	1.7	1.8	—	6.4	5.9	—
100	72.5	26.5	2.2	1.8	1.5	6.1	5.7	5.9
>100	80.7	32.1	2.9	2.1	1.7	5.4	5.3	5.4
13.4	—	—	0.8	—	—	8.4	—	—
21.8	—	—	1.1	—	—	7.7	—	—
32.8	—	—	1.2	—	—	7.1	—	—
44.7	—	—	1.3	—	—	6.8	—	—
51.9	21.8	6.4	1.5	1.3	1.0	6.6	6.0	6.1
61.5	—	—	1.5	—	—	6.3	—	—
58.3	—	—	1.7	—	—	6.1	—	—
85.9	—	—	1.6	—	—	6.0	—	—
79.7	—	—	1.9	—	—	5.8	—	—
70.7	28.0	12.2	1.9	1.3	1.2	5.7	5.6	5.6
—	32.3	13.2	—	1.5	1.3	—	5.0	5.1
—	37.2	16.5	—	1.8	1.3	—	4.3	4.6
16.0	13.5	—	1.1	0.9	—	7.7	6.9	—
27.5	18.7	—	1.3	1.0	—	6.8	6.3	—
54.4	25.0	8.3	1.7	1.3	0.9	5.8	5.5	5.6
70.4	21.3	7.5	2.0	1.6	1.0	5.1	4.8	5.0

$$[\mathrm{H}^+]_{\frac{1}{2}} = K_{\frac{1}{2}}^* = K_a \left\{1 + K_n C_{\mathrm{P}}^{n} \left(\frac{V_{\mathrm{B}}}{V_{\mathrm{S}_{\frac{1}{2}}} + V_{\mathrm{B}}}\right)^{n}\right\} \tag{5}$$

where the subscripts $\frac{1}{2}$ denote that the various quantities assume the value appropriate for the point of half neutralization. It is interesting to note that ANTIKAINEN[11,12] derived a similar expression for the apparent ionization constant of boric acid in polyol solutions by means of the minimum buffer capacity method.

Since $K = K_a K_n$ and considering that $K_a \ll [\mathrm{H}^+]_{\frac{1}{2}}$, eqn. (5) can be rearranged to give:

$$\mathrm{pH}_{\frac{1}{2}} = -\mathrm{n} \log C_{\mathrm{P}} + \mathrm{p}K - n \log \left(\frac{V_{\mathrm{B}}}{V_{\mathrm{S}_{\frac{1}{2}}} + V_{\mathrm{B}}}\right) \tag{6}$$

Hence a plot of $\mathrm{pH}_{\frac{1}{2}}$ *versus* $-\log C_{\mathrm{P}}$ should yield a straight line of slope n and intercept I given by eqn. (7):

$$I = \mathrm{p}K - n \log \left(\frac{V_{\mathrm{B}}}{V_{\mathrm{S}_{\frac{1}{2}}} + V_{\mathrm{B}}}\right) \tag{7}$$

from which pK can be calculated. Values of n and pK obtained at three different concentrations of boric acid (C_{B}) for several of the polyols examined in this study are shown in Table II.

TABLE II

VALUES OF n AND pK DERIVED FROM PLOTS OF $\mathrm{pH}_{\frac{1}{2}}$ *versus* $-\log_{10} C_{\mathrm{P}}$

Polyol	*Association number (n)*			$pK = pK_a + pK_n$		
	$C_B = 5.0 \cdot 10^{-2}$	$C_B = 5.0 \cdot 10^{-3}$	$C_B = 5.0 \cdot 10^{-4}$	$C_B = 5.0 \cdot 10^{-2}$	$C_B = 5.0 \cdot 10^{-3}$	$C_B = 5.0 \cdot 10^{-4}$
Ethylene glycol	1.0	—	—	8.6	—	—
Glycerol	2.2	2.2	2.1	7.3	7.3	7.6
Mannitol	2.2	1.9	1.8	4.1	4.2	4.6
Sorbitol	2.6	1.9	1.8	3.6	4.0	4.4
Fructose	2.9	1.4	1.6	3.7	4.6	4.8

The results for the pK values reflect the general conclusions regarding the relative applicability of the different polyols, *i.e.* the pK values increase in the order sorbitol < mannitol < fructose ≪ glycerol < ethylene glycol, although the pK value for fructose obtained at $C_{\mathrm{B}} = 5.0 \cdot 10^{-2}$ is abnormally low. It is also seen that on the whole the values for the association number (n) tend to decrease, and the values for pK tend to increase with increasing dilution of the boric acid. This is to be expected, for the extent of complexation would normally decrease with decreasing boric acid concentration. It is difficult to interpret values for n greater than 2 on stereochemical grounds, but it is interesting to note that MATEROVA AND ROZHANSKAYA[13] also obtained an association number greater than 2 in the case of glycerol. On the other hand, non-integral values of n between 1 and 2 indicate that both the species BP^- and BP^-_2 are present in solution.

SUMMARY

Boric acid reacts with several polyols to form complexes which are acidic enough to be titrated directly with alkali hydroxide solution. A detailed potentiometric study has shown that sorbitol gives slightly sharper end-points than the more commonly used mannitol, but both are satisfactory for the titration of $5 \cdot 10^{-2}$–$5 \cdot 10^{-4}$ *M* boric acid. Fructose, glycerol and invert sugar are not satisfactory for less than 10^{-3} *M* boric acid solution, and very large concentrations of the latter two reagents are needed. Ethylene glycol has limited application; glucose and sucrose cannot be used. The p*K* values of the complexes formed increase in the order sorbitol < mannitol < fructose ≪ glycerol < ethylene glycol.

RÉSUMÉ

L'acide borique forme des complexes avec plusieurs polyols; ces complexes sont suffisamment acides pour pouvoir être titrés directement avec une solution d'hydroxyde alcalin. Une étude potentiométrique a permis de conclure que le sorbitol et le mannitol peuvent être utilisés tous deux pour le titrage de l'acide borique $5 \cdot 10^{-2}$–$5 \cdot 10^{-4}$ *M*; cependant le point final obtenu avec le sorbitol est légèrement plus net. Le fructose, le glycérol et le sucre inverti ne conviennent pas pour des concentrations inférieures à 10^{-3} *M* en acide borique. L'emploi de l'éthylèneglycol est limité; glucose et sucrose ne peuvent pas être utilisés. Les valeurs de p*K* des complexes formés augmentent dans l'ordre: sorbitol < mannitol < fructose ≪ glycérol < éthylèneglycol.

ZUSAMMENFASSUNG

Borsäure bildet mit verschiedenen Polyolen Komplexe, die genügend sauer für eine direkte Titration mit Alkalihydroxid-Lösungen sind. Eine genaue potentiometrische Untersuchung hat gezeigt, dass Sorbit etwas schärfere Endpunkte ergibt als der mehr gebräuchliche Mannit; jedoch sind beide für die Titration von $5 \cdot 10^{-2}$–$5 \cdot 10^{-4}$ *M* Borsäure geeignet. Fruktose, Glycerin und Invertzucker sind für weniger als 10^{-3} *M* Borsäure-Lösungen nicht zufriedenstellend; es werden sehr hohe Konzentrationen der beiden letzteren Reagenzien benötigt. Äthylenglykol ist beschränkt anwendbar; Glukose und Saccharose können nicht angewendet werden. Die p*K*-Werte der gebildeten Komplexe nehmen zu in der Reihenfolge Sorbit < Mannit < Fruktose ≪ Glycerin < Äthylenglykol.

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SOLVENT EXTRACTION OF COPPER(II) BY SCHIFF'S BASES

J. AGGETT* AND R. A. RICHARDSON
Chemistry Department, University of Auckland, Auckland (New Zealand)

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Recent papers from this laboratory have been concerned with solvent extraction reagents which are capable of functioning as doubly-charged ligands. The reagents investigated previously have included salicylic acid and related compounds[1-3] and alkyl malonic acids[4]. This paper is concerned with an investigation of the solvent extraction behaviour of another type of potentially doubly-charged ligand, *viz.* Schiff's bases formed by the condensation of one mole of diamine with two moles of either β-diketone or salicylaldehyde. Compounds of this type are known to form quadridentate chelates with a number of divalent cations, and in particular those with copper(II) have been extensively investigated[5-7]. In addition to the establishment of solvent-extraction characteristics, the use of some of these reagents in the determination of copper(II) by spectrophotometry and by atomic absorption spectroscopy has also been investigated.

EXPERIMENTAL

Extraction procedure

Aqueous solutions which were 10^{-3} M in copper(II) were equilibrated with equal volumes of the appropriate organic phases at 25°. Optimum equilibration times were determined for each system since some variation was observed; for example, it was found that extraction into methyl isobutyl ketone (MIBK) was generally considerably faster than extraction into chloroform. After phase separation the copper(II) content of both phases was determined by atomic absorption spectroscopy. The aqueous phase was diluted with an equal volume of 4 M hydrochloric acid and the organic phase was back-extracted with 2 M hydrochloric acid for analysis.

All analyses were done on a Unicam SP90A spectrophotometer with the copper line at 324.7 nm and a premixed air–propane flame. Where methyl isobutyl ketone was used in extraction experiments, the back-extraction step was eliminated and the concentration of copper(II) in the organic phase was determined by aspirating the organic phase directly into the flame. The necessary calibration curves were prepared from standard solutions of the copper(II) complexes in methyl isobutyl ketone.

Reagents

Bis(acetylacetone)-ethylenediimine ($(Acac)_2en$), bis(benzoylacetone)-ethylenediimine ($(Bzac)_2en$), bis(trifluoroacetylacetone)-ethylenediimine ($(Tfac)_2en$) and the corresponding 1,2-diaminopropane derivatives were prepared by the method of MARTELL *et al.*[8]. Condensation products between the diamines and salicylaldehyde

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* Present address: Department of Chemistry, Imperial College, Imperial Institute Road, London S.W.7 (England).

were prepared by the method of DUBSKY AND SOKOL[9]. Attempts to condense *o*-phenylenediamine with the β-diketones resulted in the formation of 1:1 species only. The behaviour of these was not investigated. Although a 2:1 adduct between thenoyltrifluoroacetone and ethylenediamine was successfully prepared, it was not stable in solution and therefore was not investigated either.

The reagents synthesised for this work were purified by recrystallisation. Their melting points and elemental analysis data are recorded in Table I. Other chemicals were AR quality. Organic solvents were purified by standard procedures.

TABLE I

PROPERTIES OF LIGANDS

Compound and abbreviation	*Elemental analyses*	*M.pt. (°)*
Bis(acetylacetone)-ethylenediimine (Acac)$_2$en	Calc.: C 64.30, H 8.93, N 12.50 Found: C 63.99, H 8.85, N 12.61	111
Bis(acetylacetone)-propylenediimine (Acac)$_2$pn	Calc.: C 65.52, H 9.24, N 11.77 Found: C 65.72, H 9.33, N 11.75	92
Bis(benzoylacetone)-ethylenediimine (Bzac)$_2$en	Calc.: C 75.83, H 6.94, N 8.04 Found: C 76.04, H 6.97, N 7.68	185
Bis(benzoylacetone)-propylenediimine (Bzac)$_2$pn	Calc.: C 76.21, H 7.23, N 7.73 Found: C 76.55, H.7.35, N 7.80	115
Bis(trifluoroacetylacetone)-ethylenediimine (Tfac)$_2$en	Calc.: C 43.38, H 4.25, N 8.43 Found: C 42.10, H 4.08, N 8.43	126
Bis(ethylacetoacetate)-ethylenediimine (Etacac)$_2$en	Calc.: C 59.20, H 8.45, N 9.85 Found: C 59.48, H 8.48, N 9.78	135
Bis(salicylaldehyde)-ethylenediimine (Sal)$_2$en	Calc.: C 71.70, H 5.97, N 10.44 Found: C 72.08, H 6.05, N 10.81	126
Bis(5-bromosalicylaldehyde)-ethylenediimine (Br-Sal)$_2$en	Calc.: C 45.05, H 3.29, N 6.58 Found: C 44.82, H 3.25, N 6.37	194
Bis(salicylaldehyde)-*o*-phenylenediimine (Sal)$_2$phen	Calc.: C 76.00, H 5.07, N 8.86 Found: C 76.45, H 5.19, N 9.14	164
Bis(5-bromosalicylaldehyde)-*o*-phenylenediimine (Br-Sal)$_2$phen	Calc.: C 50.70, H 2.95, N 5.90 Found: C 50.94, H 3.02, N 6.11	211

Buffers

The most suitable buffer solution for the systems under study was one containing chloroacetic acid and sodium bicarbonate in varying proportions.

RESULTS AND DISCUSSION

Solvent extraction studies

pH profiles for the extraction of copper(II) into methyl isobutyl ketone by the reagents listed in Table I are shown in Fig. 1. Table II contains further extraction data in abbreviated form. While the extraction curves generally were of similar shape, that obtained with the 10^{-1} *M* bis(acetylacetone)-1,2-propylenediimine/chloroform system differed in that the percentage extraction fell to about 90% at pH 7. This is believed to be caused by decomposition of the ligand since in this pH region the curve was shown to correspond very closely with that for extraction by 10^{-1} M acetylacetone.

The data in Fig. 1 and Table II show that apart from bis(ethylacetoacetate)-ethylenediimine, all these reagents are capable of effecting quantitative extraction of copper(II). However, they do differ considerably in the pH region at which extraction occurs. Among the ligands based on β-diketones, variation of either the β-diketone or the diamine does not appear to produce major alteration to the pH of extraction. Generally, the salicylaldehyde-based reagents extract copper at lower pH than the reagents based on β-diketones. But while introduction of a bromo-group results in a small lowering of the pH$_{\frac{1}{2}}$ value, the most significant change in the extraction profile was achieved by the use of *o*-phenylenediamine. With the reagent bis(salicylaldehyde)-*o*-phenylenediimine, it is possible to extract copper(II) from aqueous solutions of about pH 1, *i.e.* copper(II) can be extracted from dilute acid solutions. The advantages of extraction from solutions of low pH are, firstly, that hydrolysis of highly-charged cations which may also be present in practical situations is minimised, and, secondly, that the pH can be very conveniently controlled with dilute sulphuric acid.

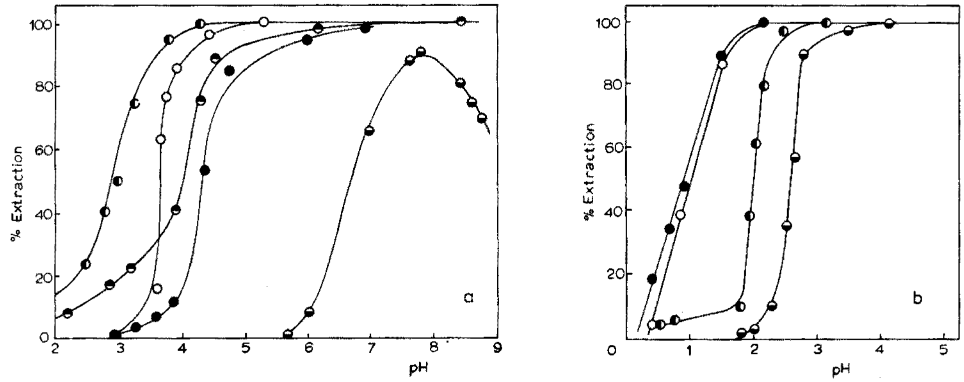

Fig. 1. pH profiles for the extraction of copper(II) with the ligands studied.
(a): (○) $(Acac)_2pn$, (●) $(Acac)_2en$, (◐) $(Bzac)_2pn$, (◓) $(Tfac)_2en$, (◒) $(Etacac)_2en$. (b): (○) $(Br\text{-}Sal)_2phen$, (●) $(Sal)_2phen$, (◒) $(Sal)_2en$, (◐) $(BrSal)_2en$.

Recently it has been reported that copper can be recovered in commercial quantities by a solvent extraction process based on a reagent LIX 64[10]. This reagent is used to extract copper(II) from dilute sulphuric acid solutions. The extraction performance of bis(salicylaldehyde)-*o*-phenylenediimine appears to be comparable with that of LIX 64. However, its stability has not yet been investigated.

The nature of the extracted species was deduced from the dependence of the distribution ratio on the ligand concentration at constant pH. Data were obtained for only one ligand, *viz.* bis(acetylacetone)-ethylenediimine. A logarithmic plot showed a straight line of slope 1.05, indicating that the species extracted is bis(acetylacetone)-ethylenediimine–copper(II). It appears very probable that the stoichiometry of the extraction process in the other systems is similar.

The observed variations in the colours of the extracts (Table II) are probably associated with differences in stereochemistry. WATERS *et al.*[6] have suggested that in

TABLE II

EXTRACTION DATA FOR COPPER(II) WITH THE VARIOUS LIGANDS

Reagent	*Concn. (M)*	*Solvent*	*pH*$_{\frac{1}{2}}$	*pH for 100% extr.*	*Colour*
(Acac)$_2$en	10^{-2}	Chloroform	3.25	5.0	Purple
	10^{-2}	Toluene	4.25	7.0	Purple
	10^{-2}	Benzene	4.02	6.2	Purple
	10^{-2}	MIBK	4.36	7.0	Purple
	$3 \cdot 10^{-2}$	Toluene	4.03	7.0	
	10^{-1}	Chloroform	2.65	4.0	
	10^{-1}	Toluene	3.54	7.0	
(Acac)$_2$pn	10^{-2}	Chloroform	2.89	5.0	Purple
	10^{-2}	Toluene	3.87	6.0	Purple
	10^{-2}	Benzene	3.58	5.0	Purple
	10^{-2}	MIBK	3.70	5.5	Purple
	10^{-1}	Chloroform	2.55	3.5	
	10^{-1}	Toluene	3.53	7.5	
(Bzac)$_2$en	10^{-2}	Chloroform	4.02	5.5	Brown
	10^{-2}	Benzene	5.43	8.5	Brown
	10^{-1}	Chloroform	2.58	3.8	Brown
(Bzac)$_2$pn	10^{-2}	Chloroform	3.60	6.0	Brown
	10^{-2}	Toluene	6.95	8.5	Brown
	10^{-2}	Benzene	5.12	7.5	Brown
	10^{-2}	MIBK	2.96	4.5	Brown
	10^{-1}	Chloroform	2.55	3.6	
	10^{-1}	Toluene	3.5	7.2	
(Tfac)$_2$en	10^{-2}	Chloroform	5.25	7.0	Purple
	10^{-2}	MIBK	4.05	8.5	Purple
(Etacac)$_2$en	10^{-2}	Chloroform	6.65	—	Brown-grey
	10^{-2}	Toluene	6.30	—	
	10^{-2}	Benzene	6.80	—	
	10^{-2}	MIBK	6.65	8.0(92%)	
(Sal)$_2$en	10^{-2}	Chloroform	2.25	3.3	Green
	10^{-2}	MIBK	2.61	4.0	Green
(Br-Sal)$_2$en	10^{-2}	Chloroform	1.36	2.1	Yellow-green
	10^{-2}	MIBK	2.00	2.8	Yellow-green
(Sal)$_2$phen	10^{-2}	Chloroform	0.92	1.5	Yellow-brown
	10^{-2}	Benzene	0.80	1.2	Yellow-brown
	10^{-2}	MIBK	1.0	2.2	Yellow-brown
(Br-Sal)$_2$phen	10^{-2}	MIBK	0.98	2.2	Orange-brown

the solid state *cis*-quadridentate copper(II) complexes are normally violet, and that the presence of a green species is indicative of higher coordination. However, little work has been reported on these species in solution and accordingly any comment must be considered speculative.

Extractive spectrophotometric determination of copper(II)

The performance of bis(acetylacetone)-ethylenediimine as a spectrophotometric reagent for copper(II) was investigated. Standard aqueous copper(II) solutions were extracted with equal volumes of 10^{-2} *M* reagent in methyl isobutyl ketone. With a 10^{-2} *M* solution of the reagent which had been pre-equilibrated with water as a blank, the variation of absorbance at 544 nm with aqueous copper(II) concentration was measured. A straight-line calibration graph was obtained over the range 0–$3.6 \cdot 10^{-3}$ *M* copper(II). The molar extinction coefficient was found to be 197 which compares well with the value of 198 obtained for solutions of the pure copper(II) complex at the same wavelength.

A similar study was made with bis(salicylaldehyde)-*o*-phenylenediimine in methyl isobutyl ketone. In this case the absorption maximum occurred at 560 nm where the molar extinction coefficient was found to be 364. However, this system was limited by precipitation at higher copper(II) concentrations.

The extent to which other cations interfere with determinations of copper(II) carried out by these procedures was also investigated. Table III contains a summary of the results of experiments on the bis(acetylacetone)-ethylenediimine system. Interference by iron(II) and iron(III) was removed by masking with fluoride, while sodium malonate was used to mask cadmium(II) interference. Palladium(II) was removed by preliminary extraction with 10^{-1} *M* acetylacetone in benzene at pH 2.

TABLE III

EFFECT OF DIVERSE IONS ON THE SPECTROPHOTOMETRIC DETERMINATION WITH $(Acac)_2en$

No interference at 10-fold amounts: Ag^+, Al^{3+}, Bi^{3+}, Ce^{3+}, Co^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Pr^{3+}, Pt^{2+}, Tl^{3+}, UO_2^{2+}, Vo^{2+}, Zn^{2+}.
Interference at equimolar concentrations: Fe^{2+}, Fe^{3+}.
Interference at 10-fold amounts: Cd^{2+}, Fe^{2+}, Fe^{3+}, Nd^{3+}, Pd^{2+}.

Interference in the bis(salicylaldehyde)-*o*-phenylenediimine system was less pronounced although iron(II), iron(III), and palladium(II) interfered when present in 10-fold amounts. Furthermore, the presence of chloride ions caused precipitation of the ligand.

Determination of copper(II) by atomic absorption spectrophotometry

The limits of detection for cations by atomic absorption spectrophotometry can be lowered by using solutions in organic solvents. In the case of copper(II), it has been reported that the sensitivity is increased almost 5-fold by preliminary extraction into methyl isobutyl ketone containing 1% ammonium pyrrolidinedithiocarbamate[11].

The behaviour of bis(acetylacetone)-ethylenediimine, bis(salicylaldehyde)-ethylenediimine, and bis(salicylaldehyde)-*o*-phenylenediimine in the determination of copper(II) by atomic absorption spectroscopy was examined and compared with that of ammonium pyrrolidinedithiocarbamate. In these experiments the two following procedures were used.

(*a*) Copper(II) was extracted from aqueous solution by an equal volume of 10^{-2} *M* reagent in methyl isobutyl ketone which was aspirated directly into the flame. For each of these reagents extracts obtained in this manner gave absorbance values approximately three times higher than those of aqueous solutions containing the same copper(II) concentration.

(*b*) A phase ratio of 1:10 was used in the extraction procedure and the methyl isobutyl ketone phase was analysed directly. This technique greatly increased the sensitivity for copper(II) (Fig. 2) and made it possible to determine concentrations of the order of 10^{-7} *M* (8 p.p.b.). These detection limits were similar to those obtained by a similar technique with ammonium pyrrolidinedithiocarbamate as the extraction reagent.

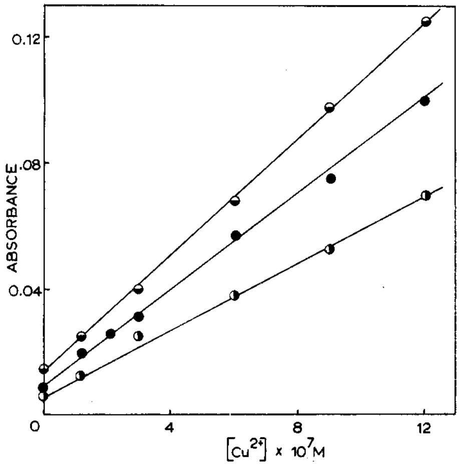

Fig. 2. Calibration graphs obtained for atomic absorption spectrophotometric determination of copper(II). (◒) $(Sal)_2en$, (●) $(Acac)_2en$, (◑) $(Sal)_2phen$.

The ability of these reagents to enhance the sensitivity of copper(II) determinations depends on the quantitative extraction of the copper(II) chelate under specified conditions, and in this respect there is little difference in their relative merits. However, because these Schiff's bases can be readily prepared from inexpensive starting materials they merit consideration as alternative reagents to ammonium pyrrolidinedithiocarbamate for the determination of copper(II).

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SUMMARY

The solvent extraction of copper(II) by a number of quadridentate Schiff's bases has been investigated. All but one of the reagents are capable of extracting copper(II) quantitatively from aqueous solution and the possibility of using these reagents for determination of copper(II) by absorption spectrophotometry and by atomic absorption spectrophotometry is described. Spectrophotometric determinations are not sensitive but the atomic absorption method allows determinations in the p.p.b. range, similar to ammonium pyrrolidinedithiocarbamate.

RÉSUMÉ

On examine l'extraction du cuivre(II) dans un solvant, par un certain nombre de bases de Schiff. Une méthode est décrite utilisant ces réactifs pour le dosage du cuivre(II) par spectrophotométrie d'absorption, et spectrophotométrie par absorption atomique. Les dosages spectrophotométriques ne sont pas sensibles. Cependant l'absorption atomique permet des dosages dans l'ordre de p.p.b., comme pour le pyrrolidinedithiocarbamate d'ammonium plus difficile à préparer.

ZUSAMMENFASSUNG

Es ist die Extraktion von Kupfer(II) durch eine Anzahl vierzähniger Schiffscher Basen untersucht worden. Fast alle Reagenzien sind fähig, Kupfer(II) quantitativ aus wässriger Lösung zu extrahieren. Die Möglichkeit der Anwendung dieser Reagenzien auf die Bestimmung von Kupfer(II) durch Absorptionsspektrophotometrie und durch Atomabsorptions-Spektrophotometrie wird beschrieben. Spektrophotometrische Bestimmungen sind nicht empfindlich; jedoch erlaubt die Atomabsorptionsmethode Bestimmungen im p.p.b.-Bereich, ähnlich Ammonium-pyrrolidindithiocarbamat, welches viel schwieriger herzustellen ist.

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THE EXTRACTION OF INDIUM FROM AQUEOUS HALIDE AND THIOCYANATE MEDIA BY SOLUTIONS OF LIQUID ANION EXCHANGERS IN ORGANIC SOLVENTS

H. M. N. H. IRVING AND A. D. DAMODARAN
Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds, 2 (England)

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The liquid–liquid extraction of indium(III) from halogen acids has been investigated for a wide range of organic solvents[1–3] and there have been several studies of its absorption on anion-exchange resins[4–6]. All these papers agree in showing that distribution involves the uni-negative anion InX_4^- ($X = Cl$, Br, I) although the distribution ratios are lower than some formally similar systems involving, for example, iron(III) and gallium(III). This could, of course, be due to the occurrence of higher anionic complexes such as $InCl_5^{2-}$ or $InCl_6^{3-}$ and indeed the failure of Raman spectroscopy to detect significant amounts of $InCl_4^-$ in concentrated aqueous solutions of indium chloride containing up to 15 *M* hydrochloric acid led WOODWARD AND TAYLOR[7] to postulate that $InCl_5^{2-}$ and $InCl_6^{3-}$ are the predominant species. On the other hand, studies of the stability constants for the system indium(III)–halide ion gave values decreasing in the order $K_1 > K_2 > K_3$ for chlorides, bromides and iodides[8] and, if the trend were continued, the formation constant for the species InX_4^- would be very low indeed and that for higher complexes still smaller. An alternative explanation[5] is that indium(III) tends to retain a coordination number of six, so that species such as $InCl_4(H_2O)_2^-$ being more hydrophilic than the tetrahedral $InCl_4^-$ would favour the aqueous phase and so reduce the distribution ratios.

Studies with liquid anion exchangers can often yield information on the composition of the participating species but they have so far been limited to chloride systems and the results are conflicting. Thus WHITE, KELLY AND LI[9] report that indium is extracted by solutions of tri-*n*-octylamine hydrochloride as the pentachloro complex, $InCl_5^{2-}$, but results from NAKAGAWA[10] for the secondary amine Amberlite LA-1 are very different. MAYDAN AND MARCUS[5] report detailed studies with solutions of tri-iso-octylamine hydrochloride in xylene and conclude that indium is extracted both as $NR_3H^+InCl_4^-$ and $(NR_3H^+)_3InCl_6^{3-}$ depending on the concentration of amine ($R =$ iso-octyl), whilst the extraction of $(NR_3H)_2HInCl_6$ and $(NR_3H)H_2InCl_6$ were postulated additionally to explain the observed differences between extractions from concentrated solutions of sodium chloride and from concentrated hydrochloric acid.

After the present work had been completed[11], GOOD AND HOLLAND[12] published a very full account of their studies with a variety of extractants. With solutions of tertiary amine hydrochlorides $NR_3H^+Cl^-$ ($R =$ hexyl, *n*-octyl and iso-octyl) in toluene, the slope of the isotherm was consistent with the extraction of $(NR_3H^+)_2InCl_5^{2-}$, possibly retaining a molecule of water attached to the indium to preserve octahedral coordination. On the other hand, the quaternary salt Alamine-336 (tricaprylmethylammonium chloride) extracted indium as a uni-negative ion, *viz.* as $R_3{}^1MeN^+InCl_4{}^-$ (or $R_3{}^1MeN^+InCl_4(H_2O)_2{}^-$) where R^1 = capryl. Diethyldihexylammonium chloride and the hydrochloride of Primene 81-R ($C_{12-14}H_{25-29}NH_2$,HCl) were much poorer extractants.

These conflicting results induce us to report our own findings which cover a wider variety of anions in the aqueous phase. With ^{114m}In ($t_{\frac{1}{2}}$ 49 days) as a tracer, the distribution of indium(III) between aqueous solutions containing chloride, bromide, iodide and thiocyanate ions and a solution of the corresponding *n*-hexylammonium halide in 1,2-dichloroethane was studied. With a constant concentration of halogen acid, a plot of the distribution ratio *D* (defined as the total concentration of indium in the organic phase divided by the total concentration of indium in the aqueous phase, both measured radiometrically) against the concentration of quaternary ammonium halide was a straight line of unit slope for both chloride, bromide and iodide (Fig. 1).

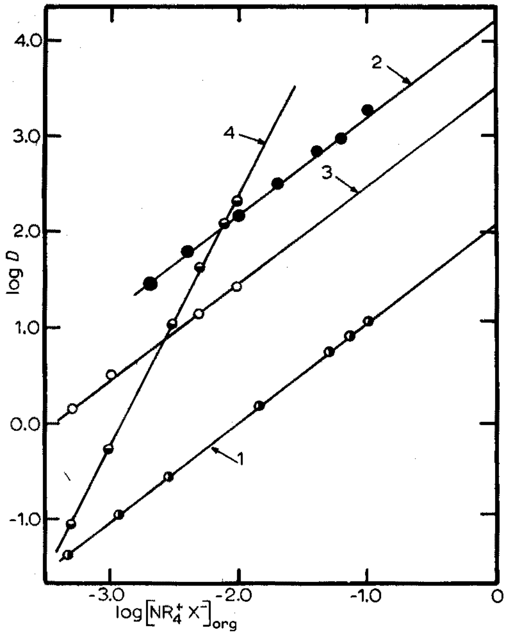


Fig. 1. The extraction of indium(III) by a solution of quaternary *n*-hexylammonium salt in 1,2-dichloroethane at 22 ± 2° from an equal volume of aqueous phase. (1) 0.72 *M* HCl, (2) 1.5 *M* HBr, (3) 0.033 *M* HI, (4) 0.1 *M* KSCN at pH = 1.

The results are consistent with the extraction of a uni-negative species, $InX_4{}^-$ (X = Cl,Br,I) according to the extraction equation

$$(NR_4{}^+X^-)_{org} + InX_4{}^- \rightleftharpoons (NR_4{}^+InX_4{}^-)_{org} + X^- \qquad (1)$$

with an extraction constant defined as follows

$$\overline{K}_2 \equiv \overline{K}_{X^-,InX_4{}^-} = \frac{[NR_4{}^+InX_4{}^-]_{org}\,[X^-]}{[NR_4{}^+X^-]_{org}\,[InX_4{}^-]} \qquad (2)$$

where R = *n*-hexyl, and the subscript org is used to distinguish species in the organic phase. It follows that the distribution ratio is given by

$$\begin{aligned} D &= [\mathrm{NR_4^+InX_4^-}]_{\mathrm{org}} \Big/ \Sigma\,[\mathrm{In}] \\ &= \bar{K}_2\,[\mathrm{NR_4^+X^-}]_{\mathrm{org}}\,\beta_4[\mathrm{X^-}]^3 \Big/ \sum_0^N \beta_j\,[\mathrm{X^-}]^j \end{aligned} \qquad (3)$$

where the overall formation constant of the j-th species InX_j^{4-j} is defined by $\beta_j = [\mathrm{InX}_j^{4-j}]/[\mathrm{In^{3+}}][\mathrm{X^-}]^j$.

Thence

$$\begin{aligned} &\log D = \log[\mathrm{NR_4^+X^-}]_{\mathrm{org}} + (\log \bar{K}_2 + \log \beta_4 \\ &+3 \log\,[\mathrm{X^-}] - \log \sum_0^N \beta_j\,[\mathrm{X^-}]^j) \end{aligned} \qquad (4)$$

which predicts the type of graph found experimentally (Fig. 1).

By extrapolation of the linear plots (Fig. 1) to the value $\log D = 0$, the values 2.1, 4.2 and 3.5 are obtained for the sum of the four terms enclosed within parentheses on the right hand side of eqn. (4) for the systems involving X = Cl, Br and I respectively. Since tracer quantities of indium were used, $[\mathrm{X^-}]$ can be equated with the total concentration of hydrohalic acid used, and it should thus be possible to calculate $\bar{K}_2$, being given the relevant values for all the stability constants. Unfortunately, this presents considerable problems, for values of K_4 for the formation of the species $\mathrm{InX_4^-}$ have rarely been measured; indeed, values reported for K_1, K_2 and K_3 by different authors and methods show a disturbing lack of agreement even when they apply to roughly the same conditions of temperature and ionic strength. To make any further progress one possibility is to estimate values for K_4 from consistent values of K_1, K_2 and K_3 [8] assuming that change in free energy in forming $\mathrm{InX_4^-}$ from $\mathrm{InX_3}$ follows the pattern set in forming $\mathrm{InX_3}$ from $\mathrm{InX_2^+}$, $\mathrm{InX_2^+}$ from $\mathrm{InX^{2+}}$, and $\mathrm{InX^{2+}}$ from $\mathrm{In^{3+}}$. This is equivalent to setting $\log K_4 = \log K_3 - \frac{1}{2}(\log K_1 - \log K_3)$.

For chloride systems with $[\mathrm{Cl^-}] = 0.72\ M$ and $\beta_1 = 10^{2.36}$, $\beta_2 = 10^{3.63}$, $\beta_3 = 10^{3.95}$ and $\beta_4 = 10^{3.25}$

$$2.1 = \log \bar{K}_2 + 3.25 + \bar{1}.572 - 3.789$$

whence $\log \bar{K}_{\mathrm{Cl^-,InCl_4^-}} = 3.1.$ (5)

For the bromide complex with $[\mathrm{Br^-}] = 1.5\ M$ and $\beta_1 = 10^{2.01}$, $\beta_2 = 10^{3.10}$, $\beta_3 = 10^{3.28}$ and $\beta_4 = 10^{2.8}$

$$4.2 = \log \bar{K}_2 + 2.8 + 0.5283 - 4.101$$

whence $\log \bar{K}_{\mathrm{Br^-,InBr_4^-}} = 5.0$ (6)

and for the iodide system with $[\mathrm{I^-}] = 0.033\ M$ and $\beta_1 = 10^{1.64}$, $\beta_2 = 10^{2.56}$, $\beta_3 = 10^{2.48}$ and $\beta_4 = 10^{1.54}$

$$3.5 = \log \bar{K}_2 + 1.54 + \bar{5}.556 - 0.454$$

whence $\log \bar{K}_{\mathrm{I^-,InI_4^-}} = 6.85$ (7)

Although these equilibrium constants show that the tendency to extract InX_4^- in place of X^- increases in the order $Cl^- < Br^- < I^-$, a more direct comparison of the relative tendency to extract the complex anions may be derived as follows.

If $\bar{K}_{A,B}$ is used to symbolise the equilibrium constant for the reaction

$$(Q^+A^-)_{org} + B^- \rightleftharpoons (Q^+B^-)_{org} + A^-$$

for the replacement of A^- in the anion exchanger by B^- (and where Q^+ stands for a quaternary ammonium ion) we can write for the overall replacement reaction

$$(Q^+InCl_4^-)_{org} + InBr_4^- \rightleftharpoons (Q^+InBr_4^-)_{org} + InCl_4^-$$

$$\bar{K}_{InCl_4^-,InBr_4^-} = \frac{[Q^+InBr_4^-]_{org}\,[InCl_4^-]}{[Q^+InCl_4^-]_{org}\,[InBr_4^-]}$$

$$= \frac{\left(\dfrac{[Q^+InBr_4^-]_{org}}{[Q^+Br^-]_{org}} \cdot \dfrac{[Br^-]}{[InBr_4^-]}\right)\left(\dfrac{[Q^+Br^-]_{org}\,[E^-]}{[Q^+E^-]_{org}\,[Br^-]}\right)}{\left(\dfrac{[Q^+InCl_4^-]_{org}}{[Q^+Cl^-]_{org}} \cdot \dfrac{[Cl^-]}{[InCl_4^-]}\right)\left(\dfrac{[Q^+Cl^-]_{org}\,[E^-]}{[Q^+E^-]_{org}\,[Cl^-]}\right)}$$

$$= \frac{\bar{K}_{Br^-,InBr_4^-} \cdot \bar{K}_{E^-,Br^-}}{\bar{K}_{Cl^-,InCl_4^-} \cdot \bar{K}_{E^-,Cl^-}}$$

where E^- represents the anion of Erdmann's salt[11,14]. Using data available for the replacement of E^- by Cl^- and Br^-[11] we obtain

$$\bar{K}_{InCl_4,InBr_4^-} = \frac{10^{5.0} \times 10^{\bar{2}.92}}{10^{3.1} \times 10^{\bar{2}.48}} = 10^{2.3} \tag{8}$$

Similarly

$$\bar{K}_{InBr_4^-,InI_4^-} = \frac{10^{6.85} \times 10^{\bar{1}.62}}{10^{5.0} \times 10^{\bar{2}.92}} = 10^{2.55} \tag{8a}$$

These figures (although the similarity is fortuitous) show that InI_4^- is extracted in preference to $InBr_4^-$ and $InBr_4^-$ in preference to $InCl_4^-$. This is precisely the order noted for the liquid–liquid extraction of the solvated ion-pairs $H^+InX_4^-$ irrespective of the solvent used[1] and for their extraction on anion-exchange resins[6]. It is also the order for the extraction or absorption of the simple halide ions $Cl^- < Br^- < I^-$ but it is precise reverse of the stability of the complex anions, *viz.* $InI_4^- < InBr_4^- < InCl_4^- \ll InF_4^-$. It would appear that size is the dominant factor and that the increased work of hole-formation in the aqueous phase as the size of the extractable ion increases determines the order of extractability. This argument would hold equally if the extracted species were hydrated, *e.g.* $InX_4(H_2O)_2^-$.

Maximum extraction of indium takes place from *ca.* 6 *M* hydrochloric acid (Fig. 2). By differentiating eqn. (4) it can be shown that the slope of the plot of log *D* against log $[X^-]$ should be $3-\bar{n}$ and the maximum should occur when the degree of formation, $\bar{n}$, equals 3. With the stability constants used in deducing eqn. (5) and putting $\bar{n}=3$ in the formula

$$\sum_{0}^{N}(\bar{n}-j)\beta_j[\mathrm{X}^-]^j = 0 \tag{9}$$

we find $[\mathrm{X}^-]=1.6$ M. This is far too low and suggests that the value of β_4 has been overestimated. Indeed, if the above values for β_1, β_2 and β_3 are retained, the value of β_4 which would predict maximum extraction from 6 M hydrochloric acid is $10^{2.08}$ corresponding to a much lower stability for the species $\mathrm{InCl_4^-}$.

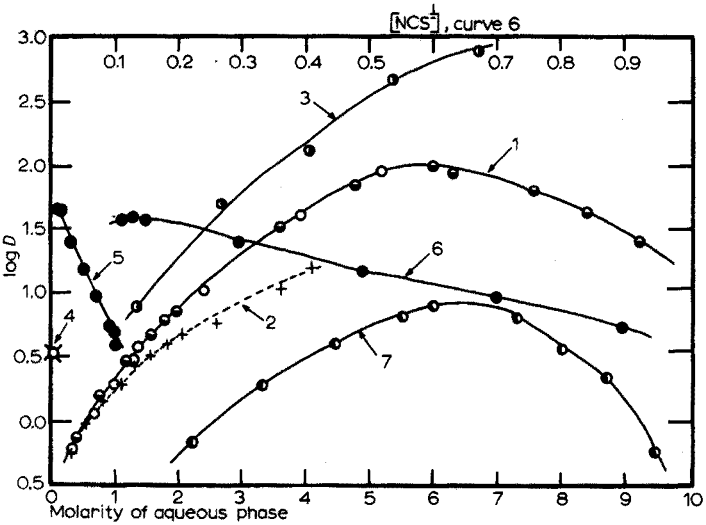


Fig. 2. The effect of halide concentration on the extraction of indium(III). (1) Extraction by 0.0152 M tetra-n-hexylammonium chloride in 1,2-dichloroethane from HCl (○) or LiCl (◒), (2) effect of replacing HCl by NaCl (+), (3) extraction from HBr by a 10^{-3} M solution of tetra-n-hexylammonium bromide in 1,2-dichloroethane. The value of log D = 0.52 when $\mathrm{Br^-}$ is replaced by $\mathrm{I^-}$ is shown by the number (4). (5) Extraction from thiocyanate solution by $6.65\cdot10^{-3}$ M tetra-n-hexylammonium thiocyanate in 1,2-dichloroethane. The pH of the aqueous phase was *ca.* 1. (6) shows the same data with a ten-fold expanded concentration scale (upper abscissa). (7) Extraction from HCl by an 0.02 M solution of tri-n-hexylamine hydrochloride in xylene.

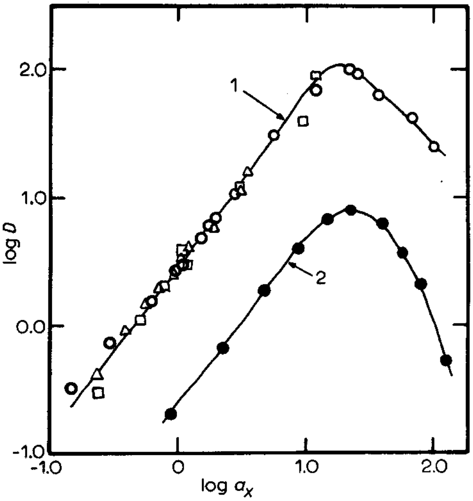
Such calculations are highly qualitative at best, since the stability constants used[8] refer to a constant ionic strength of 0.69 M ($\mathrm{HClO_4}$) whereas in the extraction work the measurements were made on solutions in which the ionic strength ranged up to nearly 10 M. A more satisfactory approach would be to consider the variation of log D with log a_x where the ligand activity is defined by $a_\mathrm{x}=m_\mathrm{HCl}\gamma_{\pm\mathrm{HCl}}$ (or by equivalent forms for solutions containing *e.g.* NaCl).

The experimental data are shown plotted in this way in Fig. 3. A more precise formulation of eqn. (4) will now be

$$\log D = \log[\mathrm{NR_4^+X^-}]_\mathrm{org} + \log \bar{K}_2' - \log\sum_{-3}^{N-3}\beta_i'^{*}a_\mathrm{x}^{i} \tag{4a}$$

where $\bar{K}_2'$ is the thermodynamic equilibrium constant for the reaction, the ratio of the activity coefficients for the species $(\mathrm{NR_4^+InCl_4^-})_\mathrm{org}$ and $(\mathrm{NR_4^+X^-})_\mathrm{org}$ is assumed constant and unity, and following MAYDAN AND MARCUS[5], stabilities are referred to the neutral species $\mathrm{InX_3}$ by the definitions $i=j-3$, $\beta_i'^{*}=\beta_j'^{*}/\beta_3'^{*}$, and $\log\beta_0'^{*}=0$.

The following values of the parameters $\beta_i'^*$ (which, by definition, are independent of the magnitude of a_x) have been calculated[5] for the system indium–chloride from distribution measurements with Dowex-1 anion-exchange resin: $\log \beta_{-2}'^* = -0.50$, $\log \beta_{-1}'^* = -0.45$ and $\log \beta_{+1}'^* = -1.6$; it was assumed that $\log \beta_{-3}'^* \sim -3$. With these data we calculate $a_x = 4.45$ when $\bar{n} = 3$ corresponding to $[HCl] = 3.2\ M$, a value much below that now found experimentally or that reported by GOOD AND HOLLAND ($\sim 5.5\ M$) for a wide variety of extractants[12].



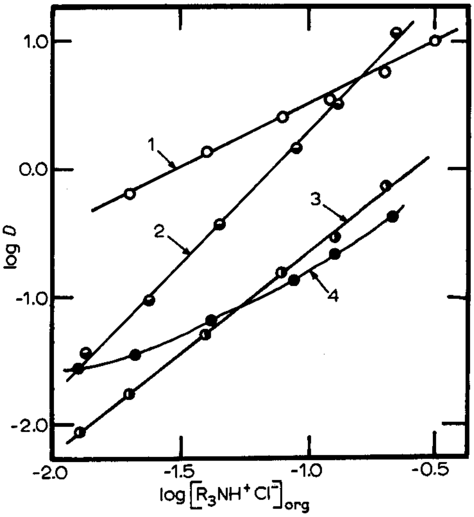


Fig. 3. The extraction of indium(III) from chloride media. (1) 0.0152 M tetra-n-hexylammonium chloride in 1,2-dichloroethane and equal volumes of HCl (○), NaCl (△) or LiCl (□); (2) 0.02 M tri-n-hexylamine hydrochloride in xylene and equal volumes of HCl.

Fig. 4. The extraction of indium(III) from 0.72 M HCl by equal volumes of tri-n-hexylamine hydrochloride dissolved in nitrobenzene (1), xylene (2), 1,2-dichloroethane (3) and benzaldehyde (4).

If the quaternary n-hexylammonium chloride is replaced by the hydrochloride of tri-n-hexylamine, $NR_3H^+Cl^-$, the extraction of indium is less effective (Fig. 2) despite the use of a somewhat more concentrated solution of extractant. However, maximum extraction (Fig. 3) occurs with the same activity (or concentration) of hydrochloric acid. This result is in full agreement with the derivative of eqn. (4a) which predicts that the maximum at $\bar{n} = 3$ will be a function of a_x and the relevant stability constants only; it should be independent of the nature of the extracting cation and of the organic solvent—though both these factors will affect the value of $\log D_{max}$—provided that the stoicheiometry of extraction conforms to eqn. (4).

That this may not be the case is shown by measurements with tri-n-hexylammonium chloride in four different solvents (Fig. 4) where the slopes of log D against $\log [R_3NH^+Cl^-]_{org}$ are 1.0, 1–1.5, 1.6 and 2.0 for nitrobenzene, benzaldehyde, 1,2-dichloroethane and xylene respectively. This increase of slope with decreasing solvent polarity may be attributed to an association reaction, *e.g.*

$$(NR_3H^+InCl_4^-)_{org} + (NR_3H^+Cl^-)_{org} \rightleftharpoons (NR_3H^+InCl_4^-NR_3H^+Cl^-)_{org}$$
$$\text{or } ((NR_3H^+)_2InCl_5^{2-})_{org}$$

which will be less favoured in highly polar solvents such as nitrobenzene where extraction takes place solely with the ion $InCl_4^-$. This tendency to form quadruples and higher aggregrates seems to be a characteristic feature of salts derived from tertiary amines.

According to eqn. (4a) the course of the extraction curve is governed by the activity of the halide ions, and it is noteworthy that plots for extraction from HCl, LiCl and NaCl are superimposable (Fig. 3). No measurements were carried out with $[LiCl] > 5.2$ *M*, hence it was impossible to establish whether, as reported by GOOD AND HOLLAND for solutions of tri-*n*-hexylammonium chloride in toluene, decrease in *D* at high concentrations of hydrochloric acid does not occur with lithium chloride.

The extraction of indium(III) from a thiocyanate medium contrasts with that from halide media. The plot of log *D* against log $[NR_4^+SCN^-]_{org}$ (Fig. 1) has a slope of 2.6 suggesting that a mixture of $In(SCN)_5^{2-}$ and $In(SCN)_6^{3-}$ is being extracted. Maximum extraction occurs with a much lower concentration of ligand (Fig. 2) in accordance with the much higher stability of the various complexes $In(SCN)_j^{3-j}$. The limiting slope of the descending portion of the curve (Fig. 2) has a slope of -3 showing that $\bar{n}$ has reached the value of 6, a result in accordance with evidence from polarography[13]. Using the published values $\beta_1 = 10^{2.08}$, $\beta_2 = 10^{3.20}$, $\beta_3 = 10^{4.24}$, $\beta_4 = 10^{4.23}$, $\beta_5 = 10^{4.81}$ and $\beta_6 = 10^{4.84}$ valid for $\mu = 2$ *M* ($NaClO_4$) at 30° [13], we calculate $\bar{n} = 3.0$ when $[SCN^-] = 0.22$, which is in satisfactory agreement with the experimental value of 0.15.

The striking differences between the extractability of thiocyanate and halide complexes of indium(III) reinforces the view that they are all 6-coordinate, the presence of coordinated water in the halide complexes giving them a greater hydrophilic character and accounting for the lower values of *D* when comparison is made under comparable conditions with the tetrahedral complexes of iron(III) and gallium(III). The differences can readily be exploited analytically.

EXPERIMENTAL

Solutions of quaternary tetrahexylammonium chloride were prepared from the iodide with an anion-exchange resin[14] and their concentrations were determined as previously described[14]. Solutions of the quaternary bromide were prepared similarly.

To prepare a solution of tetra-*n*-hexylammonium thiocyanate in dichloroethane, 100 ml of a 0.01 *M* solution of the corresponding iodide was equilibrated with an equal volume of aqueous 1 *M* ammonium thiocyanate containing a little of the disodium salt of EDTA which retained traces of extractable metals such as iron(III). The aqueous phase was rejected and the organic phase re-equilibrated with fresh aqueous ammonium thiocyanate, and this cycle was repeated three times in all, when the complete absence of iodide ion in the aqueous extract could be demonstrated by adding sodium nitrite to a portion, acidifying with hydrochloric acid and shaking up with chloroform. The solution of tetra-*n*-hexylammonium thiocyanate in dichloroethane was well washed by water before use. The concentration was determined by the method already reported[14].

Solutions of tri-*n*-hexylammonium chloride were obtained by dissolving a known weight of the pure amine (Eastman Organic Chemicals) in xylene and equilibrating with three successive portions of 1 *M* hydrochloric acid. The organic layer was then carefully washed with distilled water to remove adhering acid. Solvents were of AR quality and were redistilled immediately before use. Indium-114 obtained by irradiation of the Specpure element (Johnson Matthey) at A.E.R.E., Harwell, was dissolved in concentrated hydrochloric acid and then taken to dryness. The residue was dissolved in 10^{-3} *M* hydrochloric acid and then diluted as required. The concentration of tracer indium was generally *ca.* 10^{-5} *M*. Equilibrations were carried out with equal volumes (5 ml) of organic and aqueous phase by shaking mechanically for 1 h at $22 \pm 2°$ in stoppered centrifuge tubes. After centrifugation 2-ml aliquot portions of each phase were removed and their radioactivity measured in a well-type scintillation counter. Distribution ratios were calculated after due correction for background counts.

SUMMARY

The distribution of indium(III) at tracer levels between aqueous solutions containing chloride, bromide, iodide and thiocyanate ions and solutions of the corresponding tetra-*n*-hexylammonium salts in 1,2-dichloroethane has been studied and the composition of the extracted ion-pairs is discussed. The effect of the cations H^+, Li^+ and Na^+ on extractions from chloride media is reported, together with the results of changing the organic solvent when indium is extracted from hydrochloric acid by solutions of tri-*n*-hexylamine hydrochloride.

RÉSUMÉ

Une étude est effectuée sur le partage de l'indium(III) entre des solutions aqueuses renformant chlorure, bromure, iodure, thiocynate et des solutions du sel de tétra-*n*-hexylammonium dans le dichloro-1,2-éthane. On a examiné l'influence des cations H^+, Li^+ et Na^+ sur les extractions en milieu chlorure. On donne également les résultats obtenus pour l'extraction de l'indium en milieu acide chlorhydrique par des solutions de chlorhydrate de tri-*n*-hexylamine.

ZUSAMMENFASSUNG

Indium(III) wurde im tracer-Massstab verteilt zwischen wässrigen Lösungen, die Chlorid-, Bromid-, Jodid- und Thiocyanat-Ionen enthielten, und Lösungen der korrespondierenden Tetra-*n*-hexylammonium-Salze in 1,2-Dichloräthan. Die Zusammensetzung der extrahierten Ionenpaare wird diskutiert. Es wird über den Einfluss der Kationen H^+, Li^+ und Na^+ auf die Extraktion aus Chloridlösungen und über die Ergebnisse berichtet, die bei einem Wechsel des organischen Lösungsmittels erhalten werden, wenn Indium aus salzsaurem Medium durch Lösungen von Tri-*n*-hexylamin-hydrochlorid extrahiert wird.

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IONIC EQUILIBRIA IN MIXED SOLVENTS

MONOPROTIC ORGANIC ACIDS*

BUDDHADEV SEN AND LOUIS H. ADCOCK**
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)

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It is frequently necessary to study the thermodynamics of reversible ionic equilibria in nonaqueous or organic–water mixed solvent systems. In such studies, infinitely dilute solution in the solvent used is normally taken as the state of unit activity coefficient. In this paper we are primarily concerned with the ionization constants of the weak monoprotic (carboxylic) organic acids. The equilibrium constant of a reversible system determined in a particular solvent may be of considerable practical importance, but such a value cannot be readily compared with the equilibrium constant of a similar reversible system determined in another solvent. Therefore, it would be extremely useful if there were a method for converting the equilibrium constant of a reversible system determined in a particular solvent (nonaqueous, or organic–water mixed) to the corresponding value in some reference solvent, say water. The correction factors which enable one to perform such conversion have been termed by OWEN[1,2] as medium effects.

Thermodynamic representation of medium effects

There are two kinds of medium effect resulting from two different kinds of interactions in a solution containing electrolytes. These are the primary medium effect caused by ion–solvent interaction, and the secondary medium effect caused by ion–ion interaction; the sum of the two medium effects is called the total medium effect.

An equation correlating the two types of medium effects on hydrochloric acid may be obtained by considering the galvanic cell I,

$$\text{Pt, H}_2(1\text{ atm})\ |\text{HCl}(m),\ \text{organic}(x),\ \text{water}(y)\ |\text{AgCl–Ag}$$

where x and y are the mole fractions of organic and water, and the coupled galvanic cell II,

$$\text{Ag–AgCl}\ |\text{HCl}(m),\ \text{water}\ |\text{Pt, H}_2(1\text{ atm})\ |\text{HCl}(m),\ \text{organic}(x),\ \text{water}(y)\ |\text{AgCl–Ag}$$

The equation in its final form (see HARNED AND OWEN[2] for a detailed derivation and meaning of medium effects in terms of free energy changes) is as follows:

$$\ln \frac{{}^{\mathrm{s}}_{\mathrm{w}}\gamma_{\pm}}{{}^{\mathrm{w}}_{\mathrm{w}}\gamma_{\pm}} = \ln {}^{\mathrm{s}}_{\mathrm{w}}\gamma_{0\pm} + \ln \frac{{}^{\mathrm{s}}_{\mathrm{s}}\gamma_{\pm}}{{}^{\mathrm{w}}_{\mathrm{w}}\gamma_{\pm}} \qquad (1)$$

Total Primary Secondary

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[*] Abstracted in part from a dissertation submitted by L. H. ADCOCK.

[**] Present address: University of North Carolina at Wilmington, Wilmington, N.C.

The superscripts s and w indicate that the measurements were made in mixed solvent and water, respectively. The subscripts s and w indicate that a solution in mixed solvent and a solution in water were taken respectively as the reference states. ${}^{\mathrm{s}}_{\mathrm{w}}\gamma_{0\pm}$ is the mean activity coefficient of hydrochloric acid in infinitely dilute solution in mixed solvent with respect to infinitely dilute solution in water.

Because there is no concentration term in eqn. (1), the total medium effect ${}^{\mathrm{s}}_{\mathrm{w}}\gamma_{\pm}/{}^{\mathrm{w}}_{\mathrm{w}}\gamma_{\pm}$ describes the relative non-ideality of the two solutions, a part of which results from ion–solvent interaction (${}^{\mathrm{s}}_{\mathrm{w}}\gamma_{0\pm}$), and a second part, ${}^{\mathrm{s}}_{\mathrm{s}}\gamma_{\pm}/{}^{\mathrm{w}}_{\mathrm{w}}\gamma_{\pm}$, results from ion–ion interaction and is concentration-dependent. Computation of the primary and secondary medium effects on a symmetrical valence type electrolyte, such as hydrochloric acid, involves accurate experimental determination of potentials of appropriate galvanic cells of the type I and II.

SEN *et al.*[3] have demonstrated that an equation of the type

$$E + \frac{2RT}{F}\ln m = A_0 + A_1 m^{\frac{1}{2}} + A_2 m + A_3 m^{\frac{3}{2}} + \ldots \tag{2}$$

(in which A_0 is identical with the standard potential $E_{\mathrm{m}}{}^0$) is theoretically sound and precisely expresses the value of the standard potential. This polynomial equation can be solved by means of an appropriate program when a reliable set of E values is available. Further, the activity coefficient is given by eqn. (3) in which the constants A_i' (as well as the

$$\ln\gamma_{\pm} = A_1' m^{\frac{1}{2}} + A_2' m + A_3' m^{\frac{3}{2}} + \ldots \tag{3}$$

constants A_i in eqn. (2)) are not arbitrary constants, but are composed of a number of physical constants, the temperature, the dielectric constant of the solvent, and only one adjustable parameter, the ion-size parameter. It is reasonable to assume that the ion-size parameter is practically constant within the range of validity of the Debye–Hückel theory[2]. In such a case the activity coefficient (hence the standard potential) is primarily a function of the bulk dielectric constant of the solvent at a constant temperature. However, its direct computation is not possible because of the uncertainty of the value of ion-size parameter.

Medium effect and ionization constant of weak monoprotic (carboxylic) organic acids

Of the various types of ionic equilibria, those of weak monoprotic acids are the simplest to study and the most amenable to mathematical treatment. Addition of an organic solvent to the aqueous solution usually reduces the value of the bulk dielectric constant of the solvent, causing an increased electrostatic attraction between the cations and the anions. This provides an increased opportunity for covalent bond formation (non-coulombic interaction) resulting in a decrease in the ionization constant of the weak acid dissolved in a mixed solvent. It can be shown that the ionization constants of a weak acid HR in pure water (K_{A}) and in the mixed solvent ($K_{\mathrm{A}}{}^*$) are related by the expression

$$K_{\mathrm{A}} = \frac{{}^{\mathrm{s}}_{\mathrm{w}}\gamma_{0\mathrm{H}^+}\cdot{}^{\mathrm{s}}_{\mathrm{w}}\gamma_{0\mathrm{R}^-}}{{}^{\mathrm{s}}_{\mathrm{w}}\gamma_{0\mathrm{HR}}}\cdot K_{\mathrm{A}}{}^* = Q_\gamma \cdot K_{\mathrm{A}}{}^* \tag{4}$$

The activity coefficient quotient term, Q_γ, is obviously the medium effect term. Difficulty arises in computing single ionic activity coefficients; one cannot use mean activity coefficient as was done in the case of pure hydrochloric acid cells I and II, because, as will be seen later, of the nature of the galvanic cell employed in determining the ionization constants. This is the stumbling block in converting the ionization constant (or some other thermodynamic equilibrium constant) determined in one medium to its corresponding value in some other medium. The best way seems to be to assume some reasonable and extrapolatable function relating K_A and K_A^*. It can be seen from eqn. (4) that K_A^* approaches K_A as the medium effect term Q_γ approaches unity. From the composition of the coefficients of eqns. (2) and (3), one can further assume that Q_γ is a function of the bulk dielectric constant of the solvent at a constant temperature. The foregoing conclusions may be summarized by the following symbolic expression

$$K_A = K_A^* \cdot f Q_\gamma(\varepsilon) \tag{5}$$

Determination of ionization constant

Experimental determination of the ionization constant of a weak monoprotic acid is a relatively simple matter, and is computed from the e.m.f. data of the cell III:

Pt, H_2(1 atm)|HR(m_1), NaR(m_2), NaCl(m_3), organic(x), water(y)|AgCl–Ag

The ionization constant of the acid, HR, is given by the expression

$$E_{obs} - E_m^0 + \frac{RT}{F}\ln\frac{m_{HR}\cdot m_{Cl^-}}{m_{R^-}} = -\frac{RT}{F}\ln\frac{\gamma_{H^+}\cdot\gamma_{Cl^-}\cdot\gamma_{HR}}{\gamma_{H^+}\cdot\gamma_{R^-}} - \frac{RT}{F}\ln K_A^* \tag{6}$$

E_m^0 is the standard potential of the corresponding cell with hydrochloric acid replacing all other electrolytes. The first term on the right-hand side of eqn. (6) contains the ratio of activity coefficients which becomes unity at infinite dilution and is nearly that at low ionic strength. If the right-hand side of eqn. (6) equals $-(RT/F)\ln K_A^{*\prime}$, then the intercept of the plot $\log K_A^{*\prime}$ *vs.* μ (ionic strength), or some function of μ, at $\mu = 0$, is $\log K_A^*$. With the foregoing substitution eqn. (6) becomes

$$-\frac{RT}{F}\ln K_A^{*\prime} = E_{obs} - E_m^0 + \frac{RT}{F}\ln\frac{m_{HR}\cdot m_{Cl^-}}{m_{R^-}} \tag{7}$$

The right-hand side of eqn. (6) can be readily evaluated, because $m_{Cl^-} = m_3$, $m_{HR} = m_1 - m_{H^+} \approx m_1$, $m_{R^-} = m_2 + m_{H^+} \approx m_2$, and E_{obs} and E_m^0 are obtained experimentally.

When $x = 0$ in cell III, the value of the ionization constant is K_A, *i.e.* the value in aqueous solution.

EXPERIMENTAL

All chemicals and solvents were obtained either as commercial reagent grade, or were purified by standard procedures. The platinized hydrogen electrodes, and silver–silver chloride electrodes were prepared as described by ROY AND SEN[4]. In acetone–water systems, either an unplatinized hydrogen electrode[5] or a glass electrode[6] was used in order to prevent reduction of acetone. E.M.F. readings were taken with a L & N K-3 Universal Potentiometer calibrated against an Eppley standard cell. A L & N model 7405 expanded Scale pH-meter was used with a glass electrode (Corning No. 476022).

The calculations of E_{obs}, log $K_A{}^{*\prime}$, and all other calculations were made on an IBM 7040 or IBM 360 computer.

RESULTS AND DISCUSSION

Figure 1 represents the plot of log $K_A{}^{*\prime}$ *vs.* $\sqrt{\mu}$ for acetic acid which is representative of similar plots for other acids. Many of the p$K_A{}^*$ values for other acids were taken from the literature, but in a number of cases these values were checked in this laboratory.

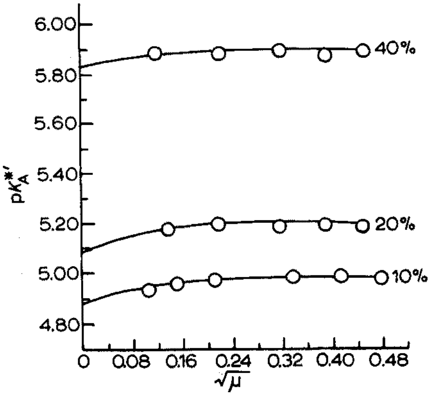

Fig. 1. p$K_A{}^{*\prime}$ *vs.* $\sqrt{\mu}$ for acetic acid in acetone–water mixtures at 25°. The percentages are weight percent of acetone.

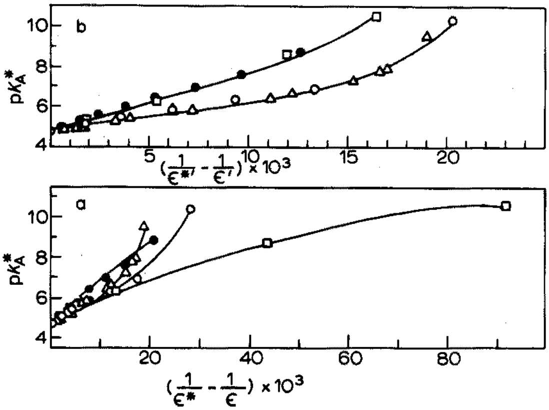

Fig. 2. Ionization constant of acetic acid *vs.* dielectric constant functions in various mixed solvents at 25°. (○) Ethanol–water, (△) methanol–water, (□) dioxane–water, (●) acetone–water; ε^* = dielectric constant of the mixed solvent; ε = dielectric constant of water; $\varepsilon^{*\prime} = \varepsilon^* + (\varepsilon_{MeOH} - \varepsilon_{org})$; $\varepsilon_{org} = \varepsilon_{EtOH}$ or ε_{acet} or ε_{diox}; $\varepsilon' = \varepsilon + (\varepsilon_{MeOH} - \varepsilon_{org})$.

The primary objective was to obtain a function of the type represented by eqn. (5), correlating $K_A{}^*$ (the value of the ionization constant at infinite dilution in mixed solvent) and K_A (the value of the ionization constant at infinite dilution in aqueous solution). In order to obtain an acceptable function, plots of p$K_A{}^*$ *vs.* various functions of bulk dielectric constants of the solvent were investigated. An acceptable plot should have the following properties.

1. It should be continuous without any maximum or minimum.

2. The plot should contain p$K_A{}^*$ values of an acid for as many systems as possible.

3. The plot should be preferably linear. The equation that fits this plot is the function sought. Further, the function should be capable of being interpreted in terms of the physical process of ionization assuming that the interactions are coulombic in nature. (This, of course, is an arbitrary choice.)

It was soon realized that the appropriate variable has to be some linear combination of the reciprocals of the bulk dielectric constants of the two solvents, for the plot to meet requirements outlined above. One would also anticipate this from a consideration of various electrostatic models[7-9] describing ionization process in solution. One of the initial plots which showed promise was p$K_A{}^*$ *vs.* $(1/\varepsilon^* - 1/\varepsilon)$, where ε^* = bulk dielectric constant of the mixed solvent and ε = bulk dielectric constant of water. Figure 2a is the plot for acetic acid which is representative of the plots for the other acids. It is obvious that a suitable term must be added to the primary variable in order to obtain all the points on the same line. The plots for methanol–water and ethanol–water systems are particularly instructive. It is evident that these two plots can be made to coincide by adding $(\varepsilon_{\mathrm{MeOH}} - \varepsilon_{\mathrm{org}})$ to both ε^* and ε (*cf.* Fig. 2b), where $\varepsilon_{\mathrm{org}}$ is the bulk dielectric constant of ethanol. A similar treatment placed the acetone and the dioxane curves together but somewhat displaced from the methanol–ethanol composite curve; the shapes of both the composite curves were, how-

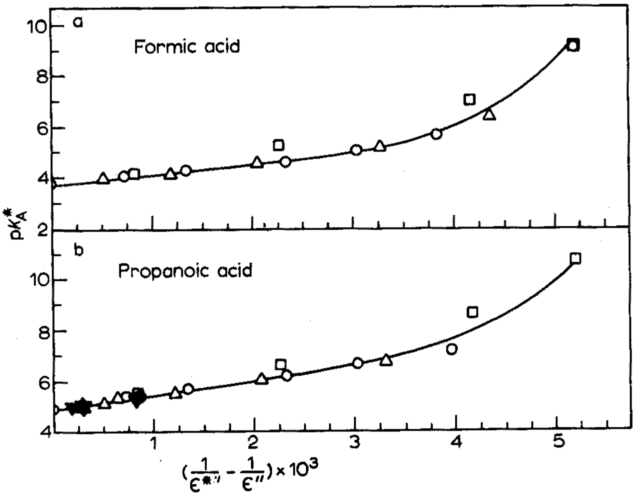

Fig. 3. Ionization constant of formic acid (a) and propanoic acid (b) *vs.* dielectric constant function in various mixed solvents at 25°. (○) Ethanol–water, (△) methanol–water, (□) dioxane–water, (▼) 2-propanol–water, (●) acetone–water; $\varepsilon^{*\prime\prime} = \varepsilon^* + (\varepsilon - \varepsilon_{\mathrm{org}})$; $\varepsilon'' = 2\varepsilon - \varepsilon_{\mathrm{org}}$; ε^* and ε as defined in Fig. 2.

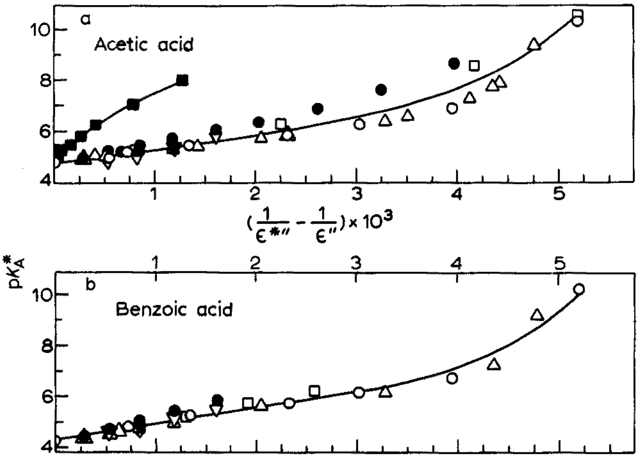

Fig. 4. Ionization constants of acetic acid (a) and benzoic acid (b) *vs.* dielectric constant function in various mixed solvents at 25°. (○) Ethanol–water, (△) methanol–water, (□) dioxane–water, (●) acetone–water, (▼) glycol–water, (▽) 2-methoxyethanol–water, (■) dimethylsulfoxide–water; $\varepsilon^{*\prime\prime}$ and ε'' as defined in Fig. 3.

TABLE I

ACIDS STUDIED, CALCULATED CONSTANTS AND BULK DIELECTRIC CONSTANTS OF THE MIXED SOLVENTS USED

Acid	pK_A			*No. of composition of each mixed solvent syst. studied Org. compound*	*Range of dielectric const.*	*Constants of eqn. (8)*			*Eqn. (9)* β	*Eqn. (12)* b'
	Expl.	*Eqn. (8)*	*Eqn. (9)*			*b*	*c*	*d*		
Formic	3.75	3.75	3.78	5(MeOH)	34–71	321	−1.80	463	110	477
				6(EtOH)	24–67					
				4(Dioxane)	10–61					
Acetic	4.76	4.76	4.87	13(MeOH)	31.5–74	530	−1.70	423	125	530
				8(EtOH)	24–73.5					
				4(Dioxane)	10–61					
				13(Acetone)	30–73					
				4(2-Methoxyethanol)	53–69					
Propanoic	4.87	4.88	4.98	6(MeOH)	42–74	508	−2.00	484	128	617
				5(EtOH)	33–67					
				4(Dioxane)	10–61					
				2(Acetone)	64–73					
				3(2-PrOH)	64–75					
Butanoic	4.82	4.85	5.00	4(MeOH)	42–71	482	−2.08	500	140	482
				5(EtOH)	33–67					
				3(2-PrOH)	64–75					
Benzoic	4.20	4.27	4.45	8(MeOH)	32–74	631	−2.80	620	152	627
				6(EtOH)	24–67					
				4(Dioxane)	34–61					
				6(Acetone)	53–73					
				4(2-Methoxyethanol)	53–69					
Chloroacetic[a]	2.86		2.98	5(EtOH)	33–67				116	530
Cyanoacetic[a]	2.47		2.47	5(EtOH)	33–67				113	471
3-Methylbutanoic[a]	4.78		4.98	5(EtOH)	33–67				141	640
Glycolic[a]	3.83		3.96	5(EtOH)	33–67				106	480
Glutaric[a]	4.34		4.40	5(EtOH)	33–67				114	552
Malonic[a]	2.75		2.90	5(EtOH)	33–67				88	420
Salicylic[a]	3.00		3.04	5(EtOH)	33–67				115	514
Succinic[a]	4.13		4.28	5(EtOH)	33–67				115	500

[a] pK_A* values of these acids in the curved region of the plots were not available and were not determined. Therefore, b, c, d could not be calculated.

ever, the same. This indicated that by using some other appropriate term all curves might be brought together. The final plots were pK_A^* *vs.* $(1/\varepsilon^{*\prime\prime} - 1/\varepsilon^{\prime\prime})$, where $\varepsilon^{*\prime\prime} = \varepsilon^* + (\varepsilon - \varepsilon_{org})$, $\varepsilon^{\prime\prime} = \varepsilon + (\varepsilon - \varepsilon_{org}) = (2\varepsilon - \varepsilon_{org})$, ε = bulk dielectric constant of water, ε_{org} = bulk dielectric constant of the organic component; some of these plots are shown in Figs. 3–5. Table I summarizes the acids investigated in different kinds of mixed solvents and the range of bulk dielectric constant encompassed by the mixed solvents.

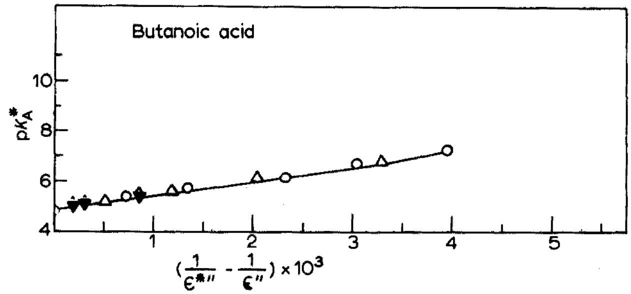

Fig. 5. Ionization constants of butanoic acid *vs.* dielectric constant function in various mixed solvents at 25°. (○) Ethanol–water, (△) methanol–water, (▼) 2-propanol–water; ε'' and $\varepsilon^{*\prime\prime}$ as defined in Fig. 3.

The only system among those studied which did not fall in line with the other systems, was the dimethylsulfoxide–water system (Fig. 4a). The ionization constant as well as the bulk dielectric constant data for this system should have been checked independently. The dielectric constant data used by MOREL[6] seem particularly doubtful. On the other hand, there could be extensive non-coulombic interactions between the solvent molecules, the ions and the solute molecules in this case, even at a low concentration of the organic component of the solvent.

The equation that fits these curves (Figs. 3–5) has the general form

$$pK_A^* = pK_A + b\left(\frac{1}{\varepsilon^{*\prime\prime}} - \frac{1}{\varepsilon^{\prime\prime}}\right) + 10^{c+d(1/\varepsilon^{*\prime\prime}-1/\varepsilon^{\prime\prime})} \quad (8)$$

The first two terms of the function represent the linear portion of the curve, where the interactions are primarily coulombic. It is interesting to note that a similar function can be written for the linear portion of the curves in Fig. 2a.

$$pK_A^* = pK_A + \beta\left(\frac{1}{\varepsilon^*} - \frac{1}{\varepsilon}\right) \quad (9)$$

Linear plots of eqn. (9) for several acids are shown in Fig. 6. Equation 9 is identical in form to BORN's equation[7] relating the ionization constant of a weak acid in two media.

$$\ln K_A - \ln K_A^* = \frac{Ne^2}{2RT}\left(\frac{1}{\varepsilon^*} - \frac{1}{\varepsilon}\right)\left(\frac{1}{r_{H^+}} + \frac{1}{r_{R^-}}\right) \quad (10)$$

$$\text{i.e.} \quad pK_A^* = pK_A + \frac{Ne^2}{4.606RT}\left(\frac{1}{\varepsilon^*} - \frac{1}{\varepsilon}\right)\left(\frac{1}{r_{H^+}} + \frac{1}{r_{R^-}}\right) \quad (11)$$

in which the symbols have their usual meaning. BORN's thermodynamic cycle is based essentially on an electrostatic model[7]. Equation 8 is a modification of BORN's equation with an additional term to account for the non-coulombic interactions. In the limiting case, when $(1/\varepsilon^{*\prime\prime} - 1/\varepsilon^{\prime\prime}) = 0$, *i.e.* in pure water, the exponential term becomes vanishingly small, making $pK_A^* = pK_A$. The linear segments of the plots of pK_A^* *vs.* $(1/\varepsilon^{*\prime\prime} - 1/\varepsilon^{\prime\prime})$ (*cf.* Figs. 3–5; separate plots of the linear parts are not shown to conserve space) are represented by the equation

$$pK_A^* = pK_A + b'\left(\frac{1}{\varepsilon^{*\prime\prime}} - \frac{1}{\varepsilon}\right) \qquad (12)$$

The constants b, c, d, b′, and β have been calculated for five acids in eight solvents (*cf.* Table I). The trends of b, b′ and β are discussed in a following paragraph.

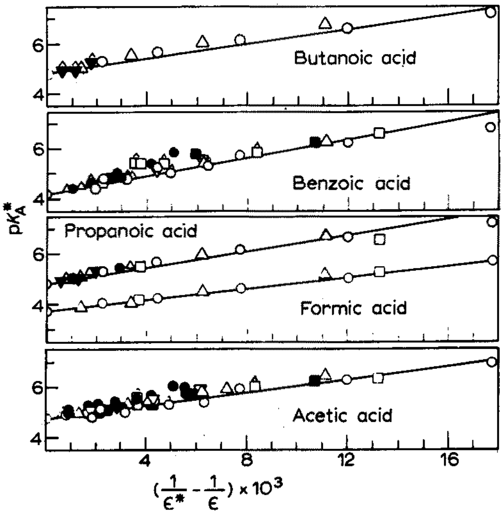

Fig. 6. Ionization constants of some acids *vs.* dielectric constant function in various mixed solvents at 25°. (Linear segment, eqn. (9)). (▽) 2-Methoxyethanol–water, (○) ethanol–water, (△) methanol–water, (□) dioxane–water, (●) acetone–water, (⧫) 2-propanol–water, (▼) glycol–water, (ô) 2-ethyoxyethanol–water, (□̂) 1,2-dimethoxyethane–water, (■) tetrahydrofuran–water; ε^* and ε as defined in Fig. 2.

Although the linear parts of eqn. (8) and eqns. (9), (11) and (12) have identical forms, yet there is a significant difference between eqns. (8) and (12) on the one hand and the other two equations. Equations (8) and (12) correlate the ionization constant of an acid in any medium with the ionization constant of the same acid in a reference medium, in this case water, whereas eqns. (9) and (11) correlate the ionization constant of an acid in two different media. There are a number of ways of testing the validity of these equations.

It is possible to compute the bulk dielectric constant of the organic component when the constants b or β are known for two acids. Actual computations showed that the values are not more than 7% in error. Equating the coefficients in eqns. (9) and (11), one obtains

$$\beta = \frac{Ne^2}{4.606RT}\left(\frac{1}{r_{H^+}} + \frac{1}{r_{R^-}}\right) \qquad (13)$$

The right-hand side of this equation cannot be computed, primarily owing to the uncertainty of the values of solvated ionic radii, r_{H^+} and r_{R^-}. Even if these were known precisely, experimental β values would almost certainly have been different from the computed values, because BORN's equation completely neglects all non-coulombic interactions which have finite contributions in all real solutions, even in solvents of high dielectric constants. Several investigators[2,10–12] have attempted to correlate the ionization constants of the monoprotic acid in two solvents and have met with various degrees of success. HARNED[2] concluded that because of the curvature in the plots pK_A^* *vs.* $(1/\varepsilon^* - 1/\varepsilon)$ at low values of dielectric constant, the BORN equation is totally inadequate. We cannot agree with this conclusion; BORN's electrostatic model is still a good model when non-coulombic interactions are taken into account at all values of dielectric constant. The contributions of these non-coulombic interactions are very small yet significant even at high values of dielectric constants, and increase very rapidly when the bulk dielectric constant is less than a certain critical value ($\varepsilon^* < 40$). Again, this critical value of the bulk dielectric constant will be different for different solvents, as it will depend on such factors as the dipole moment of the solvent molecule, its structure, Lewis basicity, polarizability, etc.; however, this difference may not be very large. Therefore, it will be futile to attempt a purely theoretical computation of β; regardless of the sophistication of the model, it must be calculated from experimental data as has been done here.

If the experimental β value and right-hand side of eqn. (13) are equated, and if a reasonable value is assumed for solvated (hydrated) protons, it is possible to calculate the solvated (primarily hydrated) anionic radii. The values of the anionic radius, r_{R^-}, of several acids are given in Table II. What do these radii mean? The term $(1/r_{H^+} + 1/r_{R^-})$ in the BORN equation is really the reciprocal of the minimum distance of approach of two ions or some function of it. In the DENNISON AND RAMSEY[11] treatment of the BORN model, this term is $1/r$, where r is the minimum distance of approach of the two ions. Implicit in the expression $(1/r_{H^+} + 1/r_{R^-})$ is the assumption

TABLE II

MINIMUM DISTANCE OF APPROACH OF HYDRATED PROTON AND SOME HYDRATED ANIONS

Acid	r_{R^-} *(Å)*	
	(r_{H^+} = 3.0 Å)	(= $r_{H^+} + r_{R^-}$)
Formic	1.3	4.3
Acetic	1.1	4.1
Propanoic	1.1	4.1
Butanoic	1.0	4.0
Benzoic	0.9	3.9
Chloroacetic	1.2	4.2
Cyanoacetic	1.2	4.2
3-Methylbutanoic	1.0	4.0
Glycolic	1.3	4.3
Glutaric	1.2	4.2
Melonic	1.7	4.7
Salicylic	1.2	4.2
Succinic	1.2	4.2
Hydroiodic[2]		5.0
Hydrobromic[2]		4.4
Hydrochloric[2]		4.3

that both ions are monoatomic and spherical; therefore, the minimum distance of approach of two ions may be apportioned as the hydronium ion radius and the anion radius. Although it might be possible to assign a value to the hydronium ion radius, the anionic radius could be quite misleading, especially when the anion is polyatomic. In fact, ROBINSON AND STOKES[12] reported that the carboxylate ion radius is of the order of 1.2 Å. Formate, benzoate, and glycolate ions cannot have the same radius, nor are they spherical. This anionic radius really is the thickness of the water sheath between the negative end of the anion and the outer periphery of the hydrated proton. Perhaps it is more realistic to report r rather than r_{R^-}, and these values are given in Table II. It is interesting to note that these are of the same order of magnitude as those for hydrogen halides reported by HARNED AND OWEN[2]. Considering all the evidence[13], we have taken $r_{H^+} = 3.0$ Å.

It seems pertinent to make some comments on the trends of b, b′ and β (*cf.* eqns. (8), (12) and (9)). Both b′ and β have definite and similar trends, as should happen. Among the similar types of acids, this trend follows the pK_A value. No such trend is observed in the value of the constant b. In computing b, the program did not attach any special importance to the points in the linear regions of the plots, hence b values are weighted by the points in the curved part of the plots, whereas eqns. (9) and (12) were evaluated by using data from graphically selected linear segments of the plots. Values of r, and consequently the degree of hydration of the anion, follow the ionization constants of the acids, but these trends are influenced by the substituents. The r values for acetic, chloroacetic, cyanoacetic and glycolic acid are indeed significant.

The results of this study encourage us to comment that it might be possible to develop similar equations for simple cationic complexes of carboxylic acids, if it could be assumed that all n-valent cations, M^{n+} ($n = 1, 2, 3$) belonging to the same period have an average solvated ionic radius. A similar treatment of lanthanide complexes is likely to be successful.

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SUMMARY

An equation correlating the thermodynamic ionization constants of monoprotic (carboxylic) organic acids in a mixed solvent and a reference solvent (water) is derived employing a curve-fitting program. The equation covers the range of bulk dielectric constant represented by that of pure water and that of very concentrated organic component. An equation for interconversion of the ionization constants between two solvents is also described. The form of the equations is similar to that of BORN's equation. Interionic distances between hydrated proton and the hydrated anions were calculated for a large number of acids using the constants of the equations, and these distances are of the right order of magnitude. The bulk dielectric constant of the organic component of the solvent may be computed utilizing the constants of the equation; the computed values of bulk dielectric constants of solvents were less than 7% off from the experimental values.

RÉSUMÉ

Une étude est effectuée sur les constantes d'ionisation thermodynamiques d'acides organiques dans un solvant organique et dans un solvant de référence (l'eau). On propose également une équation d'interconversion des constantes d'ionisation entre deux solvants. La forme de ces équations est similaire à celle de l'équation de BORN. Les distances interioniques entre le proton et les anions hydratés sont calculées pour un grand nombre d'acides en utilisant les constantes de ces équations. Ces distances sont tout à fait dans l'ordre de magnitude.

ZUSAMMENFASSUNG

Unter Benutzung eines Kurvenangleichungsprogramms wird eine Gleichung abgeleitet, die Beziehungen herstellt zwischen den thermodynamischen Ionisationskonstanten einprotoniger organischer (Carboxyl-) Säuren in einem gemischten Lösungsmittel und in einem Vergleichslösungsmittel (Wasser). Die Gleichung erfasst den Dielektrizitätskonstanten-Bereich von reinem Wasser bis sehr konzentrierter organischer Komponente. Eine Gleichung für die Änderung der Ionisationskonstanten beim Übergang von einem Lösungsmittel auf ein zweites wird ebenfalls beschrieben. Die Form der Gleichungen ist der BORNschen Gleichung ähnlich. Interionische Abstände zwischen hydratisiertem Proton und den hydratisierten Anionen wurden für eine grosse Anzahl von Säuren unter Verwendung der Konstanten der Gleichungen berechnet; diese Abstände sind in der richtigen Grössenordnung. Die Dielektrizitätskonstante der organischen Komponente des Lösungsmittels kann unter Verwendung der Konstanten der Gleichung berechnet werden; die berechneten Werte der Dielektrizitätskonstanten der Lösungsmittel unterschieden sich weniger als 7% von den experimentellen Werten.

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STOICHIOMETRY OF THE REACTION BETWEEN METHYLMERCURY(II) IODIDE AND SOLUBLE SULPHIDES

L. C. GRUEN
Division of Protein Chemistry, CSIRO, Parkville, Melbourne, Victoria 3052 (Australia)

(Received November 24th, 1969)

It has been known for some time[1] that the thiol groups of amino acids, peptides and proteins can be titrated at the dropping mercury electrode (DME) with mercury(II) chloride. This reagent, under the right conditions, combines stoichiometrically with thiols according to the equation:

$$2\ RS^- + HgCl_2 \rightarrow (RS)_2Hg + 2\ Cl^- \qquad (1)$$

More recently it has been shown that methylmercury(II) iodide (MeHgI) is more reactive and specific[2,3]. It has since supplanted mercury(II) chloride and has been extensively used in the determination of thiol and disulphide groups, both for simple thiols and soluble proteins[4,5] and for fibrous keratins[6]. The mechanism of reduction of RHgX type compounds at DME has been well characterised[7] and the two polarographic waves are believed to be associated with reductive fission of the mercury–halogen bond and of the mercury–carbon bond as follows:

$$RHgX + e \rightarrow RHg\cdot + X^- \qquad (2)$$

$$RHg\cdot + H^+ + e \rightarrow RH + Hg \qquad (3)$$

In the presence of a thiol (R'SH), the reaction is:

$$RHgX + R'SH \rightarrow RHgSR' + HX \qquad (4)$$

Thus the height of the first polarographic wave (associated with reductive fission of the mercury–halogen bond) falls, and simultaneously a new wave (ascribed to reductive fission of a mercury–sulphur bond) has been observed with simple thiols[4] and recently with mixtures of thiourea and formaldehyde[8].

Since soluble inorganic sulphides exist as HS^- in aqueous solution at alkaline pH values, they should react with mercurials in an analogous fashion to thiols. There is evidence in the literature that bismethylmercury(II) sulphide, $(MeHg)_2S$, results from the action of hydrogen sulphide on methylmercury(II) chloride in alcohol[9,10]. GRDENIC AND MARKUSIC[11] have described a more convenient preparation of $(MeHg)_2S$ involving methylmercury(II) bromide and sodium sulphide, during the course of which the sodium salt of the monosubstituted sulphide (*i.e.* $MeHg\ S^-\ Na^+$) was thought to be present but was not actually detected.

In view of doubts regarding reaction products, the present study was undertaken to investigate the stoichiometry of the reaction between the highly reactive monofunctional mercurial, MeHgI, and a typical soluble inorganic sulphide, sodium sulphide, in aqueous solution under strictly controlled conditions of ionic strength, pH and temperature.

EXPERIMENTAL

Apparatus

A Tinsley Mark 17/4 recording polarograph was used as described elsewhere[4].

Reagents

Tris (hydroxymethyl) aminomethane (Sigma Chem. Co., St. Louis, U.S.A.) and other chemicals (Hopkin and Williams, Merck or B.D.H., A.R. grade) were used without further purification. Iodine was quantitatively diluted from a B.D.H concentrated volumetric solution. Formdimethylamide (Hopkin and Williams) was freshly vacuum-distilled before use.

MeHgI solutions were prepared by the method of LEACH[4]. Dissolution was effected by adding the weighed MeHgI to a small volume of formdimethylamide before making up to volume with the aqueous buffer solution.

Sodium sulphide (Hopkin and Williams, "pure fused") was dissolved in de-ionised water, and the solution stored at pH 9.2 in a closed vessel at 0° to minimise loss of hydrogen sulphide. (Since some loss was inevitable, the sulphide concentration was always determined immediately after a polarographic experiment by oxidation with an excess of iodine followed by back-titration with thiosulphate[12].) At this pH virtually all the sulphide exists as HS^-, and there should be less than 1% present as H_2S in equilibrium solution.

Methods

A stock solution of $4 \cdot 10^{-4}$ *M* MeHgI was made up with de-ionised water and contained 0.1 *M* potassium chloride, gelatin (0.01%) and tris(hydroxymethyl)-aminomethane (*ca.* 0.03 *M*) adjusted with sufficient hydrochloric acid to yield a solution buffered at pH 9.2.

For titration of the sulphide solution with MeHgI, 10 ml of an appropriate concentration of sulphide solution was placed in the 20-ml polarograph cell. The solution was outgassed with dry nitrogen for 5 min. During the measurement of current–voltage curves, the nitrogen was diverted to pass over the top of the solution. This procedure minimised aerial oxidation of the reagents and led to well-defined polarographic curves.

RESULTS AND DISCUSSION

Amperometric titration: addition of sodium sulphide to MeHgI

An accurately measured volume of $4 \cdot 10^{-4}$ *M* MeHgI solution (9.0 ml) buffered at pH 9.2 was placed in the polarograph cell. This solution was titrated with 0.5-ml aliquots of a freshly prepared aqueous solution of sodium sulphide (*ca.* $1 \cdot 10^{-3}$ *M*, see *Iodimetric titration of sodium sulphide* below). Stirring of the mixture was effected by bubbling dry nitrogen through the solution for a few seconds after each addition and before measurement of the current–voltage curve.

The results are shown in Fig. 1, where the current arising from reductive fission of the Hg–I bond (the "first" wave, $E_{\frac{1}{2}} = -0.45$ V *vs.* S.C.E.*) and from reductive

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* All voltages quoted in this work are measured relative to that of the standard calomel electrode (S.C.E.).

fission of the Hg–S bond (the "second" wave, $E_{\frac{1}{2}} = -0.85$ V) is plotted against the volume of sulphide solution added. All the current values have been corrected for volume change accompanying successive additions of sulphide solution. It can be seen that 6.0 ± 0.1 ml of the sodium sulphide solution are required to reduce the concentration of MeHgI to zero.

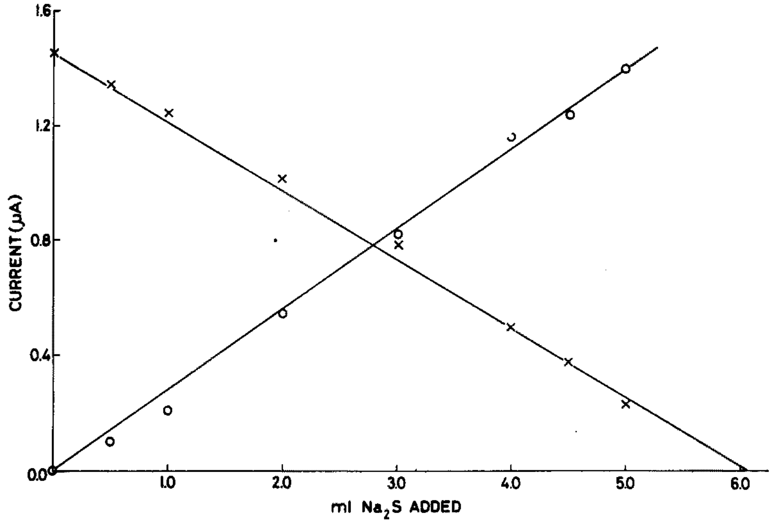

Fig. 1. Amperometric titration of MeHgI ($4 \cdot 10^{-4}$ *M*, 9.0 ml) with Na_2S solution at pH 9.2 and 20°. (×) Current due to "first" wave ($E_{\frac{1}{2}} = -0.45$ V), (o) current due to "second" wave ($E_{\frac{1}{2}} = -0.85$ V).

Iodimetric titration of sodium sulphide

Following standard practice[12], 10 ml of the above sodium sulphide solution, an excess of standardised iodine solution (10 ml of $5 \cdot 10^{-3}$ *M*) and 5 ml of concentrated hydrochloric acid were measured into a conical flask. The excess of iodine was titrated with standard thiosulphate solution (10^{-2} *M*) in the usual manner. Four such titrations, performed directly after the polarographic titration described above, agreed to better than 0.3%. The concentration of the Na_2S solution thus obtained was $2.95 \cdot 10^{-4}$ *M*.

Calculation of reaction stoichiometry

From the sodium sulphide concentration determined iodimetrically and from the result of the polarographic titration, it can be seen that the $3.60 \cdot 10^{-3}$ mmole of MeHgI required $(1.77 \pm 0.03) \cdot 10^{-3}$ mmole of sodium sulphide for complete reaction. Thus the reaction involves 2 moles of the mercurial per mole of sulphide.

Amperometric titration: addition of MeHgI to sodium sulphide

As a further check on the stoichiometry, the sulphide solution used previously was diluted ten-fold and its pH adjusted to 9.2. Then 8.0 ml of this diluted solution (corresponding to $2.36 \cdot 10^{-4}$ mmole of sodium sulphide) was titrated with the $4.0 \cdot 10^{-4}$ *M* MeHgI solution. A 1:1 reaction would require *ca.* 0.6 ml of the mercurial, whereas

2:1 stoichiometry would involve 1.2 ml. Figure 2 shows the progress of this titration upon addition of successive 0.5-ml aliquots of MeHgI. The initial anodic wave[13] at $E_{\frac{1}{2}} = -0.7$ V produced by the free sulphide ion diminishes with addition of MeHgI. The polarographic waves arising from Hg–S bond fission ($E_{\frac{1}{2}} = -0.85$ V) and Hg–C bond fission (the "third" wave $E_{\frac{1}{2}} = -1.30$ V) appear with the addition of the first aliquot of MeHgI. However the "equivalence point", which in this titration is reached when an excess of MeHgI produces the "first" wave (at $E_{\frac{1}{2}} = -0.45$ V), is not reached until more than 1.0 ml of the mercurial has been added (see Fig. 2). Although estimation of the precise equivalence point is rather more difficult here than for the reverse titration, analysis shows that 1.1±0.2 ml of MeHgI was needed. This result confirms the stoichiometry observed above.

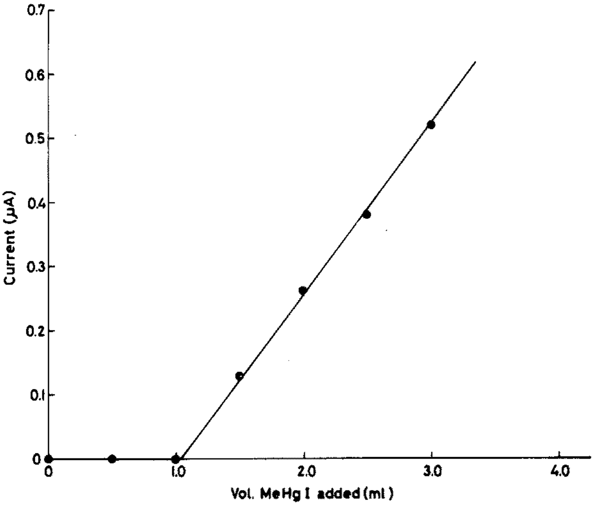

Fig. 2. Amperometric titration of Na_2S ($2.95 \cdot 10^{-5}$ *M*, 8.0 ml) with MeHgI ($4 \cdot 10^{-4}$ *M*). The shaded circles represent current due to the "first" wave ($E_{\frac{1}{2}} = -0.45$ V).

The above experiments were repeated with ammonium sulphide and similar results were obtained. Similar behaviour would presumably be found with all other soluble sulphides.

The monosubstituted compound, $MeHgS^- Na^+$, seems to behave as a reactive intermediate and is rapidly converted to $(MeHg)_2S$ in the presence of MeHgI. On the other hand bismethylmercury(II) sulphide appears to be a stable soluble entity under the conditions employed in this experiment.

In view of the precise stoichiometry, speed and sensitivity of the reaction, MeHgI should prove to be a useful reagent for the estimation of low sulphide ion concentrations in solution and studies on such polarographic analyses are currently being made.

The author wishes to thank Mr. P. W. NICHOLLS for helpful discussions and Mr. B. G. STEVENS for technical assistance.

SUMMARY

For the specific reaction between methylmercury(II) iodide and sodium sulphide, a strict 2:1 stoichiometry was observed in amperometric titrations at 20° and at pH 9.2. This stoichiometry applies up to at least pH 12.7 and to wide ranges of reagent concentrations. The reaction occurs rapidly and neither of the two steps involved appears to be rate-limiting.

RÉSUMÉ

On a déterminé un rapport stoechiométrique de 2:1 pour la réaction spécifique entre iodure de méthylmercure(II) et sulfure de sodium, en procédant par titrages ampérométriques à 20° et au pH de 9.2. Ce rapport est constant à des pH allant jusqu'à 12.7 et pour des concentrations en réactifs très variées. Cette réaction se produit très rapidement.

ZUSAMMENFASSUNG

Für die spezifische Reaktion zwischen Methylquecksilber(II)jodid und Natriumsulfid wurde bei amperometrischen Titrationen bei 20° und pH 9.2 eine strenge 2:1-Stöchiometrie beobachtet. Diese Stöchiometrie gilt bis mindestens pH 12.7 aufwärts und in einem weiten Bereich von Reagenzkonzentrationen. Die Reaktion verläuft schnell, und keine der beiden Reaktionsstufen scheint geschwindigkeitsbestimmend zu sein.

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BEITRAG ZUR MIKROBESTIMMUNG VON SAUERSTOFF IN ORGANISCHEN SUBSTANZEN IN GEGENWART VON METALLEN SOWIE IN METALLORGANISCHEN VERBINDUNGEN UND AUTOMATISCHE ENDBESTIMMUNG DER KOHLENSÄURE*

WOLFGANG MERZ
Untersuchungslaboratorium der Badischen Anilin- und Sodafabrik AG., Ludwigshafen/Rhein (Deutschland)

(Eingegangen den 28. Januar, 1970)

In den Jahren 1938 und 1939 hat SCHÜTZE[1] im Untersuchungslaboratorium der BASF, aus dem in Fortführung langjähriger Arbeiten auch dieser Bericht stammt, eine Methode zur direkten Sauerstoffbestimmung in organischen Substanzen ausgearbeitet. Sie ist heute—ausgeführt in einer der zahlreichen möglichen Modifikationen—zum Allgemeingut vieler Mikrolaboratorien geworden. Im Rahmen der hier beschriebenen Arbeit soll sowohl über eine neue Variante der Endbestimmung, als auch über Möglichkeiten zur korrekten Bestimmung des Sauerstoffs in metallhaltigen Verbindungen berichtet werden.

AUTOMATISCHE TITRATION DER KOHLENSÄURE

Grosse Verdienste für die Übertragung der Sauerstoffbestimmung in den Mikromassstab haben vor allem ZIMMERMANN[2] und UNTERZAUCHER[3]. Während ersterer die letztlich entstehende Kohlensäure gravimetrisch bestimmt, arbeitete UNTERZAUCHER eine blindwertfreie Methode mit jodometrischer Endbestimmung aus. Die neueren Modifikationen, auf die hier nicht weiter eingegangen werden soll, arbeiten im Prinzip ebenfalls nach der SCHÜTZEmethode, verwenden zur Endbestimmung jedoch weitgehend moderne massanalytische, gasvolumetrische, potentiometrische oder konduktometrische Verfahren. Daneben sind auch Methoden beschrieben, die das CO_2 über Wärmeleitfähigkeit oder Infrarotspektroskopie bestimmen. Eine übersichtliche Zusammenstellung der genannten Verfahren verdanken wir DAVIES[4]. Bereits bei der Ausarbeitung unserer Schnellmethode zur C,H-Bestimmung[5] fanden wir die Titration der Kohlensäure in nichtwässriger Phase als besonders geeignet. Auch haben langjährige Erfahrungen mit der von EHRENBERGER *et al.*[6] beschriebenen potentiometrischen Titration nach Absorption der Kohlensäure in Bariumhydroxidlösung gezeigt, dass bei höheren Sauerstoffgehalten (über 30 Prozent) die Absorption in wässriger Lösung nicht mehr quantitativ ist, wobei der Fehler mit steigendem Sauerstoffgehalt grösser wird. Auch war es naheliegend, eine einheitliche Endbestimmung sowohl für die C,H-Analyse als auch für die Sauerstoffbestimmung zu

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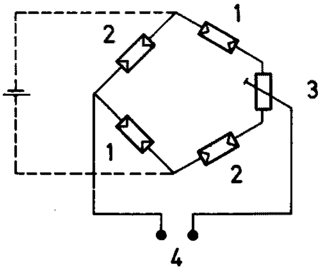
* Herrn Prof. Dr. BERNHARD WURZSCHMITT zum 75. Geburtstag gewidmet.

haben, zumal die Titration mittels kolorimetrischer Endpunktsindikation ohne grossen Aufwand vollautomatisch ausgeführt werden kann. Unser Verfahren[5], das nach dem von Brodkorb und Scherer[7] entwickelten Prinzip arbeitet, hat dabei gegenüber der von Snoek und Gouverneur[8] beschriebenen Titriereinrichtung den Vorteil, dass es wesentlich empfindlicher ist. Während bei unserer Methode durch Anwendung von diffusem Streulicht der Endpunkt der gesamten Titrierlösung bestimmt wird, ist dies bei Snoek und Gouverneur[8] nicht möglich. Die Anordnung mit einem einfachen Lichtstrahl erlaubt nur die Feststellung einer relativ lokalen Änderung der Acidität im Gesamtvolumen.

Ein weiteres Kriterium für die Empfindlichkeit unserer Titrierautomatik ist die Verwendung von zwei Interferenzfiltern in der Indikator- und dessen Komplementärfarbe, sowie der Brückenschaltung der Photowiderstände (Abb. 1). Auch ist hier die Möglichkeit gegeben, den gewünschten Farbton des Endpunktes mit Hilfe eines Potentiometers exakt einzustellen. Mittels Tastschaltung wird gegen Ende der Titration die Masslösung beliebig langsam zugegeben. Die Gefahr der Titration über den Ausgangwert hinaus, ist somit bei uns nicht gegeben. Ein weiterer gravierender Vorteil unserer Methode ist die Unbeeinflussbarkeit der Titration von aufsteigenden



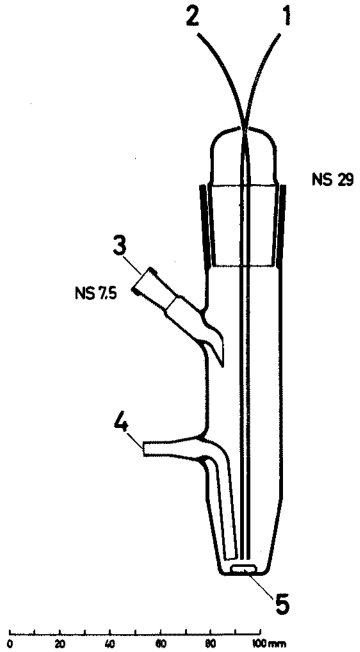


Abb. 1. Brückenschaltung des Titrators. Über den Fotowiderständen (1) und (2) sind die Interferenzfilter von 470 (1) und 610 nm (2) angeordnet. (3) Potentiometer zur Sollwerteinstellung des Farbtones. (4) Anschluss zum Steuergerät.

Abb. 2. Titriergefäss. (1) Zulauf der Titrierlösung, (2) Gaseintritt ($CO_2 + N_2$), (3) Zulauf der Absorptionslösung, (4) Absaugung von Absorptions- und Titrierlösung mittels Unterdruck, (5) Magnetrührer.

Gasblasen oder starker Rührbewegung, was bei normaler photoelektrischer Arbeitsweise durch schwankende Lichintensität zu fehlerhaften Werten führt.

Schliesslich erlaubt in unserem System ein in der Motorkolbenbürette eingebauter elektronischer Zähler eine wesentlich höhere Ablesegenauigkeit des Titriervolumens. Nähere Einzelheiten des Prinzips sowie die Titriereinrichtung* selbst sind der Originalarbeit[5] zu entnehmen. Als Absorptionslösung verwenden wir Dimethylformamid, dem Monoäthanolamin sowie als Indikator Thymolphthalein zugesetzt sind. Als Titrierlösung haben sich Tetrabutylammoniumhydroxid oder das in der Literatur[9] als stabiler beschriebene Tributylmethylammoniumhydroxid—jeweils in Isobutanol—gleichermassen bewährt. Die Form des Titriergefässes haben wir zwischenzeitlich vereinfacht (Abb. 2). In dieser verkleinerten Ausführung sind 20 ml Absorptionslösung auch bei plötzlichem Anfall der Kohlensäure ausreichend.

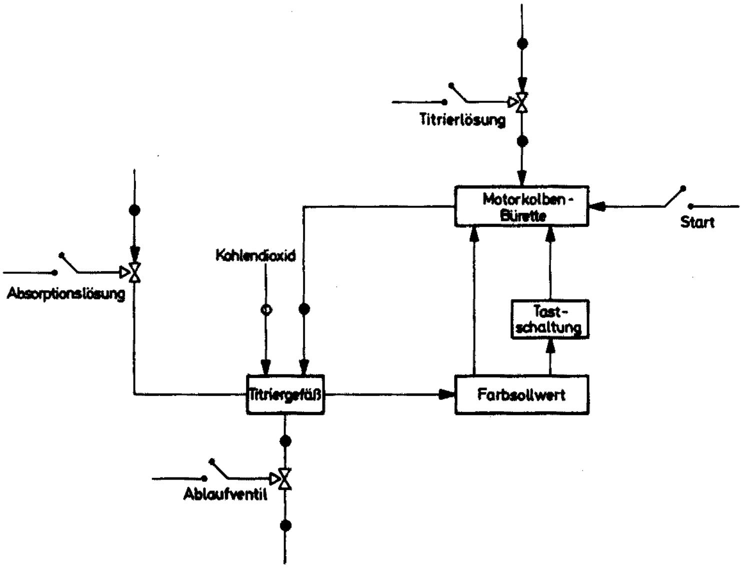


Abb. 3. Blockschaltbild der Titration. Gasleitungen sind durch einen Kreis (○), Flüssigkeitsleitungen durch einen Punkt (●) symbolisiert.

Gegenüber der vollautomatischen Anordnung bei der CH-Analyse[5] ist bei der hier beschriebenen O-Bestimmung nur die Titration selbst automatisiert. Aus dem Blockschaltbild (Abb. 3) ist zu ersehen, dass in dieser vereinfachten Anlage die Zugabe sowohl der Absorption—als auch der Titrierlösung über Magnetventile manuell ausgeführt wird. Dasselbe gilt für die Absaugung der Lösung nach Ende der Bestimmung. Über eine vollautomatische Apparatur zur Sauerstoffbestimmung soll an anderer Stelle ausführlich berichtet werden. Mit der beschriebenen Anordnung liegt die Analysenzeit bei 15 Minuten pro Bestimmung. Als Verbrennungsteil verwenden wir im Prinzip die von EHRENBERGER[6] beschriebene Apparatur mit Einschleusgabel. Eine nachgeschaltete, auf 850° erhitzte Kupferschicht verhindert Störungen bei

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* Kann komplett von der Fa. W. C. Heraeus, Hanau, bezogen werden.

schwefel- und phosphorhaltigen Substanzen. Als Treibgas verwenden wir vorgereinigten Stickstoff. Die Strömungsgeschwindigkeit liegt bei 15 ml pro Minute. Eine Erhöhung der Strömungsgeschwindigkeit führt dabei nicht zu einer Verkürzung der Ausspülzeit.

SAUERSTOFFBESTIMMUNG IN GEGENWART VON METALLEN

Während über die Bestimmung des Sauerstoffgehaltes in rein organischen Verbindungen in der letzten Zeit viel berichtet wurde, ist die Zahl der Arbeiten, die sich mit der Störanfälligkeit und den Grenzen dieser Methode beschäftigen, relativ gering. Die Verwendung von Wasserstoff anstelle des Stickstoffs als Treibgas, wie es BÜRGER[10] vorgeschlagen hat, erwies sich nicht als Allheilmittel. Auch ist bei Verwendung von Wasserstoff ein ständiger und vor allem auch schwankender Blindwert zu beachten. Das von OITA UND CONWAY[11] beschriebene Überleiten der Reaktionsgase nach Passieren des Kohlekontaktes über erhitztes Kupfer hat sich auch bei stark schwefelhaltigen Proben als ausreichend erwiesen. Störungen waren in diesem Falle auch mit Stickstoff als Treibgas nicht festzustellen. Auch phosphorhaltige Proben können auf diese Weise störungsfrei analysiert werden, wenn der Kurzbrenner eine Zersetzungstemperatur von 1000° gewährleistet. Die Annahme, dass bei Anwesenheit von Wasserstoff die Sauerstoffbestimmung auch in metallhaltigen Substanzen durchführbar ist, kann nur bedingt bestätigt werden. Es trifft dies nur auf relativ edle Metalle zu.

Wesentlich günstigere Resultate wurden durch Anwendung von Zuschlägen zur Probe erzielt. Bereits UNTERZAUCHER[12] empfahl für die Analyse metall-, speziell alkalihaltiger Verbindungen den Zusatz von Indulinbase RM, einem nicht definierten sauren Kondensationsprodukt von Anilin zur Substanzeinwaage. HUBER[13] schlug für die Sauerstoffbestimmung in alkali- und erdalkalihaltigen Proben einen Zuschlag von Silberchlorid in Gegenwart von Wasserstoff als Treibgas vor. Es spielt hier die gleiche Rolle wie Kaliumbichromat, Vanadinpentoxid oder ein anderer saurer Zuschlag bei der C-Bestimmung solcher Verbindungen. KAPRON UND BRANDT[14] empfahlen den Zusatz von Kupfer(I)-chlorid und Kohle zur Einwaage. Die Wirksamkeit dieses Zuschlages wurde von MONAR[15] bestätigt. Ein blindwertfreies Arbeiten mit diesem Kupfersalz ist jedoch ausgeschlossen, da eine Sauerstoffaufnahme des Kupfer(I)-chlorids in der Praxis nicht auszuschliessen ist. Auch der Zuschlag von Kohle, wie es bereits UNTERZAUCHER[3] beschrieben hat, ist wegen des hohen Blindwertes durch anhaftendes Wasser nicht zu empfehlen. Diese Tatsache eines derart grossen und oft schwankenden Blindwertes zwischen 0.5 und 1.5% Sauerstoff (Eigengehalt des Zuschlages), trifft aber auch auf die bereits erwähnte Indulinbase[12], sowie die von WURZSCHMITT[16] vorgeschlagenen halogenierten Paraffine, Wachse und das Polyacrylnitril zu. Sie scheiden daher für den Routinebetrieb aus. Da andererseits im Untersuchungslaboratorium der BASF 10–15% aller Sauerstoffanalysen in Substanzen mit Metallgehalten auszuführen sind, war es notwendig, die grundlegenden Arbeiten von WURZSCHMITT[16] weiterzuführen, um einen geeigneten, universell einsetzbaren Zuschlag mit möglichst niederem Sauerstoffgehalt (Blindwert) zu finden.

Grundvoraussetzung war, dass dieser Zuschlag den in den Krackrückständen verbleibenden Sauerstoff quantitativ abspaltet. Dazu muss er aber nicht nur reduzierende Eigenschaften haben, er muss auch eine intensive Berührung mit dem

Rückstand gewährleisten. Letztere Bedingung trifft auf das von HUBER[13] vorgeschlagene Silberchlorid nur zum Teil zu. Eine echte Durchmischung mit der Analysensubstanz ist nur bei solchen Proben gewährleistet, deren Krackrückstand eine Schmelze bildet. Ist dies nicht der Fall, verläuft die Reaktion nur in den Randzonen des Rückstandes quantitativ. Auch ist die reduzierende Wirkung des Silberchlorids nur im Wasserstoffstrom optimal.

Als wesentlich wirkungsvoller erwies sich das von WURZSCHMITT[16] beschriebene Ammonchlorid. Es dissoziiert in der Hitze auch unter Stickstoff in Ammoniak und Chlorwasserstoff. Der Wirkungsgrad von Ammonchlorid als Zuschlag wird weiter erhöht durch die Tatsache, dass die sublimierende Substanz die verkrackende Probe aufbläht und somit eine intensivere Berührung des Rückstandes mit den Salzsäuredämpfen gewährleistet. Nachteilig bei diesem Zuschlag ist lediglich ein geringer Blindwert von 0.1% Sauerstoff, der aber weitgehend konstant ist. Da sich andererseits aber—speziell für kohlenstoffarme Verbindungen—die Gegenwart von Kohle zur Reduktion zahlreicher Metalloxide als notwendig erwies, war Ammonchlorid allein als Zuschlag unzureichend. Die bereits erwähnte Indulinbase oder das Polyacrylnitril waren wegen ihres hohen Blindwertes nicht geeignet. Der Idealzuschlag wäre eine völlig blindwertfreie, organische Halogenverbindung, die von 100–1000° kontinuierlich Salzsäure abspaltet und dabei einen voluminösen Kohlerückstand hinterlässt. Einen solchen Zuschlag konnten wir aber nicht finden. Als Zuschlag der Wahl blieb somit nur eine Kombination mehrerer Komponenten, von denen jede eine der geforderten Aufgaben zu erfüllen hat.

In langer Versuchsreihe entdeckten wir in Hexamethylentetramin eine Substanz, die als Kohlenstoffdonator sehr geeignet war. Sie lieferte bei minimalem Blindwert von 0.2% eine ausreichende Menge Kohlenstoff, der zudem als stark voluminöser Rückstand eine genügend grosse Oberfläche für eine intensive Reaktion mit dem Probenrückstand bot. Der anorganische Rest der Substanz oder bei der Analyse von Metalloxiden die Probe selbst, liegt im Rückstand dieses Kohlenstoffdonators in relativ feiner Verteilung vor. Damit ist zwangsläufig auch eine optimale Angriffsmöglichkeit für das gleichzeitig als Zuschlag eingesetzte Ammoniumchlorid gewährleistet. Für ungeschmolzene, feste Rückstände ergab sich damit als ideale Kombination ein Mischzuschlag aus Ammoniumchlorid und Hexamethylentetramin. Entsteht jedoch bei der Pyrolyse eine klare Schmelze, so erwies sich auch dieser Kombinationszuschlag als nicht optimal. Die relativ niedrige Sublimationstemperatur des Ammonchlorids von 335° machte sich hier nachteilig bemerkbar. Bevor es noch zur Reaktion mit dem Probenrückstand kommt, sublimiert das Ammonchlorid ab und der aus dem Hexamethylentetramin stammende Kohlenstoff ist häufig allein nicht in der Lage, den Sauerstoff der Schmelze quantitativ abzuspalten. In den meisten Fällen ist die Anwesenheit von Chlor oder Chlorwasserstoff zur Reduktion unumgänglich.

Eine echte Verbesserung unseres Zuschlags brachte schliesslich die Zumischung von Silberchlorid, das in dieser Kombination eine ausgezeichnete Wirkung zeigte. Unser Universalzuschlag ist ein Dreikomponentenzuschlag mit entsprechender Arbeitsteilung. Das Hexamethylentetramin ist der Kohlenstoffdonator, während das Ammoniumchlorid die für Reduktion der Probe notwendige Salzsäure liefert und als sublimierende Substanz gleichzeitig für das Aufblähen des Krackrückstandes und damit für seine Durchmischung mit dem Kohlerest des Hexamethylentetramins verantwortlich ist. Das Silberchlorid schliesslich, das bei 455° unter langsamer Zerset-

TABELLE I

ANWENDUNGSBEREICH DER KOHLENSTOFFDONATOREN, HALOGENDONATOREN UND DES UNIVERSALZUSCHLÄGES

Verbindung	*Kohlenstoffdonatoren*		*Halogendonatoren*			*Kombinierte Zuschläge (Kohlenstoff + Halogen)*		*Universalzuschlag Hexamethylentetramin + AgCl + NH_4Cl*
	Hexamethylentetramin	*Indulinbase*	*NH_4Cl*	*AgCl*	*AgCl + NH_4Cl*	*Hexamethylentetramin + NH_4Cl*	*Hexamethylentetramin + AgCl*	
Sb_2O_3		×	×		×	×	×	×
$BaCO_3$			×	×	×	×		×
CeO_2								×
$K_2Cr_2O_7$								×
Fe_2O_3		×				×	×	×
Gd_2O_3						×		×
Co_2O_3					×	×		×
RuO_2		×			×			×
Sm_2O_3					×	×		×
SnO_2		×				×		×
$Sr(NO_3)_2$					×		×	×
WO_3			×			×	×	×
ZnO		×	×		×	×	×	×
NH_4VO_3						×	×	×
Tl_2CO_3	×	×	×	×	×	×	×	×
SeO_2	×	×	×	×	×	×	×	×
$KMnO_4$					×	×		×
$CuCO_3$								×
$(NH_4)_2HPO_4$								×
$NaAsO_2$								×

× = Theoretische Werte innerhalb der Fehlergrenze. Leerstellen = keine quantitative Erfassung des Sauerstoffs.

zung schmilzt, reagiert in dieser Form mit dem geschmolzenen Rückstand der Probe und setzt langsam den noch enthaltenen Sauerstoff in Freiheit. Jede Komponente dieses Zuschlages hat ihre eigene Aufgabe zu erfüllen. Als Einzelsubstanz nahezu unwirksam, liefert die Kombination dieser drei Verbindungen einen Universalzuschlag, der nahezu als ideal zu bezeichnen ist. Wir sind uns aber dabei völlig im Klaren, dass es sicherlich noch andere wirksame Kombinationsmöglichkeiten geben wird. Die optimale blindwertfreie Einzelsubstanz dürfte jedoch ein Wunschtraum bleiben. Wir arbeiten schon seit Jahren mit diesem kombiniertem Zuschlag aus Ammonchlorid, Silberchlorid und Hexamethylentetramin und konnten damit ausgezeichnete Erfolge verzeichnen. Die Verwendung von Platinschiffchen ist in diesem Falle aber nicht ratsam. Sie werden vom Zuschlag stark angegriffen und auch ihre Reinigung nach der Analyse ist sehr zeitaufwendig. Wir arbeiten daher ausschliesslich mit Quarzschiffchen oder dünnen Quarzröhrchen.

Letztere verwenden wir zur Analyse von pyrophoren oder hygroskopischen Substanzen sowie Substanzen mit hohem Dampfdruck. Zum Schutz der Substanz gegen Feuchtigkeit oder Luftsauerstoff wird das Röhrchen (Innendurchmesser 2–3 mm) mit einem Tropfen Paraffin verschlossen. Während sich beim Arbeiten mit Schiffchen ein Überschichten der gleichmässig über die gesamte Bodenfläche verteilten Einwaage mit dem Zuschlag empfiehlt, ist es bei Verwendung der Quarzröhrchen notwendig, den Zuschlag vor der Einwaage einzubringen, diese also zu unterschichten.

Da das Silberchlorid spezifisch schwerer als die beiden anderen Komponenten des Mischzuschlags ist, empfiehlt es sich, die drei Substanzen nur in kleinen Portionen zu vermischen. Am zweckmässigsten erwies sich dabei ein Mischungsverhältnis von einem Gewichtsteil Hexamethylentetramin und je zwei Teilen Ammonium- und Silberchlorid. Dieser Dreikomponentenzuschlag wird im Verhältnis von etwa 10:1 zur Probeneinwaage gegeben. Bei einer Normaleinwaage von 5 mg wären dies etwa 50 mg, die einen reproduzierbaren Blindwert von 0.04 mg O verursachen. Als Alternativlösung ist ebenso die Zumischung jeder Einzelkomponente zur Einwaage möglich. In diesem Falle sollte das Ammonchlorid als sublimierende Substanz zuerst zugegeben werden. Ein Unterschichten der Probe ist nicht ratsam, da damit jede nachträgliche Änderung der Einwaagengrösse ausgeschlossen ist.

Wesentlich beim Arbeiten mit Zuschlägen ist die Verwendung von vorgereinigtem Kohlekontakt. Wir verwenden CK 3-Russ der Fa. Degussa, Hanau, der nach Auswaschen mit Salzsäure 1:1 mit destilliertem Wasser absolut säurefrei gespült wird. Der bei 120° getrocknete Russ wird anschliessend 5 Stunden bei 1000° im Wasserstoffstrom geglüht. Auf diese Weise sind die meisten Kationen sowie der Schwefel entfernt und evtl. im Russ eingeschlossene organische Krackprodukte weitgehend zu Kohlenstoff reduziert.

ERGEBNISSE UND DISKUSSION DER ZUSCHLÄGE

Die allgemeine Einsetzbarkeit unseres Universalzuschlages, der sich aus Hexamethylentetramin als Kohlenstoffdonator und Ammonchlorid und Silberchlorid als Halogendonatoren zusammensetzt, soll die Tabelle I zeigen. Um den reduzierenden Einfluss organischer Verbindungen bei der Pyrolyse auszuschliessen und allein die Reduktionskraft des Zuschlages zu testen, haben wir ausschliesslich reine Metalloxide bzw. rein anorganischer Salze analysiert. Auch der an Metall gebundene Sauerstoff, der erst in eine der reaktiven Verbindungen H_2O, CO oder CO_2 übergeführt werden muss, wird so mit Sicherheit quantitativ erfasst. Während beispielsweise der Sauerstoffgehalt einer Reihe von organischen Bor- oder Phosphorverbindungen auch mit anderen Zuschlägen entsprechend der Theorie gefunden wurde[17], werden in Ammon- oder Alkaliphosphaten nur mit unserem kombinierten Zuschlag richtige Werte erhalten. Borax liefert auch mit dem Universalzuschlag zu niedere Werte. Allerdings sei darauf aufmerksam gemacht, dass die Lebensdauer der Quarzrohre bei diesen Proben sehr begrenzt ist. Dies gilt ebenso für arsenhaltige Substanzen. Mehr oder wenige starke Verschleisserscheinungen sind auch bei anderen Metallen, besonders bei Natrium und Kalium zu beobachten.

In der Zwischenzeit haben wir das hier beschriebene Verfahren auf ein sehr heterogenes Probenmaterial ausgedehnt und festgestellt, dass die Sauerstoffbestimmung nunmehr auf alle Verbindungen angewendet werden kann, die keine schwer reduzierbaren Elemente enthalten. Nach unseren Erfahrungen versagt die Methode lediglich noch in Gegenwart von Al, Si, Ti, Zr, Nb, Ta, Sc, At, Ho und Lu. Auch für fluorhaltige Substanzen haben wir noch keine allgemein anwendbare Methode. MONAR[15] leitet zur Entfernung des Fluors die Reaktionsgase vor Passieren des Kohlekontaktes über auf 800° erhitztes Bariumchlorid. Bei aliphatischen Fluorverbindungen treten jedoch auch mit dieser Methodik Störungen auf.

Aus der angeführten Tabelle ist nicht nur die universelle Einsetzbarkeit unseres Universalzuschlages zu ersehen, es ist vergleichsweise auch die Anwendungsbreite der Einzelkomponenten Ammonchlorid, Silberchlorid und Hexamethylentetramin sowie Gemische zweier dieser Komponenten aufgezeigt. Schliesslich ist auch die Überlegenheit der von UNTERZAUCHER[12] vorgeschlagenen Indulinbase als reinem Kohlenstoffdonator gegenüber dem von uns vorgeschlagenen Hexamethylentetramin zu erkennen. Stark geschmälert aber wird die Wirksamkeit der Indulinbase durch einen allzuhohen Blindwert, der nach eigenen Versuchen bei 10 Bestimmungen um 0.02 mg um den gefundenen Mittelwert von 0.20 mg Sauerstoff aus 20 mg Indulinbase schwankt. Nicht nur die Höhe des Blindwertes macht sich demnach negativ bemerkbar, auch die grosse Schwankungsbreite führt zu fehlerhaften Resultaten. Bei einer Einwaage von 5 mg einer Probe bedeuten 0.02 mg Sauerstoff einen Fehler von $\pm 0.4\%$ O, also mehr, als der normalen Fehlergrenze von $\pm 0.3\%$ absolut entspricht. In der Praxis ist dadurch mit einem Gesamtfehler von $\pm 0.7\%$ zu rechnen. Dies war schliesslich auch der Grund, dass wir auf einen Einsatz von Indulinbase verzichteten.

Aus der Tabelle ist weiterhin zu ersehen, dass Ammonchlorid als Zuschlag eine grössere Anwendungsbreite als Silberchlorid hat. Ausgezeichnete Resultate werden bereits mit einem kombinierten Zuschlag dieser beiden Chloride erhalten. Das Gemisch aus Ammonchlorid und Hexamethylentetramin war wesentlich aktiver als die Kombination des Kohlenstoffdonators mit dem Silberchlorid und würde sogar in vielen Fällen als Zuschlag ausreichen. Für Routineanalysen ist es jedoch ratsam, speziell bei unbekannten Substanzen, prinzipiell den Universalzuschlag einzusetzen, zumal der Blindwert des Silberchlorids gegenüber den Blindwerten der beiden anderen Komponenten vernachlässigbar klein ist. Der Gesamtblindwert unseres Universalzuschlages (50 mg) liegt, wie bereits erwähnt, bei 0.04 ± 0.004 mg O. Demzufolge verursacht der Blindwert unseres Universalzuschlages keinen weiteren merklichen Anstieg der Fehlergrenze der Methode.

ZUSAMMENFASSUNG

Es wird über die direkte Bestimmung von Sauerstoff in organischen Substanzen in Gegenwart von Metallen berichtet. Zur quantitativen Abspaltung des Sauerstoffs aus einer grossen Zahl von Metalloxiden erwies sich ein Kombinationszuschlag aus Ammonchlorid, Silberchlorid und Hexamethylentetramin als sehr geeignet. Die Endbestimmung erfolgt über vollautomatische Titration der Kohlensäure mittels kolorimetrischer Endpunktsindikation.

SUMMARY

The direct determination of oxygen in organic substances in the presence of metals is described. For complete removal of oxygen from metal oxides, the addition of a mixture of ammonium chloride, silver chloride, and hexamethylenetetramine was found to give the best results. The carbon dioxide is finally determined by fully automatic titration with colorimetric end-point detection.

RÉSUMÉ

L'auteur décrit un dosage direct de l'oxygène dans les substances organiques en présence de métaux. Pour l'élimination complète de l'oxygène contenu dans les oxydes métalliques, de très bons résultats ont été obtenus en ajoutant un mélange de chlorure d'ammonium, chlorure d'argent et hexaméthylènetétramine. Pour terminer, on titre automatiquement le gaz carbonique avec détection colorimétrique du point final.

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POLARITY OF THE GAS CHROMATOGRAPHIC STATIONARY PHASES AND RETENTION INDICES OF ALIPHATIC ESTERS, KETONES AND ALCOHOLS

J. MARTÍN MIRA AND L. GASCÓ SÁNCHEZ
División de Química Analítica, Junta de Energía Nuclear, Madrid-3 (Spain).

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Many attempts have been made to establish qualitative and quantitative classification of stationary phases. A logical order can be achieved by considering the relative behaviour of all stationary phases for the same class of compounds. It is possible to obtain a classification by means of the equation

$$b = \log \frac{V'_{z+1}}{V'_z} = \log r_{(z+1)z} \tag{1}$$

where V'_{z+1} and V'_z are the *n*-alkane-adjusted retention volumes for $z+1$ and z carbon atoms; the least polarity corresponds to the stationary phase whose b value is the biggest. On the basis of *n*-alkane–stationary liquid interactions, a definition of polarity has been indicated[1] where extreme values are 0 for Squalane and 1 for β,β'-hydroxydipropionitrile. Likewise, LITTLEWOOD[2] has reported that the polarity of stationary phases increases with the relative retention of polar–nonpolar compounds. This idea is connected with KOVÁTS indices, which are defined as

$$I_x = \left(z + \frac{\log r_{xz}}{b}\right) \cdot 100 \tag{2}$$

According to the definition of retention index, the plot of I *vs.* the number of carbons in an *n*-alkane homologous series is a straight line, giving a 100 units increment in the value of the index with the addition of one methylene group. This fact can be studied in homologous series other than those of *n*-alkanes in order to find out if every $-CH_2-$ group has the same behaviour. KOVÁTS[3] verified that the members of a homologous series with carbon number less than 6 gave an increment differing from 100 units; ZULAICA AND GOUIOCHON[4] and JONAS *et al.*[5] reported other differences.

ROHRSCHNEIDER[6] measured the selectivity of the stationary liquid as

$$S_x = I_x - I \text{ (}n\text{-alkane with the same number of carbon atoms)} \tag{3}$$

This equation allows the prediction of stationary phase retentions (its quantitative evaluation) by means of functional group selectivities, and also permits the study of functional group contribution at liquid phase–solute molecule interactions.

Moreover, in this empirical method, KOVÁTS[7] proposed a relation between retention indices and boiling points. When I is plotted against boiling point, linear relationships are obtained for every homologous series. The same method can also be utilized to predict retentions in any liquid phase, if the straight-line equations are known.

In this work, a study is made of the three methods described above for the quantitative evaluation of the stationary phases: *I*, selectivity and *I*–boiling point relationships. In order to compare the behaviour of phases of different polarity, retention indices from the literature as well as those obtained in the present work have been used. The columns used were of Squalane, Apiezon L[7,8], Ucon, Emulphor O[7,8], Carbowax 1540[9] and PEG 400[10], in increasing order of polarity.

EXPERIMENTAL

Apparatus

Conventional gas chromatographs with flame ionization detectors were used. The columns were copper tubes, 2 m in length and 4.8 mm in internal diameter. Stationary phases were 2% Ucon 50LB 1200X (F.M.) and 2% Squalane (Hopkins and Williams). Supports were Chromosorb G a.w. 80–100 mesh, deactivated by acetic acid digestion and coated with 0.05% tetrahydroxyethylethylenediamine. Column temperatures were 50° and 70°. Flow rate of gases in the FID were 60 ml/min for argon, 35 ml/min for hydrogen and 625 ml/min for air.

Retention index measurement

Retention indices of 71 compounds (aldehydes, ketones, alcohols and esters) were measured by means of eqn. (2) on two columns of Squalane and Ucon 50LB 1200X at 50° and 70°. The data are given in Table I. The value of *b* was calculated as

TABLE I

RETENTION INDICES AT 50° AND 70° IN COLUMNS OF 2% OF STATIONARY PHASE ON CHROMOSORB G ACETYLATED BY DIGESTION AND MODIFIED WITH 0.05% THEED

Compound	*B.P.*	*Squalane*		*Ucon 50LB 1200X*	
		I_{50}	I_{70}	I_{50}	I_{70}
Acetaldehyde	21	346	—	482	—
Propionaldehyde	48.8	437	422	580	589
Isobutyraldehyde	62.5	506	501	635	639
Butyraldehyde	75.7	535	533	680	681
Isovaleraldehyde	92.5	604	—	739	—
Valeraldehyde	103.4	640	639	785	785
Hexanal	131	742	743	887	888
Furfural	161.7	—	748	—	1046
2-Hexanal	150	—	781	—	974
Heptanal	155	—	842	—	991
Octanal	163.4	—	943	—	1094
Acetone	56.5	426	—	594	609
2,3-Butanedione	88	523	—	714	—
Methyl ethyl ketone	79.6	533	524	694	696
Methyl propyl ketone	101.7	624	623	781	782
Methyl isobutyl ketone	115	680	682	826	827
Methyl butyl ketone	127.2	726	727	883	883
Methyl formate	31.5	373	—	526	—
Ethyl formate	54.3	456	—	617	—
Isopropyl formate	71.3	516	—	663	—
n-Propyl formate	81.3	559	—	723	—

TABLE I (*continued*)

Compound	*B.P.*	*Squalane*		*Ucon 50LB 1200X*	
		I_{50}	I_{70}	I_{50}	I_{70}
n-Butyl formate	106.8	660	—	823	—
Isoamyl formate	123.5	727	—	885	—
n-Amyl formate	132.1	765	—	927	—
Methyl acetate	57.1	470	—	623	—
Ethyl acetate	77.1	548	540	700	695
Isopropyl acetate	93	596	—	739	—
tert.-Butyl acetate	97	639	—	769	—
n-Propyl acetate	101.6	646	—	800	—
Isobutyl acetate	116.5	708	—	852	—
n-Butyl acetate	126.5	745	—	901	—
Isoamyl acetate	142.5	812	—	956	—
n-Amyl acetate	148	848	—	1000	—
n-Hexyl acetate	169.2	—	946	—	1096
Methyl *n*-propionate	79.9	569	—	720	—
Ethyl *n*-propionate	99.1	646	642	791	787
Isoamyl *n*-propionate	160.2	—	908	—	1038
Methyl isobutyrate	92.6	623	—	762	—
Ethyl isobutyrate	111.7	695	694	825	824
Isobutyl isobutyrate	148.7	853	—	970	—
n-Butyl isobutyrate	—	—	891	—	1012
Isoamyl isobutyrate	168.8	—	955	—	1069
Methyl *n*-butyrate	102.3	660	—	807	—
Ethyl *n*-butyrate	121.3	737	736	877	876
n-Propyl *n*-butyrate	143	834	—	970	—
Isobutyl *n*-butyrate	—	—	892	—	1018
Isoamyl *n*-butyrate	184.8	—	998	—	1120
Methyl isovalerate	116.7	716	—	855	—
n-Butyl isovalerate	—	—	989	—	1108
Ethyl *n*-valerate	146	837	837	976	976
Methyl *n*-hexanoate	149.5	—	861	—	1008
Ethyl *n*-hexanoate	168	—	935	—	1073
Methanol	64.6	420	—	648	646
Ethanol	78	422	—	686	678
2-Propanol	82.5	476	—	705	—
n-Propanol	97.2	521	508	795	784
2-Butanol	100	567	—	802	—
2-Methyl-1-propanol	108.4	589	580	858	847
2-Methyl-2-butanol	101.8	614	—	809	—
n-Butanol	118	625	—	901	—
3-Pentanol	115.6	665	—	892	—
2-Pentanol	119.3	665	—	902	—
3-Methyl-1-butanol	130.5	697	692	973	960
2-Methyl-1-butanol	128	700	—	972	—
n-Pentanol	138	730	722	1008	996
1-Hexen-3-ol	—	746	—	—	987
3-Hexanol	135	761	—	988	—
2-Hexanol	140	766	—	1004	—
3-Hexen-1-ol	156	813	—	—	1064
n-Hexanol	157.2	831	—	—	1099
n-Heptanol	176	—	923	—	—
Values of *b*		0.425	0.378	0.385	0.351

the mean of the logarithm of relative retention for successive *n*-alkanes from $z=3$ to $z=10$. The *n*-alkane standard and the homologous compounds to be eluted in a known sequence were introduced as samples; the amount of each compound was *ca.* 0.1 μg.

RESULTS AND DISCUSSION

Retention indices and boiling points

It has been possible to establish the well-known linear relationships between the retention indices and the boiling points of the homologous series investigated (Table I). Linear equations permit the extrapolation of the retention index values of other homologous compounds not actually measured. Straight-line relationships between I and boiling point in Ucon and Squalane for aliphatic and saturated aldehydes, ketones, esters and alcohols, are presented in Table II. Boiling points (t) are expressed in degrees centigrade. Furthermore, the standard deviations of the straight-line adjustments (S), of the y-intercept (S_a) and of the slope (S_b) were calculated. It can be observed from the experimental data that alcohols give the highest standard deviations; also, when the alcohols were adjusted as a whole, they gave bigger values than when they were adjusted by sub-groups as primary and secondary alcohols. The decrease in the values of the standard deviation when the adjustments were made by sub-groups is especially important for Squalane.

TABLE II

CORRELATION BETWEEN RETENTION INDICES (I) AND BOILING POINTS (t) FOR COMPOUNDS OF SOME HOMOLOGOUS SERIES

Stationary phase	*Homologous series*	*Correlation*	*Standard deviations*		
			S	S_a	S_b
Squalane	Aldehydes	$I = 3.61t + 267$	6.6	6.2	0.07
Ucon	Aldehydes	$I = 3.70t + 399$	2.1	2.0	0.008
Squalane	2-Ketones	$I = 4.24t + 190$	4.6	8.1	0.08
Ucon	2-Ketones	$I = 4.02t + 370$	4.9	8.7	0.09
Squalane	Straight and branched esters	$I = 4.11t + 234$	7.9	5.6	0.05
Ucon	Straight and branched esters	$I = 3.95t + 397$	7.8	5.5	0.05
Squalane	Straight and branched primary and secondary alcohols	$I = 4.87t + 77$	24	33	0.29
Ucon		$I = 5.09t + 302$	10	14	0.13
Squalane	Primary alcohols	$I = 5.18t + 20$	8.4	15	0.13
Ucon	Primary alcohols	$I = 5.43t + 265$	6.8	15	0.13
Squalane	Secondary alcohols	$I = 5.10t + 63$	12	47	0.38
Ucon	Secondary alcohols	$I = 5.09t + 297$	6.1	23	0.19

Retention indices and molecular structure

The retention index increments, ΔI, with the $-CH_2-$ addition in homologous series other than *n*-alkanes (such as aldehydes, ketones, alcohols and esters) were calculated to check if every member of the family fulfills the condition $\Delta I = 100$. The data derived from Table I, together with some derived from published retention index data (Apiezon L, Emulphor O, Carbowax 1540 and PEG 400) are given in Table III. Some of the results denote that the methylene group in the *n*-alkane family shows a different behaviour in the other homologous series; likewise, this indicates that the interactions of the $-CH_2-$ are not equal in different phases. It can be observed in the case of the more volatile esters that ΔI decreases when the polarity of the stationary phase increases. This effect can not be related with the difference of temperatures at which retention indices were measured, as in the case of Apiezon L and PEG 400, because although the temperature affects the I value, this effect is of little importance for two successive members of a series. If it is supposed that the more volatile ester has a polarity greater (more capacity as acceptor) than that of the next member, this can be interpreted to mean that the stationary phase is more polar (more donor groups), and the solute–phase interactions will be stronger, decreasing the difference in the retentions and, consequently, decreasing ΔI. When the chain length increases, the nonpolar–nonpolar interactions become more important, and ΔI is nearer to 100; then it can be said that the solute–solvent interaction forces are the same for two successive members. An analogous interpretation can be made for aldehydes and ketones. The interpretation is more difficult for alcohols, because the temperature significantly influences the I values in a nonpolar phase, and the interaction with the siliceous support is greater (principally for methanol, the smallest and most polar molecule), the I values depending on the quantity of sample injected (it should be noted that quantities of the order of 10^{-1} μg were introduced into the Squalane and Ucon columns). Accordingly, the ΔI values for methanol to ethanol are quite different in different supports, but generally low in polar phases, owing to the different donor capacity of the two alcohols. The other alcohols show values higher than 100;

TABLE III

RETENTION INDEX INCREMENTS CAUSED BY ADDITION OF THE $-CH_2-$ GROUP TO THE LEADING MEMBERS OF ESTERS, ALCOHOLS, ALDEHYDES AND KETONES

	Squalane 50°	*Apiezon L*		*Ucon 50LB 1200X 50°*	*Emulphor O 130°*	*Carbowax 1540 80°*	*PEG 400*	
		70°	*130°*				*60°*	*100°*
Et Ac–Met Ac	78	82	79	77	62	57.6	57	56
Prop Ac–Et Ac	98	97	101	100	95	88.4	87	89
But Ac–Prop Ac	99	103	109	101	97	95.8	95	97
Et Ac–Et For	92	89	92	83	65	62.2	—	—
Et Prop–Et Ac	98	97	98	91	80	70.8	68	67
Et But–Et Prop	91	87	93	86	85	—	74	75
Ethanol–Methanol	2	85	117	38	45	33	34	32
Propanol–Ethanol	99	112	127	109	104	100.2	98	99
Butanol–Propanol	104	106	116	106	108	104.3	103	102
Pentanol–Butanol	105	—	106	107	114	—	107	106
Propanal–Ethanal	91	112	119	98	99	85.8	—	—
Butanal–Propanal	98	102	104	100	91	85.6	—	—
2-Butanone–Acetone	107	100	101	100	84	82.6	—	—
2-Pentanone–2-Butanone	91	91	93	87	86	76.3	—	—

TABLE IV

MEAN VALUES FOR THE SELECTIVITY OF SOME HOMOLOGOUS SERIES

	Squalane	*Apiezon L*	*Ucon 50LB 1200X*	*Emulphor O*	*Carbowax 1540*	*PEG 400*
n-Methyl esters	166.6 ± 5.6	166.8 ± 4.8	316.8 ± 9.0	410.2 ± 22.3	519.5 ± 35.6	—
n-Formates[a]	158.3 ± 2.4	174.0 ± 15.5	321.0 ± 3.6	413.8 ± 0.5	519.9 ± 4.5	—
n-Acetates[a]	146.6 ± 1.3	151.2 ± 3.9	299.4 ± 2.1	374.0 ± 3.4	476.9 ± 9.4	537.3 ± 10.7
n-Propionates[a]	146	149.0 ± 2.9	291	351.2 ± 5.8	456.8	—
n-Butyrates[a]	135.5 ± 2.7	139.2 ± 1.0	273.5 ± 6.2	332.8 ± 8.7	—	—
n-Ketones[2]	127.2 ± 4.4	147.4 ± 2.4	288.0 ± 6.3	384.4 ± 11.5	503.9 ± 24.3	—
n-Aldehydes	140.7 ± 4.1	161.1 ± 13.1	285.6 ± 5.2	393.0 ± 4.0	493.8 ± 13.9	—
Alcohols (primary)	224.5 ± 4.4	215.8 ± 18.2	497.5 ± 10.7	584.7 ± 12.5	741.6 ± 2.7	870.8 ± 4.8
Alcohols (secondary)	164.8 ± 2.6	156.5 ± 11.5	397.6 ± 6.9	469.0 ± 4.4	—	753.5 ± 8.0

[a] Except methyl.

from the above argument, such values in a nonpolar stationary phase can indicate that the alcohols with a longer hydrocarbon chain will be comparatively strongly retained.

By means of ROHRSCHNEIDER's selectivity equation (eqn. 3), it is possible to evaluate the increment in the retention index when one functional group is added to an *n*-alkane molecule. Table IV presents mean selectivity values obtained from the same six stationary phases for esters, ketones, aldehydes and alcohols; standard deviations are given. The results for esters indicate that the selectivities of formates, acetates, propionates and butyrates are representative, but aldehydes and ketones are not distinct except in Squalane, while the differences of selectivity between primary and secondary alcohols increase with increased polarity of the phase.

SUMMARY

Retention indices of 71 compounds (aldehydes, ketones, esters and alcohols) were measured on Squalane and Ucon 50LB 1200X at 50° and 70°, and 12 straight-line relationships were established between retention indices and boiling points. By means of these indices and those obtained by other authors on Apiezon L, Emulphor O, Carbowax 1540 and PEG 400, a comparative study was made of retention index increments caused by the addition of a $-CH_2-$ group in the leading members of some homologous series, and of mean values of the selectivity of some series in every stationary phase.

RÉSUMÉ

Une étude est effectuée sur la chromatographie gazeuse de 71 composés (aldéhydes, cétones, esters et alcools) sur Squalane et Ucon 50LB 1200X à 50° et 70°. On compare les indices obtenus avec ceux d'autres auteurs ayant travaillé sur Apiezon L, Emulphor O, Carbowax 1540 et PEG 400, en mesurant les augmentations des indices de rétention causées par addition des groupes $-CH_2-$.

ZUSAMMENFASSUNG

Es wurden die Retentionsindices von 71 Verbindungen (Aldehyden, Ketonen, Estern und Alkoholen) an Squalan und Ucon 50LB 1200X bei 50° und 70° gemessen. 12 Geraden-Beziehungen zwischen Retentionsindices und Siedepunkten wurden festgestellt. Mit Hilfe dieser Indices und jener, die von anderen Autoren für Apiezon L, Emulphor O, Carbowax 1540 und PEG 400 erhalten worden sind, wurden die Retentionsindex-Inkremente, die durch eine zusätzliche $-CH_2-$ Gruppe in den führenden Gliedern einiger homologer Reihen hervorgerufen werden, mit den Mittelwerten der Selektivität einiger Reihen für jede stationäre Phase verglichen.

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INTERET DU CALCUL AUTOMATIQUE DANS LA RECHERCHE DES CONDITIONS EXPERIMENTALES OPTIMA EN FLUORESCENCE X*

G. VOS
Section de Chimie Analytique et Minérale, EURATOM, Commission des Communautés Européennes, C.C.R. Etablissement, Ispra (Italie)

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Il est assez fréquent, dans le cas d'une analyse effectuée par une méthode physique telles que la spectrographie d'émission ou la fluorescence X, d'utiliser pour l'étalonnage une série d'échantillons témoins. A partir de ceux-ci on trace une courbe de calibrage. Souvent, on considère qu'il s'agit d'une droite.

On peut en estimer les paramètres, pente et ordonnée à l'origine par la méthode classique de la régression. Cette méthode est bien connue et ne demande que des calculs élémentaires. Toutefois, ces derniers sont plutôt longs et fastidieux, s'ils sont effectués à la main et comportent des risques d'erreurs. Aussi, renonce-t-on à les utiliser dans la pratique courante. L'introduction croissante des machines à calculer programmables et des ordinateurs permet actuellement d'effectuer ces opérations très rapidement. De plus, les différents paramètres statistiques de la droite de régression peuvent être facilement obtenus. L'un d'eux, en particulier, la variance résiduelle, est caractéristique de la dispersion des points utilisés pour le tracé de la droite de calibrage.

Plusieurs auteurs, dont LINNING ET MANDEL[1] ont souligné la relation existant entre cette dispersion et la précision des déterminations exécutées à partir de cette droite. Si l'on veut bien se rappeler du nombre de facteurs qui peuvent influencer cette dispersion, c.à.d. les conditions opératoires de la technique d'analyse, la gamme des standards utilisés, etc., on se rend compte que l'on se trouve en présence d'une variété de paramètres dont l'analyste ne peut estimer à priori l'importance relative. Dans ces conditions, le choix des conditions analytiques optima n'est pas aussi évident qu'il pourrait paraître.

On verra, ci-dessous, comment à l'aide du calcul des caractéristiques statistiques de la droite de régression on peut mieux parvenir à la connaissance de ces conditions.

DROITE DE CALIBRAGE OBTENUE PAR RÉGRESSION ET QUELQUES-UNES DE SES CARACTÉRISTIQUES STATISTIQUES

Les considérations qui suivent sont au moins partiellement classiques et peuvent être trouvées exposées de manière plus complète dans des ouvrages spécialisés tels que BROWNLEE[2].

La Figure 1 représente la droite de calibrage calculée par régression linéaire (ou des moindres carrés). y en abscisse est le signal reçu (intensité de la raie en fluo-

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rescence X), x correspond aux concentrations de l'élément à doser. La droite de calibrage s'exprime par l'équation

$$y = a + bx \tag{1}$$

où a, l'ordonnée à l'origine, peut être assimilée au fond continu.

La valeur de b peut être estimée par la relation

$$b = \frac{\Sigma(x_i - \bar{x})(y_i - \bar{y})}{\Sigma(x_i - \bar{x})^2} \tag{2}$$

Σ est équivalent à $\sum\limits_{i=1}^{N}$; toutes les sommations sont effectuées de 1 à N, N étant égal au nombre d'étalons utilisés.

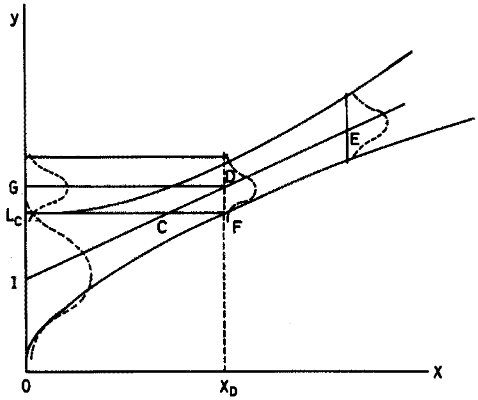

Fig. 1. Droite de calibrage obtenue par régression avec indication des limites de décision L_C et de détection x_D.

$\bar{x}$ et $\bar{y}$ sont respectivement les moyennes de toutes les valeurs de x et de y servant à l'étalonnage. Quant à a, il est donné par la relation

$$a = \bar{y} - b\bar{x} \tag{3}$$

La variance résiduelle autour de la droite de régression est un concept des plus utiles car elle permet de calculer un certain nombre de caractéristiques de la droite de calibrage. Elle est estimée par la relation

$$V_R = \frac{\Sigma(y_i - y_i')^2}{N-2} \tag{4}$$

où les y_i' sont les valeurs recalculées de y à partir de la droite de calibrage pour les différentes valeurs x_i des étalons. V_R correspond aux fluctuations résiduelles de y autour de la droite de régression. On peut, la connaissant, calculer l'intervalle de confiance du facteur analytique b.

On a dessiné sur la Fig. 1 les intervalles de confiance pour un certain niveau de probabilité (95% p.ex.) autour de la droite de calibrage. Ces intervalles sont décrits par des courbes dont le décalage par rapport à la droite de régression parallèlement à l'axe des y est égal à S_y. S_y au point x est donné par la relation

$$S_y{}^2 = V_R t^2 \left[1 + \frac{1}{N} + \frac{(x-\bar{x})^2}{\Sigma(x_1-\bar{x})^2}\right] \tag{5}$$

où t est le facteur de Student. Ces courbes sont hyperboliques. On peut en déduire l'intervalle de confiance autour d'un résultat d'analyse x_0. En posant $S_{x_0} = S_{y_0}/b$, on obtient l'intervalle qui a la probabilité (on choisit 95% en général) correspondant au facteur t adopté de contenir la valeur vraie de x lorsque y est observé. Cet intervalle est donné approximativement par la formule

$$x_0 \pm S_{x_0} t/\sqrt{n} \tag{6}$$

si n est le nombre de mesures effectuées sur l'échantillon à analyser.

D'autre part HUBAUX ET VOS[3] ont montré qu'il était possible de calculer deux concepts appelés limite de décision (L_C) et limite de détection (x_D) à partir de la variance résiduelle. Ces concepts ont été introduits par CURRIE[4] qui a indiqué qu'ils correspondaient respectivement aux erreurs de première et deuxième espèce. En effet, pour L_C, on a une probabilité α (dans ce cas 2.5%) de déclarer que la substance à analyser est présente alors qu'elle est absente (erreur du premier ordre). D'autre part pour une concentration égale à x_D on a, a priori, une probabilité β (ici 2.5%) de déclarer que cette concentration ne peut être distinguée de zéro (erreur du deuxième ordre).

On a représenté sur la Fig. 1 la distribution gaussienne de la probabilité d'un signal en un point quelconque E, au point I correspondant à l'intersection de la droite de calibrage avec l'axe des y, et au point D dont nous verrons plus loin le mode de calcul. Au point L_C, correspondant à l'intersection avec l'axe y de la limite supérieure du domaine de confiance à 95%, on a effectivement 2.5% de chance de détecter un signal non nul alors que la substance est absente (non nul, s'entend après déduction du fond continu). OL_C est équivalent à la limite de décision telle qu'elle est définie par CURRIE.

Sa valeur OL_C est égale à $OI + IL_C$

$$(IL_C)^2 = V_R t^2 \left[1 + \frac{1}{N} + \frac{\bar{x}^2}{\Sigma(x_i-\bar{x})^2}\right] \tag{7}$$

Si l'on prolonge la parallèle à l'axe des x L_CC jusqu'à son intersection F avec la limite inférieure du domaine de confiance, on se trouve en un point où l'on a β% (dans ce cas 2.5%) de chance d'avoir un signal inférieur à L_C pour une concentration réelle correspondant à x_D et par conséquent non distinguable d'une concentration nulle. C'est ce que représente la courbe de Gauss dessinée sur la Fig. 1 et dont le centre se trouve en D. L'abscisse de ce point correspond à la limite de détection déjà définie OL_D et par conséquent à la concentration x_D.

Par suite de la forme hyperbolique des limites du domaine de confiance, un calcul exact de x_D est relativement laborieux. Toutefois on peut, en première approximation, assimiler dans cette région ces limites à des parallèles à la droite de régression. Dès lors x_D, qui est égal à IG/b, avec la relation approchée

$$(\mathrm{IG}) = V_{\mathrm{R}}^{\frac{1}{2}} t \left[1 + \sqrt{1 + \frac{1}{N} + \frac{\bar{x}^2}{\Sigma(x_i - \bar{x})^2}} \right] \tag{8}$$

On trouvera un développement plus exhaustif et des formules plus exactes dans le travail de HUBAUX ET VOS[3].

L'examen des formules (5),(6) et (7) démontre l'interdépendance qui existe entre la variance résiduelle d'une part, la précision et la sensibilité de détection d'une détermination, d'autre part. Dès lors, il sera intéressant de vérifier de quelle manière influe le choix des conditions expérimentales et des standards sur ces deux caractéristiques principales d'une méthode analytique classique comme la fluorescence X.

RECHERCHE DES CONDITIONS EXPÉRIMENTALES OPTIMA EN FLUORESCENCE X

Cinq cas typiques seront décrits ci-dessous:

1. recherche du temps de comptage optima,
2. influence du choix des standards sur la limite de détection,
3. choix des conditions d'excitation optima,
4. recherche de la surface minima utilisable pour l'analyse d'un échantillon d'aluminium,
5. comparaison entre deux méthodes de dosage de Cl dans un caloporteur organique.

On comparera chaque fois la limite de détection calculée selon la formule (7) et appelée "expérimentale" à celle égalée à trois fois la racine carrée du fond continu, appelée "limite théorique".

Recherche du temps de comptage optimum

On a choisi une gamme d'échantillons témoins permettant le dosage de faibles teneurs de Fe et de Si dans l'aluminium. Les limites de détection théoriques sont, comme il est bien connu, nettement différentes, étant donné la différence de nombre atomique de ces deux éléments. Les témoins utilisés, de fabrication privée, sont employés normalement pour le dosage spectrographique des impuretés les plus courantes de l'aluminium[5]. Néanmoins celles-ci sont pour la plupart déterminables par fluorescence X. Toutes autres conditions demeurant égales, on trace la droite de calibrage pour différents temps de comptage, pour lesquels on calcule les deux limites de détection théorique et expérimentale.

Ces mesures ont été effectuées dans quatre cas: (*a*) le dosage de Fe dans l'aluminium normal (qualité A5) à l'aide de 5 témoins; (*b*) le dosage de Si dans l'aluminium normal (qualité A5) à l'aide de 5 témoins; (*c*) le dosage de Fe dans l'aluminium AG 2-3 avec 4 témoins; (*d*) le dosage de Si dans l'aluminium AG 2-3 avec 4 témoins.

La Fig. 2 montre l'évolution de la limite de détection de Fe dans Al en fonction du temps de comptage. On constate que le facteur de dispersion, c.à.d. la variance résiduelle, joue un rôle tellement important qu'il est pratiquement illusoire d'augmenter le temps de comptage au-delà de quelques secondes, contrairement à ce que l'on pourrait déduire de la limite de détection théorique.

Il en est de même pour la précision relative; la variance résiduelle divisée par le facteur analytique c.à.d. par la pente de la droite de calibrage ne varie pratiquement pas avec le temps de comptage. Rappelons que la variance résiduelle est un paramètre statistique et que, par conséquent, une seule gamme de mesures n'en donne qu'une estimation. Les limites de détection indiquées dans la Fig. 2 sont d'ailleurs la moyenne d'au moins trois mesures et il n'est pas rare d'avoir un écart type sur la variance résiduelle (et, par conséquent, sur la limite de détection) de l'ordre de 30%. D'autre part, notons que les limites de détection expérimentales de Fe dans Al obtenues avec ces témoins sont de l'ordre de 200 p.p.m., contrairement à la limite théorique estimée à 5 p.p.m. (pour un temps de comptage de 40 sec). Cela s'explique notamment par la valeur élevée du témoin à concentration la plus basse, 500 p.p.m. On peut montrer d'ailleurs que la distribution des témoins influe fortement sur la limite de sensibilité par l'intermédiaire du 3e terme du membre de gauche de l'éqn. (7). Cette influence pourra être réduite par l'emploi de témoins plus exacts et la multiplication d'échantillons à basses teneurs. Les mêmes analyses, effectuées avec les quatre échantillons témoins d'AG 2-3 (0.50, 0.28, 0.13 et 0.07% Fe) donnent des résultats pratiquement similaires, la limite de détection étant de l'ordre de 200 à 300 p.p.m. selon les essais effectuées.

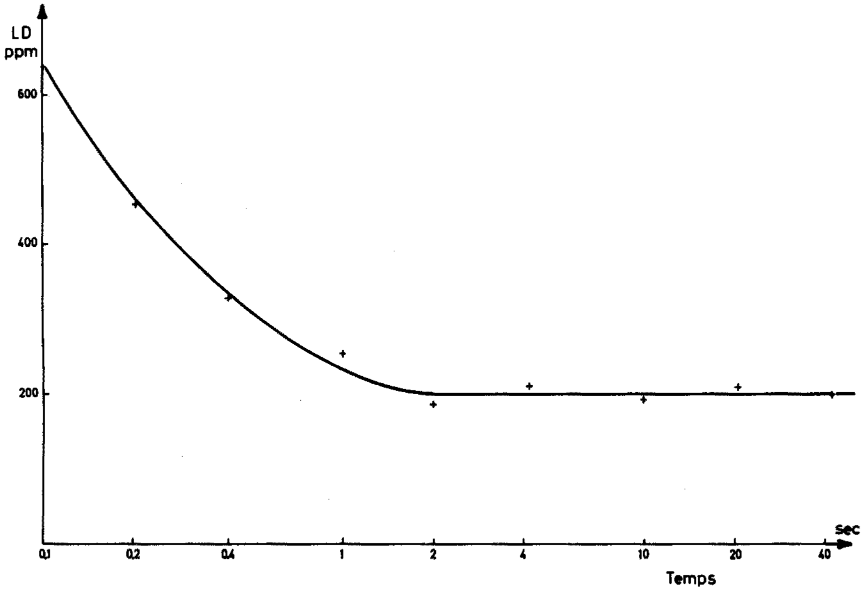

Fig. 2. Dosage de Fe dans l'aluminium (5 témoins). Limite de détection expérimentale en fonction du temps de comptage. Conditions: tube W; cristal LiF; raie Kα Fe; collimateur 160 μ; tension 40 kV; ampèrage 40 mA; compteur à flux gazeux sous vide.

Dans le cas du dosage de silicium, on se trouvait en présence d'une situation différente. On disposait, au départ, des gammes de concentration de 0.22, 0.11, 0.08, 0.04 et 0.02% de Si, pour l'Al normal, et 0.24, 0.12, 0.07 et 0.04% de Si dans l'AG 2-3.

On a représenté sur la Fig. 3 l'évolution de la limite de détection de Si en fonction du temps de comptage dans l'aluminium et les alliages AG 2-3. Comme on peut s'en rendre compte, un temps de comptage de l'ordre de 100 sec est souhaitable pour avoir une bonne sensibilité de détection. En effet, passant de 10 à 100 sec, la limite de détection est réduite d'environ un facteur 2. Ce facteur de réduction reste néanmois inférieur au facteur de réduction théorique, qui est égal à la racine carrée du rapport des temps de comptage soit 3.16. D'autre part, pour 100 sec, la limite de détection théorique est de l'ordre de 50 p.p.m., pratiquement du même ordre que la valeur expérimentalement trouvée. Cela tient en partie au fait que les témoins utilisés sont situés dans le domaine de concentration de cet ordre de grandeur et que, d'autre part, le signal émis par l'élément à doser est d'intensité relativement faible par rapport au fond continu. Par conséquent, la contribution à l'incertitude sur les déterminations provenant des fluctuations du comptage devient prépondérante, si l'on adopte un temps de comptage trop réduit, moins de 100 sec en pratique. Entre 100 et 400 sec, par contre, d'autres facteurs tels que l'instabilité de l'électronique, la dispersion autour de la droite de calibrage provenant de l'inexactitude des témoins eux-mêmes, jouent le rôle le plus important. Notons à ce propos que l'écart standard sur la pente est pour Si et un temps de 100 sec de l'ordre de 2%, alors que pour Fe il est déjà de 0.5% pour 4 sec. On remarque ici la corrélation existant entre les conditions expérimentales (appareillage, témoins, etc.) et la sensibilité et la précision d'une méthode physique d'analyse.

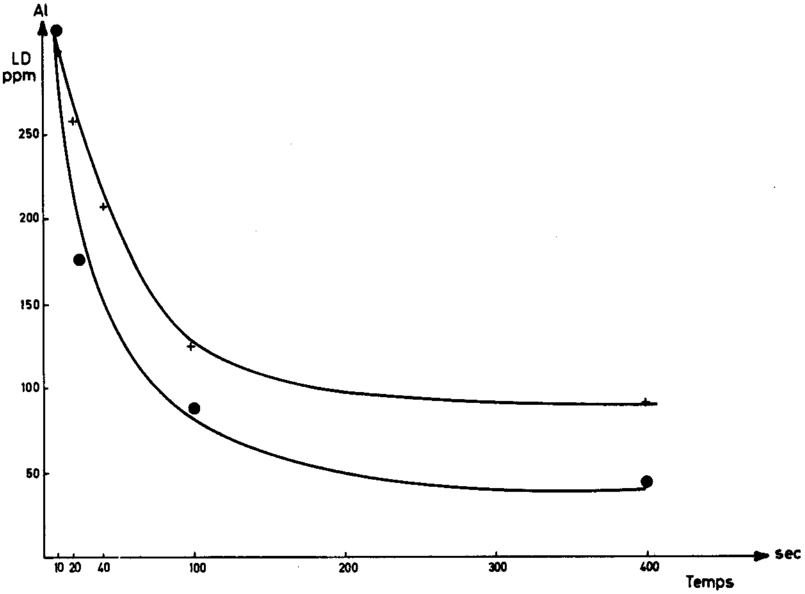

Fig. 3. Dosage de Si dans l'aluminium (+) (5 témoins) et les alliages AG 2-3 (●) (4 témoins). Limite de détection expérimentale en fonction du temps de comptage. Conditions: tube Cr; cristal EDDT; raie Kα Si; collimateur 480 μ; tension 40 kV; ampèrage 40 mA; compteur à flux gazeux sous vide.

Choix des témoins et limite de détection

Il peut arriver que l'analyste doive décider s'il veut tenter d'améliorer la sensibilité de détection, ou d'augmenter le nombre de témoins ou d'accroitre le temps de comptage.

Un exemple d'une situation de ce genre est donné par le cas du dosage de Sn dans l'acier peu allié. Utilisant Lα Sn comme raie analytique, on a regroupé 6 standards dont on disposait de 4 manières différentes, excluant chaque fois l'un d'entre eux (voir Tableau I). Toutes les autres conditions sont maintenues identiques. L'expérience a été répétée trois fois à des jours différents, afin de tenir compte autant que possible de la statistique des facteurs instrumentaux. On constate effectivement à la lecture du Tableau I, une variation non négligeable de la limite de détection d'un jour à l'autre.

TABLEAU I

DOSAGE DE Sn DANS L'ACIER. INFLUENCE DU CHOIX DES TÉMOINS SUR LA LIMITE DE DÉTECTION
(Tube W–40 kV–40 mA. Raie Lα Sn. Cristal LiF. Coll.: 160 μ. Compteur à flux gazeux sous vide)

Gamme de témoins (p.p.m.)					*Limites de détection (p.p.m.)*			*Moyenne des limites de détection*
50	90	130	430	1000	54	66	38	52 ± 14
50	90	130	220	1000	115	91	78	95 ± 18
50	220	430	660	1000	97	58	58	71 ± 22
50	90	130	660	1000	47	67	39	51 ± 14

Néanmoins le choix de la gamme de standards n'est pas complètement indifférent et en particulier la première et la dernière disposition paraissent légèrement supérieures. Une analyse de variance montre par exemple qu'il y a plus de 70% de chance que ces deux limites de détection c.à.d. 52±14 et 51±14 p.p.m. sont significativement différentes de la deuxième et que par conséquant la deuxième disposition des standards est moins conseillable. Il faudrait répéter les expériences un plus grand nombre de fois pour acquérir une certitude dans ce domaine. Dans cet exemple, on n'est pas en mesure de choisir les témoins avant leur achat. En revanche, s'il s'agit de témoins synthétiques ou d'échantillons analysés par une autre méthode, cette opération de triage est assez facilement réalisable. D'ailleurs, même si la disposition des standards n'exerce pas d'influence sur la variance résiduelle, elle en exerce une en revanche, sur la limite de détection[3].

Optimisation des conditions d'excitation en fluorescence X

Cette opération peut évidemment s'effectuer à l'aide du critère de qualité de SPIEGELBERG ET BRADENSTEIN[6]. Ce dernier est basé sur la limite de détection théorique: on choisit alors les conditions expérimentales qui donnent la valeur maxima au produit $R\sqrt{B}$ (ou R est le rapport pic sur fond et B le fond continu). Dans ce cas on aurait la limite de détection théorique minima.

Néanmoins, il est souhaitable de contrôler si l'emploi de la limite de détection calculée à partir de la variance résiduelle conduit aux mêmes conclusions. Dans ce but on a, à titre de comparaison, tracé sur la Fig. 4 les courbes montrant la relation entre la limite de détection experimentale de Si dans Al et le temps de comptage pour les tubes à anticathode de chrome et d'argent. Les témoins utilisés étaient les mêmes que précédemment, de même que les conditions expérimentales autres que les tubes excitateurs. Outre qu'ils confirment la nécessité d'utiliser un temps de comptage d'au moins 100 sec, les résultats démontrent également la supériorité du tube à anticathode de chrome par rapport à celui d'argent. Ce dernier est d'ailleurs à peine meilleur que celui à anticathode de tungstène (LD = 220 p.p.m. pour 40 sec.)

Les limites de détection théoriques pour les trois tubes et un temps de détection de 100 sec atteignent respectivement les valeurs de 150 p.p.m. pour W, 45 p.p.m. pour Ag et 40 p.p.m. pour Cr. Il semble donc qu'un autre facteur que le simple rapport pic sur fond intervienne dans le comportement de ces tubes et influe sur la sensibilité de détection de chacun. Ce facteur pourrait être une moindre stabilité du tube à anticathode d'argent, limitant la précision et la sensibilité des dosages avec ce tube.

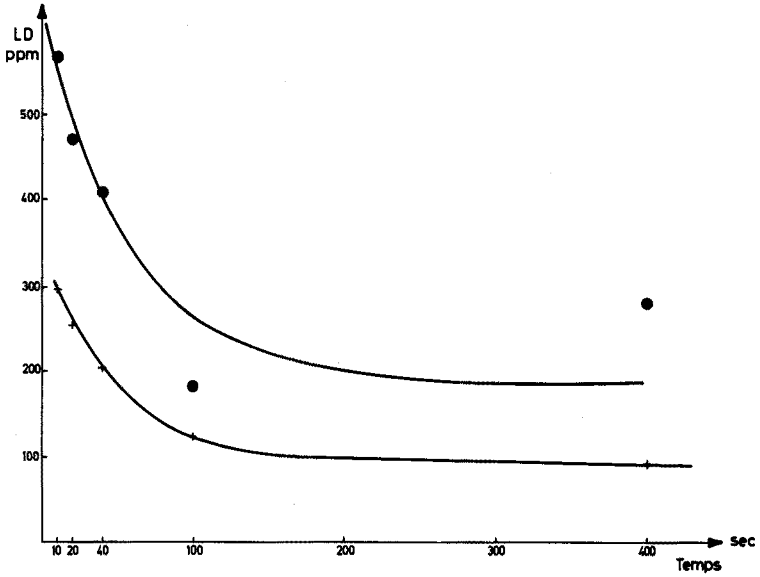

Fig. 4. Dosage de Si dans l'aluminium (5 témoins). Limite de détection expérimentale en fonction du temps de comptage pour les tubes de Cr (+) et d'Ag (●). Conditions: cristal EDDT; raie Kα Si; collimateur 480 μ; tension 40 kV; ampèrage 40 mA; compteur à flux gazeux sous vide.

Effectivement, si l'on compare les écarts types sur la pente de la droite de calibrage de Si dans Al, on obtient avec W, 2.34%, Ag 2.90% et Cr 1.44%, le temps de comptage étant de 40 sec.

On connait le rôle que joue la position relative des raies excitatrices par rapport à la discontinuité d'absorption. Toutefois, si la position relative de Kα Cr plus favorable que celle de Lα W explique le meilleur rendement du tube au chrome, pour Si, par contre bien que le tube d'Ag produise les raies L d'Ag de plus grande longueur d'onde encore, d'autres facteurs tels que l'instabilité déjà citée, ou l'influence de l'état de surface de l'échantillon paraissent réduire la sensibilité de détection.

Surface utile d'irradiation

Dans les porte-échantillons usuels, le diamètre d'échantillon que l'on peut y introduire est d'environ 30 mm. Néanmoins, il peut arriver que l'on ne dispose que d'un échantillon plus petit, ne permettant que la préparation d'un disque de diamètre inférieur, tel que la tache d'irradiation du tube à rayons X déborde de la surface utile de l'échantillon. Ce dernier est alors placé sur un masque qui intercepte une partie du rayonnement X, contribuant de la sorte au fond continu total. D'autre part, il est évident que plus réduite sera la surface irradiée, moins intense sera le rayonnement de fluorescence de l'élément à doser et par conséquent plus médiocres seront la précision et la sensibilité de détection du dosage.

A l'aide de la gamme d'échantillons témoins de Fe dans l'aluminium déjà mentionnée et en gardant toutes les autres conditions expérimentales identiques, on a étudié de quelle manière évoluait la limite de détection expérimentale de cet élément en fonction de la surface irradiée. La Fig. 5 donne une représentation graphique de cette évolution en fonction du diamètre du masque employé. On a également indiqué l'allure de la courbe intensité par unité de concentration en fonction du diamètre. On constate que, alors que la limite de sensibilité reste pratiquement inchangée jusqu'à un diamètre de 10 mm, l'intensité a déjà chuté à ce moment d'environ 75%. Ceci exprime le fait que même à ce diamètre réduit, le facteur de dispersion autour de la droite de régression introduit par les témoins demeure d'une importance telle que la sensibilité de détection n'est pratiquement pas affectée par la diminution de la taille de l'échantillon.

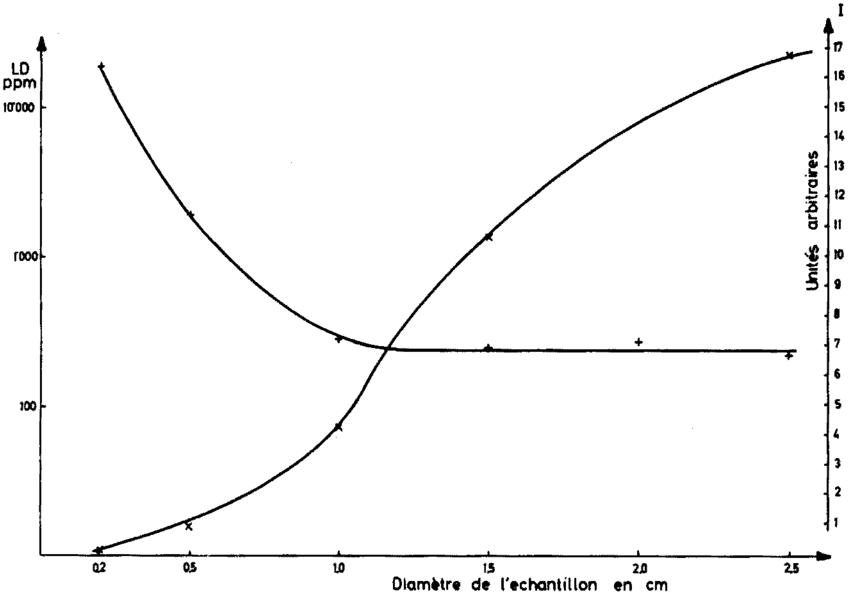

Fig. 5. Dosage de Fe dans l'aluminium (5 témoins). Limite de détection expérimentale LD (+) et intensité I (×) par unité de concentration en fonction du diamètre de l'échantillon. Conditions: tube W; cristal LiF; raie Kα Fe; collimateur 160 μ; tension 40 kV; ampèrage 40 mA; compteur à flux gazeux sous vide; temps de comptage 40 sec.

Il est certainement utile pour l'analyste de savoir à quels inconvénients, notamment la perte de sensibilité et de précision, il s'expose quand il opère sur un échantillon de taille réduite. Il faut noter que, pour le cas du dosage de Fe ici considéré, si le diamètre n'est que de 2 mm, une analyse de la variance de la régression de la droite de calibrage montre que les variables intensité de la raie analytique et concentration de l'élément à doser ne peuvent plus être considérées comme dépendantes pour un niveau de confiance de 95%. En effet si l'on compare la variance due à la régression à la variance résiduelle, leur rapport est inférieur au coefficient de Snedecor donné pour ce niveau de confiance[7].

Importance des conditions de préparation des témoins

Le dosage par fluorescence X de chlore dans une matrice hydrocarbonée est bien connu. Le manque de sensibilité de détection de cet élément ne permet toutefois guère de dépasser le p.p.m. si l'on effectue l'analyse sur l'échantillon tel quel. Or, dans le cas des polyphényles utilisés comme réfrigérants dans certains types de réacteurs, l'expérience a montré qu'il était souhaitable que la concentration de Cl ne dépasse pas un niveau de l'ordre du dixième de p.p.m.[8].

Récemment SERRINI ET LEYENDECKER[8] utilisant un chalumeau à combustion, ont mis au point une technique de récupération de traces de chlore dans les polyphényles par destruction de la partie organique. Les chlorures étant recueillis en solution aqueuse, il est possible en suivant le procédé proposé notamment par GARSKA[9] de précipiter ceux-ci sous forme d'AgCl et filtrer ce précipité sur un filtre millipore ayant un diamètre de pore de 0.3 μm. Ce filtre que l'on a eu soin de choisir d'un diamètre adéquat est ensuite exposé au rayonnement X excitateur. Dans le Tableau II on a comparé les limites de détection obtenues par cette technique et l'analyse directe. Pour cette dernière méthode, les limites de détection théorique et expérimentale sont du même ordre de grandeur, ce qui revient à dire que la sensibilité de détection est essentiellement limitée par la statistique de comptage. D'autre part on constate une différence de parfois plusieurs ordres de grandeur entre les limites de détection théorique et expérimentale pour la 2e technique. Il faut noter également que la variance résiduelle, c.à.d. la dispersion autour de la droite de calibrage est de la même importance que l'on utilise comme raie analytique Kα Cl, Lα Ag ou Kα Ag, toutes autres conditions demeurant égales. On peut interpréter ces faits expérimentaux par la nature hétérogène des dépots d'AgCl sur les filtres. Par contre le caractère stoechiométrique du précipité parait respecté et il ne semble pas qu'un excès d'Ag soit demeuré par suite d'un lavage incomplet, puisque le calibrage peut s'effectuer aussi bien à partir d'Ag que de Cl. Il est donc évident que cette hétérogénité intervient de façon prépondérante dans l'incertitude de la détermination. Par contre la statistique

TABLEAU II

DOSAGE DU CHLORE DANS UN CALOPORTEUR ORGANIQUE (THERMIQ). COMPARAISON DES SENSIBILITÉS DE DÉTECTION PAR FLUORESCENCE X POUR DEUX TECHNIQUES

Technique de dosage	*Raie analytique*	*Racine carrée de la variance résiduelle (p.p.m.)*	*Limite de détection théorique (p.p.m.)*	*Limite de détection expérimentale (p.p.m.)*
Analyse directe de l'échantillon	Kα Cl	0.93	3.43	3.92
Séparation de la matrice par calcination de la partie organique; précipitation de Cl sous forme d'AgCl filtrée sur millipore Calculs pour un échantillon de départ d'un poids de 1 g	Kα Cl	0.72	0.046	1.40
	Lα Ag	0.70	0.029	1.47
	Kα Ag	0.73	0.241	1.66

du comptage n'y contribue que de façon négligeable, puisqu'une amélioration d'un facteur 10 de la limite de détection théorique en passant de la raie analytique Kα Ag à Lα Ag ne modifie pas la limite de détection expérimentale. Il faut signaler également qu'une mesure de reproductibilité de blanc c.à.d. d'une série de filtres ayant subi le même traitement à part la précipitation d'AgCl que les standards, a donné un écart type relatif de l'ordre de 8%, bien que l'écart type sur la distribution des poids de ceux-ci ne soit que 2.5%. Notons enfin que l'emploi du dispositif faisant tourner l'échantillon n'a pas amélioré la précision des déterminations. En conclusion, la nécessité d'atteindre une limite de sensibilité de 0.1 p.p.m. environ implique un choix; si l'on veut utiliser la méthode combinant la destruction de la partie organique, suivie de précipitation et de dosage d'AgCl par fluorescence X on devra soit travailler sur une quantité élevée d'échantillon (20 g par exemple), soit réussir à réduire la dispersion de la droite de calibrage par amélioration du mode de préparation des standards.

DISCUSSION ET CONCLUSION

Les quelques exemples qui précèdent montrent l'intérèt de l'utilisation du calcul statistique en analyse par fluorescence X. Son application pratique a été rendue plus aisée par la préparation d'un programme de calcul qui donne un certain nombre de paramètres statistiques de la droite de régression: variances de la régression et résiduelle, écart type de la pente de la droite de calibrage, etc. Les avantages dérivant de l'emploi du calcul statistique en analyse sont bien connus, mais jusqu'à présent le caractère laborieux de ce genre de calcul en avait limité l'utilisation. Il est certain que l'emploi croissant des ordinateurs et calculatrices, doit permettre de serrer de plus près les conditions optima de travail et de comparer plus fréquemment entre elles les techniques et méthodes analytiques.

Tout ceci démontre l'importance en fluorescence X de deux facteurs, en vue d'obtenir des déterminations analytiques précises et sensibles: la préparation de témoins de grande exactitude et l'emploi d'appareillages dotés de bonnes qualités de stabilité. Un progrès dans ces deux directions ne peut que contribuer à améliorer les sensibilités de détection propres à cette technique.

L'auteur exprime ses remerciements à W. De Spiegeleer, pour l'exécution des mesures, à W. Leyendecker et G. Serrini pour la collaboration dans la préparation des échantillons et à A. Hubaux pour la revue critique de ce manuscrit.

RÉSUMÉ

Dans le cas d'un étalonnage linéaire pour une analyse par fluorescence X, les méthodes de calcul par régression, donnent la possibilité de répondre à différentes questions: choix objectif du temps de comptage, influence de la grandeur de la surface irradiée sur la précision du dosage, sensibilité de détection expérimentale et théorique, etc. Différents paramètres statistiques (variances de régression résiduelle, écart type de la pente de la droite de calibrage) ont été calculés pour un certain nombre d'exemples types: dosage de Fe et Si dans l'aluminium, de Cl dans les substances organiques, et de Sn dans l'acier peu allié en faisant varier les conditions expérimentales. Les résultats permettent soit de réduire notablement le temps de comptage (cas de Fe

dans Al), soit encore de choisir sans équivoque le tube excitateur (cas de Si dans Al) et mettent en évidence l'importance de la qualité des échantillons.

SUMMARY

In the case of linear calibration curves for X-ray fluorescence analysis, regression calculation methods make it possible to establish the most appropriate counting time, the influence of the magnitude of the irradiated surface on the accuracy of the determination, and the experimental and theoretical detection limits. Different statistical parameters were calculated for a certain number of typical examples: determination of iron and silicon in aluminum, of chlorine in organics, and of tin in low alloyed steel for various experimental conditions. The results enabled the counting time to be greatly reduced for iron in aluminum, and the excitation X-ray tube to be selected without doubt for silicon in aluminum; the importance of the quality of the standards is emphasized.

ZUSAMMENFASSUNG

Bei der Röntgenfluoreszenzanalyse ist es im Falle von linearen Eichkurven durch Methoden der Regressionsrechnung möglich, die geeignetste Zähldauer, den Einfluss der Grösse der bestrahlten Oberfläche auf die Genauigkeit der Bestimmung und die experimentellen und theoretischen Nachweisgrenzen festzustellen. Verschiedene statistische Parameter wurden für eine Auswahl von typischen Beispielen berechnet: Bestimmung von Eisen und Silicium in Aluminium, Chlor in organischen Substanzen und Zinn in niedriglegiertem Stahl für verschiedene experimentelle Bedingungen. Auf Grund der Ergebnisse kann die Zähldauer im Falle von Eisen in Aluminium beträchtlich reduziert und im Falle von Silicium in Aluminium die anregende Röntgenröhre eindeutig festgelegt werden; die Bedeutung der Art der Standardproben wird besonders hervorgehoben.

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Short Communications

Some preliminary studies concerning the analytical potentialities of an augmented diffusion flame

A major problem with atomic spectroscopic methods of analysis is the conversion of the sample solution into an atomic vapour. Usually the presence of oxygen in most flames is the limiting factor because of the formation of refractory oxides of many elements. Plasmas appear to offer some advantages and hence their use as atom reservoirs in analytical spectroscopy is of considerable interest. Those types which have found most application in analytical chemistry are based on the d.c. arc plasma jet[1] and the radio-frequency (r.f.) coupled plasma[2].

Some of our previous studies concerning the use of flames of atomic hydrogen[3] as a means of increasing the temperature of what would otherwise have been a cool hydrogen diffusion flame[4] showed promise and hence the r.f. coupled or augmented hydrogen diffusion flame described here was also investigated. Essentially the plasma production involves the coupling of a hydrogen diffusion flame to an r.f. field generated inside the tank coil of an r.f. oscillator valve. Once the r.f. power is coupled to the flame gases an increase in bulk enthalpy takes place and the effective temperature increases considerably.

Experimental

The plasma cell design (Fig. 1) consists of a standard Unicam burner stem and circular acetylene emission head. This arrangement was used in conjunction with conventional nebuliser units utilising argon (*ca.* 15 psi) as nebulising gas and a hydrogen flow rate sufficient to give a steady diffusion flame. The Radyne SC15 plasma generator unit was used to provide r.f. power (at 36 MHz) up to 2.5 kW. Various flames were studied initially and all were found to be capable of coupling the r.f. power when seeded with a 0.1 *M* solution of potassium chloride which provided sufficient ions to initiate and carry the discharge. It was found that a quartz sheath was necessary to shield the r.f. copper coil from the resulting plasma to prevent the r.f. current from shorting between the turns of the coil. It was also found necessary to use a stabilising electrode which was best attached to the burner head and held at ground potential (Fig. 1). With this arrangement a stable plume of plasma some 8 cm in length and 1 cm in diameter was observed emanating from the tip of the 1-mm diameter tungsten electrode stabiliser. R.f. power inputs as low as 0.5 kW were capable of producing a stable plasma.

The suitability of a number of stabilising electrode materials was investigated, but most fused, melted in the plasma and yielded an emission spectrum characteristic of the electrode material. Carbon was effective in producing a stable discharge, but gave a high background radiation. Tungsten, however, showed little background emission and relatively little burn-up. Under those conditions the background radiation produced in the tail flame (*ca.* 2 cm above the copper coil) showed a region of continuum with a maximum at 550 nm over the spectral range 450–650 nm which corresponds to the NO+O reaction. The only emission observed in the ultraviolet

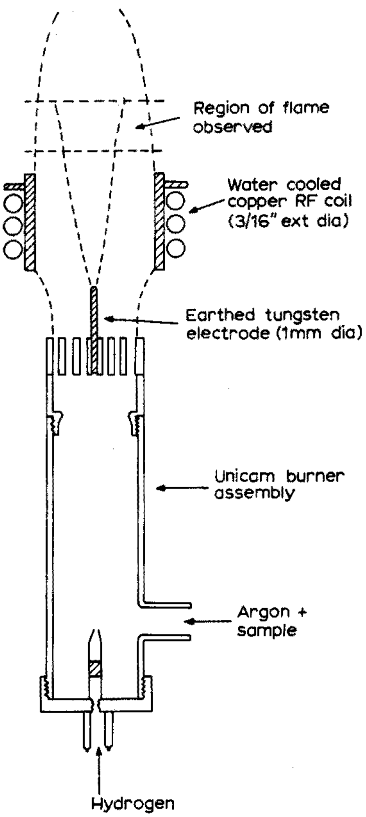

Fig. 1. Diagram of plasma cell.

TABLE I

EMISSION FROM VARIOUS METAL ION SOLUTIONS[a]

Element	*Wavelength*	*Emission signals (μA)*[b]		
(200 p.p.m.)	*(nm)*	*A/H_2*	*r.f. coupled A/H_2*	*Air/H_2*
Li	670.8	0.84	91.0	1.00
	610.4	0.20	190	0.40
Ca	422.7	0.00	16.0	0.00
Sr	460.7	0.00	183	0.00
	483.2	0.00	6.00	0.00
Ba	553.5	0.06	42.0	0.80
Hg	546.1	0.00	24.0	0.00
	253.7	0.00	1.20	0.00
Zn	334.5	0.00	2.30	0.01
	213.9	0.00	1.20	0.00
Na[c]	589.0	3.10	140	14.0
	589.6			
Cs[c]	455.5	0.02	5.00	1.50
	459.3			

[a] Measurements made with a modified Beckman DU spectrophotometer with 900 V EHT applied to an EMI 9601B photomultiplier with slit width of 0.4 mm. All aqueous solutions were 200 p.p.m. in metal ion and 0.1 *M* in potassium chloride. All emission intensities were corrected for background radiation. An r.f. power of 1.5 kW was coupled to the diffusion flame.

[b] The minimum measurable signal with the system used was 0.005 μA.

[c] Unresolved spectral lines.

region was due to OH-band emission at *ca.* 280 nm and 310 nm, which was some 40 times less intense than that observed in a typical pre-mixed air–hydrogen flame; no tungsten lines were observed in this region of the plasma although strong emission was observed from the potassium resonance lines at 404.0 nm and 404.7 nm. The glare produced at the electrode tip was shielded from the view of the spectrophotometer.

In these preliminary studies, the thermal emission intensities thus obtained were compared with those observed in the non-augmented diffusion flame and a typical pre-mixed air–hydrogen flame burning on the same burner assembly for several metal ion solutions (Table I).

The r.f. coupled diffusion flame described is relatively easy to operate and maintain and appears to exhibit little background radiation in the ultraviolet region of the spectrum. These observations and the results in Table I indicate that the augmented flame may be of some application in analytical emission spectroscopy.

The r.f. power coupled to the flame and the gas flow rates used may be varied over a wide range without significantly affecting the plasma obtained. In our experience these parameters are less variable with the conventional argon plasma (obtained using a Radyne SC15 generator) which requires a minimum r.f. power of *ca.* 2.5 kW to produce a stable discharge. Moreover, a conventional argon plasma is not always able to provide sufficient thermal energy to vaporise solid particles which then pass through the plasma region without significant excitation occurring; analyses of powdered samples can therefore present serious problems. A further difficulty encountered with low-powered argon plasmas is continuous operation whilst nebulising aqueous solutions. All of these problems may be reduced using the augmented flame described.

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Chemistry Department,
Imperial College,
London, S.W.7 (England)

K. M. ALDOUS
R. M. DAGNALL
L. C. EBDON
T. S. WEST

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Determination of silicon in plutonium metal by differential linear-sweep oscillographic polarography*

The polarography of silicon was first reported by DE SESA AND ROGERS[1], who reduced the yellow silicomolybdate complex and used ammonium nitrate as the electrolyte. GRASSHOFF AND HAHN[2] investigated the polarography of the yellow silicomolybdate complex more thoroughly in a citrate buffer at pH 2. The polarographic behavior of the reduced silicomolybdate at pH greater than 7 was investigated by SEN AND CHATTERJEE[3].

Silicon has been determined in plutonium and plutonium alloys by a modified gravimetric procedure following a perchloric acid dehydration separation[4]. PIETRI AND WENZEL used a cation-exchange separation and a spectrographic procedure to determine silicon in plutonium[5]. Silicon has also been determined in plutonium by spectrophotometry[6,7] and by atomic absorption spectrophotometry[8].

This paper reports a polarographic method for the determination of silicon in plutonium metal, based on reduction of the yellow silicomolybdate complex in a citrate buffered medium at pH 1.5.

Apparatus

A Davis Differential Cathode Ray Polarotrace, Type A–1660 (Southern Analytical, Ltd., Camberley, England) equipped with an electrode stand and a constant temperature bath, was used. This instrument has a voltage sweep rate of 0.25 V sec^{-1}, a sweep time of 2 sec, and a delay period of 5 sec. All polarographic measurements were made at 30°. A polarographic cell with a mercury pool anode was used throughout the investigation. The differential mode of operation was used with the second cell containing a reagent blank.

Dual 15-cm long capillaries were used to obtain all measurements. The $m^{\frac{2}{3}}\,t^{\frac{1}{6}}$ value, obtained at 0 V *vs.* mercury pool in a blank solution, was 1.08.

The pH values of the solutions were measured with a Beckman Model 76 Expanded Scale pH meter and a glass electrode. The pH was adjusted with hydrochloric acid or ammonia solution.

The distilling apparatus used for the volatilization of the silicon tetrafluoride was the same as described by HOLT[9] except that a graduated 50-ml polypropylene beaker (Sherwood Medical Industries, Bridgeton, Mo., U.S.A.) with a hollowed-out, 3.5-cm Teflon cap was used in place of the 15-dram plastic vial.

Reagents

The silicon standards were prepared by diluting a Chemtram (Bio-Rad Laboratories, U.S.A.) silica ionic standard to the desired concentration.

The citric acid electrolyte was prepared by dissolving 6.431 g of citric acid monohydrate in 61.2 ml of 1 *M* sodium hydroxide and diluting to 306 ml with water; 77 ml of 1 *M* hydrochloric acid and 40 ml of methyl ethyl ketone were then added and this mixture was diluted to 1 l with water.

Ammonium molybdate soln.: prepared by dissolving 10 g $(NH_4)_6MO_7O_{24}\cdot 4H_2O$

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in water and diluting to 100 ml. The hydrofluoric–nitric acid mixture was prepared by combining 5 ml of hydrofluoric acid (48%) with 25 ml of concentrated nitric acid.

All other chemicals were reagent grade and prepared in the usual manner. Purified nitrogen was used to deaerate the test solutions.

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

Procedure for sample preparation

A weight of plutonium metal was selected so that 25–100 µg of silicon were present, and this was dissolved in the platinum distilling vessel with 6 *M* perchloric acid. After the metal had completely dissolved, the distilling vessel was closed, a vacuum hose was attached to the distilling arm of the vessel, and vacuum was applied. A 150–260° heat gun was used to heat the vessel. The temperature of the vessel was gradually increased to 215–220° over a 30–33 min period. The vessel was cooled for *ca.* 2 min. While the vessel was cooling an absorbing solution was prepared by transferring 2.5 ml of a saturated boric acid solution to a 50-ml polypropylene beaker followed by 0.5 ml of the ammonium molybdate solution. The vacuum hose was detached from the distilling vessel and attached to the outlet side of the beaker cap. The polypropylene beaker was attached to the distilling arm of the distilling vessel and vacuum was applied. Hydrofluoric–nitric acid mixture (0.3 ml) was added, and the sample was distilled for 10 min at 245–250°. The beaker was cooled for 2 min and then removed from the distilling arm of the distilling vessel. The pH of the solution was adjusted to *ca.* 1.4, and permitted to come to equilibrium. After 10 min the pH of the solution was readjusted to 1.5, and the solution was transferred to a 25-ml volumetric flask and diluted to volume with a hydrochloric acid wash solution (pH 1.5). The solution was permitted to stand overnight. A 1-ml aliquot of the solution was then transferred to a 5-ml volumetric flask, and diluted to volume with the electrolyte solution.

The 5-ml solution was transferred to the electrolysis cell, and the solution was purged of oxygen by passing purified nitrogen gas for 15 min. The peak current was read at −0.40 V *vs.* Hg pool.

Calibration curve

A calibration curve for silicon was prepared by transferring an appropriate portion of a silicon solution into the platinum distilling vessel containing 5 ml of 6 *M* perchloric acid, and following the procedure described above. Thirty silicon solutions of six different concentrations were prepared and polarographed. The mean results are given in Table I and show that the peak current is proportional to the silicon concentration. The relative standard deviation for all polarograms at all concentrations was 9.3%.

Results and discussion

An investigation of the effect of pH on the peak current was made using solutions which contained 0.374 µg Si/ml. The procedure was the same as described above except that the pH was adjusted to the desired value after the solution had been first brought to pH 1.4. The transfer and diluting solutions were hydrochloric acid at the same pH as the desired pH. The influence of the pH on the peak current is apparent if the peak current is plotted against the pH (Fig. 1). Below pH 1.4 the peak current increases as the pH increases. In the pH range 1.4–1.9 the peak current is constant, but above pH 1.9 the peak current increases in a very erratic manner.

TABLE I

PEAK CURRENT AS A FUNCTION OF THE SILICON CONCENTRATION

Si concn. (μg/ml)	i_p *(μA)*	i_p*/Si concn. (μA/μg/ml)*
0.19	0.58	3.05
0.28	0.84	3.00
0.37	1.13	3.06
0.47	1.49	3.17
0.56	1.72	3.07
0.75	2.28	3.04

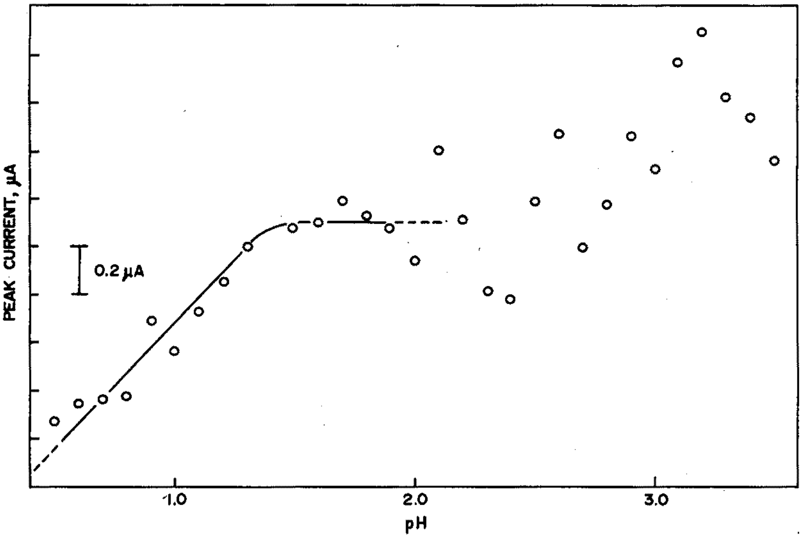

Fig. 1. Variation of peak current with pH. 0.374 μg Si/ml. 0.04% $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. 8 ml buffer solution.

Investigation of impurities. Twenty-two impurities commonly found in plutonium metal were investigated to determine their effect on the silicon determination. The results are shown in Table II. The ratio of the impurity ion to the silicon is at the maximum ratio normally found in plutonium metal. The ratio of the impurities to silicon should normally be low enough that there will be no interference. If the ratio of the impurities of cadmium, chromium, copper, iron, lead, nickel should be too great, these impurities can be removed by electrolysis in a semi-micro electrolysis cell[10]. If molybdenum and titanium[11] ratios are too great, these elements may be separated from silicon by means of anion-exchange resin.

TABLE II

INVESTIGATION OF IMPURITIES

Ion added	*Weight ratio ion/Si*	*Error in recovery of Si (%)*	*Ion added*	*Weight ratio ion/Si*	*Error in recovery of Si (%)*
Ag	0.1:1	[a]	K	0.5:1	22
Al	10:1	−25		0.2:1	[a]
	2.5:1	[a]	Mg	4:1	[a]
Ba	0.4:1	−30	Mn(II)	0.6:1	[a,b]
	0.2:1	[a]	Mo(VI)	0.8:1	[a]
BO_3^{3-}	0.4:1	[a]	Ni	20:1	16
Ca	0.8:1	−37		2.5:1	[a]
	0.4:1	[a]	Pb	4:1	−21[b]
Cd	0.2:1	[a]		0.5:1	[a,b]
			Sb(III)	0.2:1	[a]
Cr(III)	16:1	13[b]	Sn(II)	0.2:1	[a]
	8:1	[a,b]	Sr	0.2:1	[a]
Cu(II)	1:1	[a]	Ti	2:1	[a,b]
Fe(III)	16:1	[a]	U(VI)	2:1	[a]
Ga(III)	3:1	[a]	Zn	2:1	[a]

[a] Error $< \pm 10\%$ is regarded as tolerable and is indicated as zero.
[b] Precipitate formed.

Analysis of standard silicon solutions. Twenty silicon solutions covering the range of 0.20–0.75 μg of silicon per ml were analyzed as described above, except that plutonium was absent. The recovery was 97.3–103.9% with an average of 99.8%.

Recovery of silicon in the presence of plutonium. The effect of plutonium on the determination of silicon was examined by spiking plutonium solutions with standard silicon solutions. Fifteen solutions containing 0.5–1.0 g of plutonium were spiked so that the final silicon concentration ranged from 0.20 to 0.75 μg/ml. These solutions were taken through the sample preparation procedure and analyzed. The recovery ranged from 94.5 to 103.9% with an average of 99.4%.

Chemistry Research and Development,
The Dow Chemical Company,
Rocky Flats Division,
Golden, Colo. 80401 (U.S.A.)

C. E. Plock
J. Vasquez

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The determination of lead in silicate rocks by atomic absorption spectrophotometry with long-path absorption tubes

Atomic absorption spectrophotometry is a well established method for the determination of lead in various materials, because it is almost free of interference effects. DAGNALL AND WEST[1] when investigating the effect of about 50 elements, found only slight interferences due to "mechanical sequestration" by aluminum, thorium, phosphate and silicate anions besides those precipitating lead ions. The application of atomic absorption spectrophotometry to the analysis of silicate rocks is, therefore, limited rather by the limit of detection of the method than by other factors.

The Clark value of lead in the earth crust is about 16 p.p.m.[2]; among igneous rocks it is somewhat higher in granites (30 p.p.m.) than in basic rocks. The lowest contents have been reported for gabbras (around 5 p.p.m.). Compared to these values, 0.5 p.p.m. of lead is needed in a pure aqueous solution for 1% absorption. The detection limit reported for a Perkin-Elmer 303 spectrophotometer with a hydrogen–air flame and a three-slot burner is 0.02 p.p.m.[3]. If interferences are ignored this should allow the determination of about 2 p.p.m. Pb in solid samples. With the sample boat technique the reported detection limit is considerably better, namely, 0.001 p.p.m. Pb[4]. However, no thorough investigations on interference effects have so far been made and the precision of the technique still leaves much to be desired.

Because lead is a volatile element with a relatively easily dissociating oxide ($D_{\mathrm{PbO}} = 90$ kcal/mol), its degree of atomisation stays high even in cooler hydrogen–air flames as well as in those parts of the flame which are rich in oxygen. This is evident from absorption profiles of free burning flames[5] as well as from absorption profiles in long-path absorption tubes[6,7]. With this device it should therefore be possible to improve the detection limit considerably. The crucial point is obviously whether the improvement in sensitivity is not outweighed by the effect of increased background absorption caused by accompanying species in the silicate rock.

Experimental

Apparatus. The apparatus used has been described in detail previously[8]. A hydrogen–air flame from a Beckman burner is directed into a tube made from low reflecting opaque fused silica with an inner diameter of 12 mm. A neon-filled hollow-cathode lamp was used instead of the earlier argon-filled one. The line Pb 2170 Å provided a sensitivity 10 times better than that obtained with the Pb 2833 Å line. For measurements of background absorption, a hydrogen arc lamp was used.

The electric furnace is switched on, and after 30 min the measurements are started with the air and fuel flows set to values to give a fuel-rich mixture in the tube[9].

Standard solutions. A lead stock solution is prepared by dissolving metallic lead in nitric acid. From this stock solution, standards covering the range 0.01–0.5 p.p.m. Pb are prepared by dilution with 1:10 hydrochloric acid. The analytical curve is linear in the whole range.

Recommended procedure. Decompose 0.5–1 g sample by treatment with hydrofluoric and perchloric acids. After evaporation to dryness, dissolve the residue in dilute hydrochloric acid and transfer to a 50-ml volumetric flask; dilute to the mark with 1:10 hydrochloric acid. From this stock solution, pipette an aliquot containing 0.1–10 µg Pb into a 25-ml flask and dilute to the mark with 1:10 hydrochloric acid. This solution is ready for measurement.

Correct the absorbance values of the samples for background absorption by subtracting the absorbance read at the Pb 2203 Å line.

Results and discussion.

Relatively good "sensitivity" values for 1% absorption have been reported by different authors. Thus, ŠTUPAR[6] found 0.03 p.p.m., RAZUMOV *et al.*[10] 0.015 p.p.m., KOIRTYOHANN AND FELDMAN[11] with an oxygen–hydrogen flame, 0.02 p.p.m. With the present device and an air–hydrogen flame, a value of 0.005 p.p.m. Pb was found for 1% absorption.

Background absorption. At the short wavelength of the lead line, background absorption caused by other elements present in the sprayed solution may be particularly severe. BILLINGS[12], using a propane–air flame, found rather high background absorption caused by calcium, magnesium, iron, potassium and sodium. However, in the present work, when these elements, as well as aluminum and titanium, were investigated in diluted hydrochloric and nitric acid solutions, it was found that the background absorption was not serious. In all cases, it could be corrected by subtracting the background absorption measured on the non-absorbing line Pb(II) 2203.5 Å, as the background is practically constant in the spectral region between the two lines. The sulphate ion, which causes severe background absorption, is generally not present in the samples in sufficiently high concentration. Corrections for background absorption as applied for samples are shown in Table I.

Another possible source of error could be the occlusion of lead atoms in unevaporated particles of the sample concomitants. On synthetic solutions it was found that there was no blocking effect by calcium, aluminum, iron and titanium, up to concen-

TABLE I

BACKGROUND CORRECTIONS FOR DIFFERENT SAMPLE DILUTIONS

Sample no.	*g of sample per 25 ml of final solution*	*Absorbance*		*p.p.m. Pb in sample found*
		Pb 2170 Å	*Pb 2230 Å*	
5013	0.1	0.082	0.013	21
	0.06	0.055	0.008	23
5014	0.1	0.098	0.013	26
	0.06	0.072	0.009	31
5016	0.1	0.97	0.011	27
	0.06	0.061	0.008	27
5017	0.1	0.044	0.008	11
	0.06	0.028	0.005	11
5020	0.1	0.210	0.025	57
	0.06	0.123	0.015	56
	0.05	0.101	0.014	54
G-1	0.1	0.153	0.023	50
	0.06	0.114	0.015	51
668	0.05	0.155	0.013	83
	0.03	0.095	0.008	83
745	0.05	0.153	0.012	85
	0.025	0.081	0.010	88

trations of 5000 p.p.m., 1000 p.p.m., 1000 p.p.m. and 1000 p.p.m., respectively, in the solution, either separately or in combination. A further confirmation that no such effect occurred is given by the comparison of results evaluated from the analytical curve and by the addition methods (see Table II).

TABLE II

COMPARISON OF RESULTS EVALUATED BY ANALYTICAL CURVE AND ADDITION METHODS

Sample	*Analytical curve (p.p.m.)*	*By addition (p.p.m.)*	*By X-ray fluorescence (p.p.m.)*
5013 glauconitic sandstone	22	21	20
5014 glauconitic sandstone	28	27	26
5016 sandstone	27	24	26
5017 sandstone	12	14	10
5020 claystone	54	47	50
5021 schist	73	71	69

TABLE III

RESULTS FOR STANDARD ROCK SAMPLES

Sample	*This method (%)*	*Recommended value (%)*
G-1	0.0050	0.0050[13]
W-1	0.00088	<0.001
T-1	0.0036	0.0037
Basalt ZGI	0.0014	0.0011[14]
Shale ZGI	0.0010	0.0009
Granite ZGI	0.0039	0.0030

Precision and accuracy. The precision of the method was estimated from repeated decomposition and measurement of one sample containing 0.0054 % lead; different aliquots of the sample were used in the final solution measured. The coefficient of variation calculated from ten such determinations was 6.4%.

The accuracy was checked by analysing the standard rock samples G-1 and W-1 prepared by the U.S. Geological Survey and those prepared by the Zentrales Geologisches Institut in Berlin. From the results in Table III, the method seems reasonably accurate.

Geological Survey,
Kostelní 26,
Prague 7 (Czechoslovakia)

Bedřich Moldan
Ivan Rubeška
Miroslav Mikšovský

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Determination of ammonium and potassium in plutonium(VI) salts by an ion exchange–tetraphenylborate method*

The determination of macro amounts (1–10%) of ammonium and potassium ions in polyplutonates was needed to determine the composition of two new plutonium salts. A combined ion exchange–tetraphenylboron method was therefore developed.

Sodium tetraphenylboron, $NaB(C_6H_5)_4$, one of the newer salt-forming organic precipitants, was first introduced in 1949[1-3]. It precipitates potassium, ammonium and substituted ammonium ions, and many precipitation conditions and applications have been made[4,5], including instrumental applications[6]. None of the tetraphenylborate methods has been specifically applied to the determination of ammonium and potassium in plutonium compounds. Plutonium was separated before the tetraphenylboron precipitation by an ion-exchange method developed by Hayden[7] from current literature[8,9]. The plutonium as the anionic chloride complex is effectively absorbed by the resin while the ammonium and potassium ions are not. The tetraphenylboron precipitation technique of Sporek and Williams[4] was used.

Apparatus and reagents

Sodium tetraphenylboron solution. A 2%(w/v) sodium tetraphenylboron (Fisher) solution (filtered) in 0.01 *M* sodium hydroxide was prepared fresh daily and cooled to 0° before use.

Wash solution. A saturated solution of ammonium and potassium tetraphenylboron was prepared daily, cooled to 0° and filtered before use.

Standards. Baker reagent-grade ammonium and potassium chloride solutions (50 mg/ml) were prepared.

Dowex 1 anion-exchange resin was used in the separation.

Procedure

The ammonium content in the ammonium-containing plutonyl salts usually averaged about 1%, hence 200–300 mg samples were the minimum possible. The potassium in the potassium plutonyl salts varied between 5 and 10%, and 100-mg cuts were usually made. Both salts were treated as follows.

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

Dissolve an aliquot in 5–10 ml of concentrated hydrochloric acid and pass through 5 ml of Dowex 1 resin pretreated with this acid. Rinse the resin with about 30 ml of concentrated hydrochloric acid and evaporate the combined effluent and wash in an Erlenmeyer flask to 2–6 ml. Add 50 ml of chilled water to the cooled solution, and place the flask in an ice bath. Add 25 ml of 2% sodium tetraphenylboron reagent to the 50-ml sample solution and swirl for several minutes in the ice-bath. Finally, filter the precipitate on a 30-ml, medium-porosity, sintered-glass crucible. Wash three times with 10-ml volumes of wash solution and vacuum-dry at 28–30° overnight.

Results and discussion

Low ammonium results from standards were found when less than 75 ml of 1% tetraphenylboron solution was used for *ca.* 33 mg of ammonium ion. Therefore, the established lower limit was *ca.* 20 mg of ammonium per 25 ml of 2% sodium tetraphenylboron. No upper limit was established. The limit of 50 mg of potassium per 25 ml of 2% sodium tetraphenylboron reported by SPOREK AND WILLIAMS[4] was found satisfactory.

Although in established procedures the potassium tetraphenylboron precipitate is dried at 110–120° (tetraphenylboron salts of ammonium are stable to 130°)[10], vacuum drying at 28–30° was preferred and was found to give identical results.

SPOREK AND WILLIAMS[4] found that a readily filterable form of potassium tetraphenylboron is obtained when the final acidity concentration is above 0.2 *M*; they also varied the acidity up to 0.66 *M* with identical results. The effect of final acid concentration (0.40–1.6 *M*) on ammonium recovery was investigated in the present

TABLE I

RECOVERY OF AMMONIUM AT THE 16-mg LEVEL AND POTASSIUM AT THE 39-mg LEVEL

NH_4^+ taken (mg)	*No. of detns.*	*NH_4^+ found Mean (mg)*	*Av. error (%)*	*K^+ taken (mg)*	*No. of detns.*	*K^+ found Mean (mg)*	*Av error (%)*
16.7	1	16.6	−0.60	39.0[a]	4	39.0	±0.13
17.1	1	17.2	+0.59	39.0	1	39.5	+1.3
15.9[a]	4	15.95	±0.03				
15.9	6	15.90	±1.48				

[a] Not through column.

TABLE II

PRECISION STUDY: FIVE SEPARATE WEIGHINGS OF TWO DIFFERENT PLUTONIUM SALTS

	% NH_4^+	% K^+
	0.535	5.15
	0.543	5.28
	0.638	5.17
	0.546	5.15
	0.582	5.12
Std. dev.	±0.043	±0.062
Rel. std. dev. (%)	7.51	1.20

work. The ammonium ion results were found to be higher when the acidity was above 0.80 *M*; therefore the range used was 0.25–0.70 *M*. This acidity margin is reasonable for estimating the 2–6 ml volume after reducing the larger volume by boiling.

Recovery of standards. Table I contains the results of ammonium and potassium standards run with samples. The average recovery with the standards was within 1.5%.

Precision study. Five different aliquots of two plutonyl salts, containing ammonium and potassium respectively, were analyzed (Table II). The precision for the ammonium and potassium contents were 7.51 and 1.20% respectively. The analyses of the salts were in agreement with their reported stoichiometry.

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Dow Chemical Company,
Rocky Flats Division,
P.O. Box 888,
Golden, Colo. 80401 (U.S.A.)

JAMES D. NAVRATIL

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Mixed ligand chelates of copper(II) with 8-quinolinol and arylhydroxycarboxylic acids

Part IV. Electronic absorption spectra of copper(II) chelates with 5-halogeno-8-quinolinols and arylhydroxycarboxylic acids*

Copper(II) forms 1:1:1 chelates with 5-halogeno-8-quinolinolate anions and some arylhydroxycarboxylate anions[1-3]. The electronic spectroscopy of these compounds is of interest because of their unusual compositions and their possible complication of spectrophotometric analyses and other analytical procedures.

It has been stated that a metal ion in a solution containing two or more different ligands will be chelated in such a way as to distribute itself among the different ligands in a manner consistent with the dissociation constants of the ligands and the stability constants of the chelates with each ligand[4,5]. For example, in a neutral solution containing equal amounts of 8-quinolinol and salicylic acid, a small amount of copper should be chelated by 8-quinolinolate in preference to salicylate by a factor of 200,000:1. This means that 8-quinolinol should be quantitatively separable from salicylic acid under these conditions. In fact, it is found that these conditions greatly favor the formation of the mixed ligand chelate so that separation of 8-quinolinol from salicylic acid by chelation with copper cannot be carried out in aqueous solution. The formation constant of the mixed chelate must also be known if calculations of species distributions in such multicomponent systems are to have any validity.

This study is concerned with the absorption spectra in pyridine and in chloroform of eight mixed chelates of the type CuL_1L_2, where L_1 was either 3,5-diiodosalicylate or 4-bromo-3-hydroxy-2-naphthoate, and L_2 either 5-fluoro-, 5-chloro-, 5-bromo-, or 5-iodo-8-quinolinolate.

Experimental

The preparation and purity of the mixed chelates have been previously reported[3]. Spectro-quality pyridine and chloroform (Matheson, Coleman, and Bell, New Jersey) were used. Spectra were taken on a Cary Model 15 recording spectrophotometer with 1-cm silica cells.

Absorbance spectra were obtained on $1.00 \cdot 10^{-4}$ *M* solutions of the chelates in pyridine. That these types of compounds are stable in this solvent was established polarographically[6]. Because of the low solubilities of the mixed chelates in chloroform, only saturated solutions were employed. Consequently, molar absorptivities and *d–d* spectra were not recorded in chloroform.

Results and discussion

The band maxima of the electronic absorption spectra of the mixed ligand chelates in pyridine and chloroform are presented in Table I.

The electronic absorption spectra of the 5-halogeno-8-quinolinols and of their copper(II) bis-chelates[7] and of the arylhydroxycarboxylic acids and their copper(II) bis-chelates[6] have been studied. The pH dependences of the 5-halogeno-8-quinolinol spectra and their red shifting upon chelation with copper(II) indicate strong charge-

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TABLE I

ELECTRONIC ABSORPTION SPECTRA OF THE MIXED CHELATES CuL_1L_2 IN PYRIDINE OR CHLOROFORM

L_1[a]	L_2[b]	*Pyridine media*					*Chloroform media*	
		$\bar{\nu}(d\text{-}d)$ (cm^{-1})	$\bar{\nu}_A$ (cm^{-1})	$\log \varepsilon_A$	$\bar{\nu}_B$ (cm^{-1})	$\log \varepsilon_B$	$\bar{\nu}_A$ (cm^{-1})	$\bar{\nu}_B$ (cm^{-1})
A	Fluoro	14,810	23,400	3.54	28,660	3.90	23,500	29,000
A	Chloro	14,700	23,600	3.67	28,890	3.88	23,300	28,900
A	Bromo	14,560	23,710	3.65	28,910	3.82	23,300	29,000
A	Iodo	14,770	24,800	3.62	29,190	3.87	24,250	29,250
B	Fluoro	14,600	24,900	3.60	28,530	3.76	23,600	29,000
B	Chloro	14,780	24,620	3.68	28,700	3.62	23,400	28,900
B	Bromo	14,680	24,620	3.68	28,800	3.66	23,500	28,900
B	Iodo	14,760	24,990	3.69	29,190	3.78	25,920	29,250

[a] A = 3,5-diiodosalicylate; B = 4-bromo-3-hydroxynaphthoate.

[b] L_2 = 5-halo-8-quinolinolate.

transfer from metal to ligand in both ground and excited singlet states of the chelated ligands. On the other hand, the small pH and chelation dependences of the arylhydroxycarboxylate spectra indicate very little charge-transfer interaction between metal and ligand in ground or excited states.

The data in Table I show that the mixed ligand chelates and the corresponding bis(8-quinolinolato)copper(II) chelates have similar absorption maxima, except that one of the bands in each mixed chelate is substantially displaced from its counterpart in the bis(8-quinolinolato)copper(II) chelate. The spectra of the bis(arylhydroxycarboxylato)copper(II) chelates consist each of a single band, that of the 3,5-diiodosalicylate having a maximum close to those of the ^1L_b bands (the high energy bands of the 5-halogeno-8-quinolinolates[7]) of the 5-halogeno-8-quinolinolates, while that of the 4-bromo-3-hydroxy-2-naphthoate has a maximum close to the ^1L_a bands of the 5-halogeno-8-quinolinolates.

The mixed ligand chelate spectra differ from the bis(8-quinolinolato)copper(II) spectra in that those mixed chelates containing 3,5-diiodosalicylate have high energy bands which are distorted and displaced from the ^1L_b bands of the corresponding bis-(5-halogeno-8-quinolinolato)copper(II) chelates. The low energy bands of these mixed chelates are very close, in form and position, to the ^1L_a bands of the corresponding bis(5-halogeno-8-quinolinolato)copper(II) chelates. The opposite is true for those mixed chelates containing 4-bromo-3-hydroxy-2-naphthoate. None of the mixed chelates appear to have absorption bands lying outside the regions of absorption by the bis(8-quinolinolato)copper(II) or the bis(arylhydroxycarboxylato)copper-(II) chelates.

These results show the absorption spectra of the mixed ligand chelates to be qualitatively similar to a superposition of the spectra of the bis(5-halogeno-8-quinolinolato)copper(II), and the bis(arylhydroxycarboxylato)copper(II) chelates. It appears that in the mixed chelates there is strong charge-transfer from the copper-(II) ion to the 8-quinolinolate ligand but not to the arylhydroxycarboxylate ligand. It is also apparent that there is little interaction between the two different ligands attached to the same metal ion. The data taken in chloroform are in agreement with those taken in pyridine.

The *d–d* spectra of the mixed chelates were found to consist of a single very broad band. Owing to the absence of symmetry in these compounds it seems likely that there are several transitions buried under each broad absorption envelope, although a maximum was distinguishable in each case. The maxima are generally closer to those of the bis(arylhydroxycarboxylato)copper(II) chelates than to those of the bis(5-halogeno-8-quinolinolato)copper(II) chelates. The significance of this is difficult to assess as the asymmetry of the mixed ligand chelates relative to the bis-chelates may result in very different ligand field splittings for the different types of chelates. The asymmetry of these molecules will also make ligand field calculations difficult if not impossible.

The spectra of the mixed ligand chelates demonstrate differences from the spectra of the bis-chelates. Although these differences are small by comparison with those to be expected if there were considerable interaction between the two different types of ligands, they may still cause serious errors in quantitative spectrophotometric analyses of multicomponent chelate systems. What is worse, in the case of the compounds studied here, is that, because of the similarities between the spectra of the mixed ligand chelates and those of the bis-chelates, the transitions caused by different species are extremely difficult to resolve.

Since chelates of 8-quinolinol, salicylic acid and their derivatives are employed in a number of biological and chemical procedures, the mixed chelates may play a significant role in understanding biological phenomena and evaluating analytical methods. The stability constants of these compounds have been determined[3,8] and have been found to be comparable to those of the corresponding bis(8-quinolinolato)-copper(II) chelates. Furthermore, the mixed ligand chelates form in the same pH region in which the bis(8-quinolinolato)copper(II) chelates form.

The biological significance of these compounds derives from the possibility of converting biologically inactive chelates into biologically active ones by mixed chelate formation. For example, fungitoxically inactive bis(5-bromo-8-quinolinolato)copper(II) can be converted into an active fungitoxic mixed chelate in the presence of the copper(II) bis-chelate of 4-bromo-3-hydroxy-2-naphthoic or 3,5-diiodosalicylic acid.

Boyce Thompson Institute for Plant Research, Inc.,
1086 North Broadway,
Yonkers, N. Y. 10701 (U.S.A.)

STEPHEN G. SCHULMAN*
HERMAN GERSHON

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* Present address: University of Florida, Gainesville, Fla. 32601.

Neutron activation analysis for mercury

Neutron activation analysis has been applied to the determination of trace quantities of mercury in biological materials[1-8], high-purity metals[9,10], meteorites[11] and rocks[8,12,13]. Since the previous methods mostly have involved several complicated chemical separations before mercury activities can be measured, the procedures are tedious and time-consuming.

This work was undertaken in order to develop a neutron activation method of analysis for mercury which would be generally applicable to a variety of samples. Rice, dried cuttlefish and rock were chosen as representatives. These materials were neutron-irradiated and induced mercury activities were separated by a single-step anion exchange based on the selective adsorption of mercury on DEAE in thiocyanate media. Mercury activities thus obtained are sufficiently pure to allow direct gross γ-activity measurement.

Experimental

Irradiation. About 0.4–0.5 g of rice, dried cuttlefish or powdered rock was weighed into a polyethylene ampoule and sealed. Before use, the inside of the ampoule was washed thoroughly with 6 *M* nitric acid, water and acetone, successively, and dried. A mercury(II) nitrate solution (100 μl containing 20.16 μg Hg) was applied to a small piece of filter paper placed into a polyethylene ampoule, which was sealed and served as a reference standard. The sample and the reference standard were packed with aluminum foil, put into a polyethylene capsule, and irradiated for 5 h in the Triga-II reactor of Musashi Institute of Technology, Kawasaki, at a neutron flux of $3 \cdot 10^{12}$ n cm^{-2} sec^{-1}.

Dissolution of irradiated samples. After 3 days cooling, transfer the irradiated rice or cuttlefish quantitatively to a 500-ml Kjeldahl flask containing 2.0 ml of a standard mercury(II) nitrate solution (10.16 mg Hg/ml of 0.5 *M* nitric acid) as a carrier. Add 5 ml of concentrated nitric acid and 3 ml of concentrated sulfuric acid, and boil gently until white fumes of sulfur trioxide appear. Add 0.5–1 g of potassium permanganate, dilute to 20 ml with water, and heat for about 30 min to complete the decomposition. Centrifuge to remove precipitated manganese dioxide. Adjust the pH of the supernate to 1–2 with 10 *M* sodium hydroxide. If manganese dioxide appears again, centrifuge it off. Collect the supernate. Continue with the *Radiochemical separation*.

Transfer the irradiated rock sample quantitatively to a 50-ml-capacity platinum dish containing 2.0 ml of the standard mercury(II) nitrate solution. Add 10 ml of water, 3 ml of concentrated sulfuric acid and 10 ml of 40% hydrofluoric acid, and warm on a water bath to complete the decomposition. Never heat on a hot plate to expel hydrofluoric acid so that white fumes of sulfur trioxide may appear. Dilute to 20 ml with water, add 0.2–0.3 g of boric acid and warm to obtain a clear solution. Adjust the pH of the solution to 1–2 with 10 *M* sodium hydroxide. Continue as described below.

Radiochemical separation of mercury. Add 0.5–1 ml of 1 *M* ammonium thiocyanate solution to *ca.* 50 ml of the buffered solution obtained above. Allow the thiocyanate solution to pass through a 1.0-g DEAE (thiocyanate form) column (1.5 cm i.d.)

previously conditioned with 0.01 *M* ammonium thiocyanate–0.1 *M* hydrochloric acid solution at a flow rate of about 0.5 ml/min. Discard the effluent. Wash the column with 50 ml of 0.01 *M* ammonium thiocyanate–0.1 *M* hydrochloric acid solution and discard the effluent. Strip mercury(II) ion with 10–15 ml of 6 *M* hydrochloric acid and collect the whole effluent. Add *ca.* 10 ml of tin(II) chloride solution (1 g $SnCl_2 \cdot 2H_2O$/ml of conc. hydrochloric acid). Centrifuge. Discard the supernate. Wash the metallic mercury twice with 3 *M* hydrochloric acid and once with water. Dissolve the mercury in 1 ml of concentrated nitric acid. Transfer the solution to a polyethylene vial and dilute to 4.0 ml with water. Subject to the activity measurement. Treat the reference standard in a similar way.

Determination of activity and chemical yield. Total γ-ray activities from ^{197m}Hg, ^{197}Hg and ^{203}Hg in the final solution were measured by a conventional well-type γ-ray scintillation counter with a 3 × 3 in NaI(Tl) crystal. The activities of the reference standard were measured in exactly the same manner as the sample. The chemical yield was determined by EDTA titration with Cu–PAN as an indicator. Radiochemical purity was checked with a TMC 400-channel pulse-height analyzer coupled with a 1.5 × 1 in NaI(Tl) crystal. The γ-decay rate was also measured to ascertain the freedom of foreign activities in the final solution.

Results and discussion

The results on replicate determinations of mercury in rice, dried cuttlefish, and the international standard rock[14], G-2, are summarized in Table I, together with the precision data. Recently, values for trace elements in the standard rocks have been compiled by FLANAGAN[15]. For mercury, values of 0.039 and 0.050 p.p.m. for G-2 are reported; these results were obtained by a neutron activation method and atomic absorption spectrometry, respectively. There is probably no significant difference between the values found in the present work and those[15] given previously, because the mercury content in G-2 is extremely low.

TABLE I

MERCURY CONTENTS OF RICE, DRIED CUTTLEFISH, AND THE INTERNATIONAL STANDARD ROCK, G-2

	Hg (p.p.m.)		
	Rice	*Dried cuttlefish*	*G-2*[a]
	0.17	0.39	0.12
	0.15	0.43	0.11
	0.18	0.44	0.13
	—	0.47	—
Average	0.17	0.43	0.12
Standard deviation (%)[b]	9.3	7.7	8.3

[a] The U.S. Geological Survey Silicate Rock Standard[14]; G-2 = Westerly Granite (from Sullivan Quarry, Bradford, Rhode Island).
[b] Based on the final results not on the counting data.

It has been demonstrated[16] that the adsorption of mercury on DEAE in aqueous ammonium thiocyanate media is highly selective, thus permitting mercury to be separated from about 40 metal ions, including alkali metals, alkali earth metals, Sc, Y, trivalent rare earths, Th, U(VI), Zr, V(IV), Cr(III), Mn(II), Re(VII), Fe(III), Co(II), Ni, Cu(II), Zn, Cd, Al, Ga, In, Tl(I), Ge, Sn(IV), Pb, As(III), Sb(III), Bi(III), Se(IV) and Te(IV). This chromatographic process was tested in the present work in the radiochemical procedure for mercury. Comparisons between the γ-ray spectra of samples and reference standard and analyses of the decay curves showed that no activities other than those of mercury were present in the final solutions. Thus, the radiochemical procedure, which consists primarily of the single-step anion exchange, brought about the isolation of sufficiently pure mercury activities that allow the direct gross γ-ray measurement.

Because of the simplicity of the procedure, 8 samples can easily be treated by one worker at the same time with high chemical yields of about 75%. To keep the chemical yield high for biological materials, it is of primary importance to use a large Kjeldahl flask in the decomposition process. Fuming sulfuric acid up does not cause any appreciable loss of mercury in the large flasks. However, the fuming process must be avoided for the decomposition of silicate materials; the small fraction of hydrofluoric acid remaining should be masked by the addition of boric acid. The average time needed to perform the whole radiochemical procedure is only about 2 h.

It is known that the effects of neutron shielding in biological and rock samples are insignificant because of the low activation cross-sections of the major matrices and because of the low abundance of mercury in these materials. Also no such effect has been found in the reference standard so far as less than 30 μg of mercury is concerned[1]. There are no apparent interfering nuclear reactions leading to the formation of ^{197m}Hg and ^{197}Hg. ^{203}Hg formed through the reactions ^{203}Tl(n,p)^{203}Hg and ^{206}Pb(n,α)^{203}Hg is likely to be insignificant because of the very low cross-sections of the reactions unless the samples contain large amounts of thallium and lead.

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Laboratory for Analytical Chemistry, Faculty of Engineering, K. Ishida
University of Chiba, Yayoi-cho, Chiba (Japan)
Chemistry Division, National Institute of Radiological Sciences, S. Kawamura
Anagawa-cho, Chiba (Japan) M. Izawa

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Compleximetric determination of bismuth with EDTA in trichloroacetic acid medium with arsenazo III as metallochromic indicator

Arsenazo III is widely used as an organic reagent in spectrophotometry, since it forms many valuable highly coloured complexes with metals. However, because the complexes formed with arsenazo III are generally very strong, its use as a compleximetric metallochromic indicator has been very limited. It appears that arsenazo III has been applied only once as a metallochromic indicator, *viz.*, for the titration of lanthanons in alumino-silicate zeolites with DTPA[1].

The reaction of bismuth(III) with arsenazo III has been reported by SAVVIN[2], and this reaction has been utilized for the determination of bismuth in copper ores and concentrates and leached lead-containing mineral residues[3]. Arsenazo III builds with bismuth(III) a complex species of the ML_2 type which shows maximum absorption at 610 nm, the molar absorptivity[3] being $(2.7 \pm 0.5) \cdot 10^4$; the dissociation constant of the complex[3] is only $(5.54 \pm 3.7) \cdot 10^{-15}$.

Preliminary experiments showed that bismuth(III) and arsenazo III form a highly coloured complex species which exhibits the interesting property of being decomposed by EDTA in a trichloroacetic acid–sodium trichloroacetate medium (pH 1–2). Further investigation indicated that the reaction might prove most valuable for the compleximetric determination of bismuth; in addition to the normal advantages shown by good compleximetric procedures, its unusual—for compleximetric methods—sensitivity (see Table I) makes the method attractive. Another good feature is that the end-point appears very clearly and instantaneously in the cold; the initial bluish colour turns very sharply to red-crimson on addition of the stoicheiometric amount of EDTA required by the formation of a 1:1 EDTA:bismuth(III) complex compound. Furthermore, the relatively good tolerance of the method towards many foreign ions (Table II) makes it very promising. The sharpness of the colour-change at the end-point is at least as good as that of pyrocatechol violet which is at present the best indicator for this titration[4].

Reagents

Since the method is very sensitive, 0.005 *M* EDTA solutions can be used to

TABLE I

COMPLEXIMETRIC TITRATION OF BISMUTH(III) WITH EDTA IN ABSENCE OF FOREIGN IONS

Bi(III) taken (mg)	*EDTA consumption*			
	Molarity	*No. of titns.*	*Average observed (ml)*	*Theor. (ml)*
1.000	0.001	6	4.77 ± 0.01	4.786
1.000	0.002	3	2.39 ± 0.01	2.393
2.500	0.005	11	2.42 ± 0.02	2.393
5.000	0.005	10	4.79 ± 0.01	4.786
10.00	0.01	11	4.79 ± 0.01	4.786
20.00	0.02	3	4.76 ± 0.01	4.786
50.00	0.05	3	4.76 ± 0.00	4.786
50.00	0.1	4	2.385 ± 0.005	2.393
100.0	0.1	3	4.76 ± 0.01	4.786

TABLE II

APPLICABILITY OF THE PROPOSED COMPLEXIMETRIC METHOD IN THE PRESENCE OF DIFFERENT IONS

(For 5 mg Bi, the theoretical consumption of 0.005 *M* EDTA is 4.786 ml, and for 2.5 mg, 2.393 ml. 3–4 titrations were done in each case and the averages are reported)

Bi(III) taken (mg)	*Diverse ion*	*Tested concentration range*		*Tentative method(s) tested to eliminate the interference posed by the introduced ion*	*Average 0.005 M EDTA consumed (ml)*
		Lower limit (mg)	*Upper limit (mg)*		
5	Ni(II)	2.5			4.76 ± 0.01
5	Ni(II)		25[a]		4.79 ± 0.01
5	Ca(II)	—	18[a]		4.77 ± 0.01
5	Th(IV)	—	0.05[b]	Oxalic, tartaric and citric acids; SO_4^{2-}; triethanolamine; acetylacetone; tiron	—
5	Th(IV)		0.05[c]	F^-	—
5	Th(IV)		0.05[d]	None	4.756 ± 0.005
5	Pd(II)	—	0.5	100 mg $NaNO_2$	4.78 ± 0.02
5	Pd(II)	—	0.5	100 mg thiourea	4.77 ± 0.02
5	Pd(II)	—	0.5[b]	$S_2O_3^{2-}$; thioacetamide	
5	Ce(III)	—	1.0[b,d,e]	F^-	
5	Zr(IV)	—	0.5[b,e]	SO_4^{2-}, oxalate	
5	Fe(III)	—	5.0[c,f]	$NH_2OH \cdot HCl$	
5	Fe(III)	—	5.0[a]	300 mg ascorbic acid	4.76 ± 0.01
5	U(VI)	—	1.0[b]	F^-; tartaric and sulfosalicylic acid	
5	Pb(II)	2.5			4.78 ± 0.02
5	Pb(II)		100[a]	250 mg SO_4^{2-}	4.80 ± 0.01
2.5	Sn(IV)	0.5[b,f]	—	Tartaric and citric acids; triethanolamine	
2.5	Sn(II)	0.5[b,f]		Tartaric acid	
2.5	PO_4H^{2-}	5			2.40 ± 0.01
2.5	PO_4H^{2-}		10[d]		2.41 ± 0.01
2.5	AsO_2^-	100[d]			2.41 ± 0.01
2.5	AsO_2^-		125[g,d]		
2.5	PO_4H_3	—	25[d]		2.41 ± 0.01
2.5	Se(IV)	10			2.43 ± 0.01
2.5	Se(IV)		50[a]		2.43 ± 0.01
2.5	Te(IV)	2.5			2.41 ± 0.01
2.5	Te(IV)		5[d,f]		2.40 ± 0.01
2.5	Tl(I)	25			2.41 ± 0.01
2.5	Tl(I)		100[a]		2.41 ± 0.01
2.5	Cd(II)	1			2.41 ± 0.01
2.5	Cd(II)		25[a]		2.41 ± 0.01
2.5	Sb(V)	1[e,i]		30 mg tartaric acid	2.42 ± 0.00
2.5	Sb(V)		10[d,f,h]	75 mg tartaric acid	2.42 ± 0.00
2.5	Sb(III)	—	2[d,f,h]	60 mg tartaric acid	2.40 ± 0.00

[a] No greater amounts of the tested ion were investigated.

[b] Negative results were obtained because the diverse ion was not properly masked or because of a more or less extensive competitive demasking effect of the reagents added on Bi(III) from the arsenazo III complex.

[c] In the presence of an excess of masking agent, EDTA does not liberate Bi(III) from its arsenazo III complex, or Bi(III) does not react properly with arsenazo III.

[d] No prospect is foreseen for titration of Bi(III) in the presence of amounts of the interfering ion greater than the indicated value.

[e] No prospect is foreseen for titration of Bi(III) directly in the presence of the particular interfering ion.

[f] The upper limit of interference could not be established due to the complementary interfering nature of some of the ions (Cl^-, free acidity, etc.) accompanying the tested interference in the available test solution.

[g] Before the addition of Bi(III) and diverse ion, NaOH or $HClO_4$ was added in order to neutralize high values of free acidity or alkalinity exhibited by the solution of the interfering ion in order to create optimum titration conditions.

[h] A diluted perchloric acid medium was used instead of trichloroacetic acid–sodium trichloroacetate in order to minimize the initial chloride content.

titrate 1–5 mg amounts of bismuth(III). Special care must be observed in the preparation of such dilute EDTA solutions, which are obtained by suitable dilution of stock standard 0.1 *M* EDTA solutions[4]. The titer of the 0.1 *M* EDTA standard solution was checked against bismuth as described below. A 3 *M* trichloroacetic acid–3 *M* sodium trichloroacetate buffer was prepared by carefully neutralizing half the required amount of trichloroacetic acid with the calculated equivalent amount of sodium hydroxide as a concentrated solution.

An aqueous 0.1% (w/v) arsenazo III solution was prepared from a "Schuchardt" preparation (this solution is stable for years). Solutions containing 5–25 mg Bi(III)/ml were prepared by dissolution of a 99.9999% (Koch-Light) metallic bismuth sample in 4–6 *M* nitric acid with gentle warming. The solutions were diluted to the desired volume so that the final acidity was 0.5–1.5 *M* in nitric acid.

All the reagents used were of p.a. quality from well established firms.

Procedure

Pipette 1 ml of trichloroacetate mixture into a 50-ml magnetically stirred glass beaker and add a few ml of distilled water and 4 drops (*ca.* 0.2 ml) of the 0.1% arsenazo III solution. Then add the test solution containing 1–5 mg of bismuth, and dilute to about 25 ml with distilled water. Titrate with 0.005 *M* EDTA solution from a 5-ml high-precision burette. As the titration progresses, the approach of the end-point is indicated by the gradual fading of the blue colour, and at the equivalence point, the original bluish colour turns very sharply to weak red-crimson which is the colour of the free arsenazo III in acidic solution; the colour change is observed within a 1–2 drops interval. The initial pH value (1.7 ± 0.1) remains practically unchanged at the end-point because only small amounts of bismuth are involved. The titration can be done very quickly, once a little experience with the method has been achieved.

Results and discussion

Table I shows the results obtained for the titration of 1–100 mg amounts of bismuth with EDTA solutions of different normality. The results indicate clearly that the accuracy and precision of the method can be considered as practically constant throughout the wide concentration interval tested. Moreover, the clarity of the end-point is such that trouble-free titrations are possible at all the concentration levels tested. It would seem feasible to extend the titration interval down to the 0.25–0.50 mg Bi level with careful control of the experimental details.

In Table II the results of a comprehensive interference study on the titration of bismuth with EDTA are presented. It can be concluded that the tolerance of the method for foreign ions is good, since a relatively great number of elements do not interfere even when present in very large amounts compared to bismuth (I-A, II-A, III-A, and some of the V-A, VI-A, I-B, II-B, VI-B, VII-B and VIII group elements of the Periodic Table do not interfere). In other cases, the interfering elements can be readily and effectively masked to varying extents by very simple means, *e.g.* in the case of Pb(II), Fe(III), Pd(II), Sb(III), Sb(V) and Te(IV).

Certain elements interfere so much that their preliminary separation is essential: elements of group III-B, the lanthanons, the actinides, Zr(IV), Hf(IV), Sn(II) and Sn(IV). Fortunately, with the exception of tin, these elements will rarely accompany bismuth. Tin can be easily separated from bismuth as the insoluble white β-stannic acid by carrying out the attack of the samples with concentrated nitric acid.

Qualitative spot tests were done to investigate the influence of various anions on the bismuth(III)–arsenazo III reaction. Three different groups were distinguished:

(*a*) Anions which cause sequestration of bismuth from its arsenazo III complex, *e.g.* aminopolycarboxylic acids; halide, citrate and tartrate ions when present in very great excess over bismuth; thioglycolic and vanadate ions.

(*b*) Anions which are tolerated even in very large amounts, *e.g.* nitrate, acetate, sulfate, tartrate (up to 175 mg), chlorate, succinate, biphthalate, formate, borate and chloride (up to 60 mg).

(*c*) Anions which interfere owing to secondary effects (colorations, formation of precipitates in the trichloroacetic–trichloracetate medium, discoloration of the arsenazo III complex brought about by the strong oxidative or reducing power, of the anions, etc.), *e.g.* SCN^-, $PO_4H_2^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, ClO_4^-, $C_2O_4^{2-}$, IO_3^-, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, WO_4^{2-} and $Mo_2O_7^{2-}$.

Particularly interesting is the behaviour exhibited by chloride and tartrate ions since comparatively large amounts of these ions can be safely tolerated by the compleximetric method. Some chloride ion (0.5–5.0 mg/sample) is always present, since chloride is released from the trichloroacetic–trichloroacetate buffer; the amount of chloride is a function of time as a result of ageing of the 6 *M* solutions over long periods. This explains why in especially critical cases (*e.g.* antimony, Table II) the acid medium was changed to perchloric acid in order to increase the tolerance of the method for Sb, since Sb(III) and Sb(V) samples were available in very concentrated HCl solutions.

The judicious addition of tartrate ion provides effective masking of a few elements (see Table II).

Applicability

The compleximetric method described here has so far been applied only to synthetic solutions. Further work is in progress to test the practicability of the method in analyses of low-melting bismuth alloys, print metal, soldering metal, lead bricks of the type used for nuclear protection against irradiation, lead–copper ores, concentrates, etc.

The proposed method provides an interesting linkage between spectrophotometric microgram methods and titrimetric milligram methods. The remarkable simplicity, reproducibility and accuracy shown even at the 1–5 mg level of bismuth make the method very attractive and versatile.

Consejo Superior de Investigaciones
Científicas,
Departamento de Química Analítica,
Universidad de Madrid,
Madrid-3 (Spain)

J. A. PÉREZ-BUSTAMANTE
D. ALVAREZ JIMÉNEZ
F. BURRIEL-MARTÍ

1 W. W. MARSH AND G. MYERS, *Anal. Chim. Acta*, 43 (1968) 511.
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ANNOUNCEMENT

MEETINGS OF THE GESELLSCHAFT DEUTSCHER CHEMIKER, 1970

20–21 February	GDCH-DIVISION *Chemical Education.* Foundation Meeting in Heidelberg.
12–15 April	GDCH-DIVISION *Macromolecular Chemistry.* Symposium in Bad Nauheim.
29 April–2 May	MEETING *Biochemical Analysis.* Jointly organized by the Society for Biological Chemistry, the German Society for Clinical Chemistry, the German Pharmacological Society, the German Pharmaceutical Society, and the GDCH-DIVISIONS *Analytical Chemistry* and *Food and Forensic Chemistry* in Munich.
4–6 May	GDCH-DIVISION *Nuclear-, Radio- and Radiation Chemistry.* Discussion Meeting on *General Radiochemistry* in Karlsruhe.
4–6 May	GDCH-DIVISION *Water Chemistry.* Symposium in Bad Nenndorf.
11–15 May	4TH INTERNATIONAL COLOUR SYMPOSIUM. In Lindau (Lake Constance).
Beginning of June	DANISH–GERMAN MEETING OF FOOD CHEMISTS IN COPENHAGEN (DENMARK). Organized by the Danish Society of Food Technology and Hygiene, and the GDCH-DIVISION *Food and Forensic Chemistry.*
22 June	CHEMISTRY DAY AND FESTIVE MEETING. Of the Gesellschaft Deutscher Chemiker on the occasion of the ACHEMA, Frankfurt (M).
23 June (presumptive)	GDCH-DIVISION *Private Consulting Chemists.* Meeting in Frankfurt (M).
7–10 September	IUPAC-SYMPOSIUM *Cycloaddition Reactions.* In Munich.
13–16 September	GDCH-DIVISION *Food and Forensic Chemistry.* Symposium in Würzburg.
14–16 September (presumptive)	SYMPOSIUM *Radiochemical Methods.* In Graz (Austria) jointly organized by the WORKING-PARTY RADIO- AND RADIATION CHEMISTRY of the Society of Austrian Chemists, and the GDCH-DIVISION *Nuclear-, Radio- and Radiation Chemistry.*
29 September–3 October	GDCH-DIVISION *Pigments and Dyes.* 36th Symposium in Bad Nauheim.
End of Sept./Beginning Oct.	GDCH-DIVISION *Solid State Chemistry.* Symposium *Experimental Methods for Investigating the Chemical Bond in Solids* in Aachen.
6 October	CHEMISTRY DAY WITH FESTIVE MEETING OF THE GESELLSCHAFT DEUTSCHER CHEMIKER. On the occasion of the 106th Assembly of the German Society of Natural Scientists and Physicians, in Düsseldorf.

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15 and 16 October	GDCH-DIVISION *Applied Electrochemistry.* Symposium *Chloride Electrolysis* in Frankfurt (M)–Höchst.
25–31 October	EUCHEM-CONFERENCE *Photophysical Primary Processes of Organic Compounds in Condensed Phases.* Schloss Elmau/Mittenwald (participation is limited to 100 persons).
11–12 November	GDCH-DIVISION *History of Chemistry.* In Frankfurt (M).
16–19 November	SYMPOSIUM *Data Handling in Analytical Chemistry and Progress in Instrumental Analysis.* In Basel (Switzerland), jointly organized by the Swiss Society for Analytical Chemistry and Applied Chemistry, the Society of Swiss Microanalysts, the Austrian Society of Microchemistry and Analytical Chemistry in the Society of Austrian Chemists, and the GDCH-DIVISION *Analytical Chemistry.*

Details of the Meetings listed above may be obtained from: GESELLSCHAFT DEUTSCHER CHEMIKER, 6000 Frankfurt (M), Germany, Postfach 119075.

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BOOK REVIEWS

Vth International Congress on X-ray Optics and Microanalysis, Tübingen, September 1968, Edited by G. MÖLLENSTEDT AND K. H. GAUKLER, Springer-Verlag, Berlin, 1969, xii + 612 pp., price DM 198.—.

This is the latest in the triennial series of Symposia which began at Cambridge in 1956. Originally entitled *X-ray Microscopy and Microradiography*, the subsequent efflorescence of electron probe microanalysis has led to the change of title. These Symposia are now established as the acknowledged international forum for reporting advances in this field of research and their success is apparent from the continuing high standard of the majority of papers presented.

X-ray optics and electron probe microanalysis are highly instrumental fields. Instruments take time to develop, apply and evaluate. Three yearly Symposia allow this process to proceed to fruition and thus timing is also a component in the success of the meetings. In 1968 one third of the papers were on instrumental aspects compared with 15% at the 1965 Paris Congress. This increase is partially accounted for by enhanced interest in electron energy microanalysis but improved instrumentation for the electron probe still remains a very active area. The provision, in a single instrument, of facilities for transmission or scanning electron microscopy combined with electron probe microanalysis is another development reflected in an increasing number of papers. These trends seem likely to continue in subsequent meetings.

The format for these proceedings was undecided at the time of the meeting. The detailed preparation of the manuscript, including redrawing all the diagrams, was left to the publishers Springer-Verlag, who must be highly commended on the quality of this volume and the rapidity with which it has appeared. Although expensive, it is required reading for all research workers in this field and should be an automatic acquisition for libraries concerned with Materials Science.

D. A. MELFORD (Saffron Walden)

Annual Review of NMR Spectroscopy, Vol. 2, Edited by E. F. MOONEY, Academic Press, London and New York, 1969, xi + 467 pp., price 120 s.

There are at present three review series on magnetic resonance spectroscopy; one of these entitled *Advances in Magnetic Resonance*, has a strong theoretical bias and is not solely devoted to nuclear magnetic resonance whereas the volume under review is particularly intended for organic and analytical chemists who use n.m.r. for compound identification and structure determination.

Three of the eight chapters are devoted to proton resonance and are as follows: *General Review of Proton Magnetic Resonance* by P. BLADON; *N.M.R. Spectroscopy in the Study of Carbohydrates and Related Compounds* by T. D. INCH; *Solvent Effects on Proton Magnetic Resonance Spectroscopy* by J. RONAYNE AND D. H. WILLIAMS. The chapter by T. D. INCH is particularly opportune; the last review on this subject was published in 1964 and since then the introduction of more sophisticated techniques for obtaining and interpreting spectra has resulted in much more useful information being made available to the carbohydrate chemist.

In an authoritative chapter on *Nuclear Electron Double Resonance in Liquids*, by R. A. DWEK, R. E. RICHARDS AND D. TAYLOR, the theory behind the intensity enhancement of nuclear resonance signals when an electron transition is saturated (Overhauser effect) is discussed. Although this experiment has limited applications, the enhancement of carbon-13 and phosphorus-31 signals has proved useful and the nuclear–nuclear Overhauser effect has revealed remarkably subtle details of molecular conformation. The editor of the series, E. F. MOONEY, has contributed to three of the chapters: carbon-13 and nitrogen spectroscopy with P. H. WINSTON and boron-11 spectroscopy with W. G. HENDERSON. Work in these fields is extensively reviewed. It is noteworthy that carbon-13 spectroscopy is becoming increasingly important due to the availability of more sensitive detection systems using heteronuclear decoupling and time averaging techniques. The book is concluded with a lengthy chapter on the *Phosphorus-31 Spectra of Co-ordination Compounds* by J. F. NIXON AND A. PIDCOCK.

Whether the subject can support three review series is questionable—too frequent coverage of certain topics can hardly be justified. However, the present volume contains some interesting and informative articles and can be recommended, especially to those interested in the n.m.r. study of inorganic compounds.

R. SPRATT (Belfast)

Organic Reaction Mechanisms, 1968, Edited by B. CAPON AND C. W. REES, Interscience Publishers–J. Wiley, New York–London, 1969, xi+583 pp., price £9.0.

Organic Reaction Mechanisms has now clearly established itself as a continuing series. The editors have enlisted the aid of a number of colleagues, which has ensured that the mounting volume of literature is adequately appraised before it is surveyed in print.

Over 3500 references have been culled from the 1968 literature. Many are discussed and the rest are listed. The subject has been dealt with under the same headings as before. Expansion seems to have occurred in the fields of electrophilic aliphatic substitution, radical reactions, and oxidation and reduction. It is noteworthy that each of these chapters covers some organometallic chemistry.

The book has once again appeared promptly, although it would have been even quicker in a softback edition. The inclusion of a cumulative index will make it a suitable reference volume, thereby giving it an additional rôle to its original purpose of "current awareness".

The book is well produced and will be widely read. The slight increase in size from the previous volume hardly seems to warrant a 50% increase in price. At £9.0, it is now for library purchase only, which is a pity since it is just the sort of book which young researchers should purchase.

E. J. FORBES (Birmingham)

Encyclopedia of Industrial Chemical Analysis. Vol. 7. Benzene to Brewery Products, Edited by F. D. SNELL AND C. L. HINTON, Interscience Publishers–J. Wiley, New York, 1969, xi+712 pp., price £21.25 (subscription price £15.5).

This volume of the *Encyclopedia* contains articles on benzene, benzoic acid, benzyl alcohol, beryllium (and its alloys, compounds and determination), bile acids and salts, bioassay, bismuth (and its alloys and compounds), bleaching agents, bonded abrasives, boron (and its compounds), brake fluids and linings, and brewery products. The longest articles are those on brewery products (204 pp.) and bleaching agents (73 pp.).

With such a very wide variety of themes in each volume, no reviewer can competently assess the true worth of each section of this encyclopedia. Standard and other well tested methods for most of the topics covered are given in detail, and in general, the treatment appears to be satisfactory. There are however, some points that require comment. Five of the 16 topics in this volume have been dealt with by the editorial staff and can hardly be regarded as authoritative; whether or not this is preferable to long delays whilst a few authors produce their pieces is arguable, but at least the method ensures that the majority of authors who obey deadlines see their work in print before it is outdated. Further, certain parts of this volume are reminiscent of the Holy Roman Empire; the information may be useful but it is certainly neither chemical nor analytical. For example, extensive descriptions are given of bench and road testing for brake linings, and of TAPPI physical testing methods for paper and paperboard. Surely, people who must carry out these tests have the full instructions laid down by the standardizing bodies to hand, and other readers would find a brief description adequate. Another criticism is the dubious propriety of reproducing material from one Treatise or Encyclopaedia in another, even though the publishers hold the copyright of both.

As one contemplates the progress of this vast work, one wonders again who will buy it. Relevant sections will provide very useful information to less experienced analytical chemists and the whole will be a godsend to the consultant analyst with a large practice, as well as a source of endless interest, even amusement, to anyone with a genuine feeling for analytical work who can spare the time to browse through it.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 50 (1970) 361–362

G. SCHWARZENBACH AND H. FLASCHKA, *Complexometric Titrations*, 2nd English Edn., translated by H. M. N. H. IRVING, Methuen and Co., Ltd., London; Barnes and Noble, New York, 1969, xxii + 490 pp., price £4.50.

In the 12 years that have passed since the last English translation of SCHWARZENBACH AND FLASCHKA's authoritative text on compleximetric titrations, very extensive developments have taken place in this field. The German text reached its 5th edition in 1965, and this English version of the 5th edition would have appeared much earlier but for various disasters that ensued in its production. However, the delays have had the advantage that it has been possible to introduce new material in collaboration with the authors.

For readers who are unfamiliar with the German edition, a brief summary of the contents may be useful. In Part I, separate chapters deal with titrating agents, basic theory, colour and fluorescence indicators, metallochromic indicators, instrumental indication methods, the different titration techniques available, and methods of improving selectivity. In Part II, titration procedures are given for most of the elements that can be determined by means of EDTA and similar reagents, and the literature is fully surveyed for each element. The only adverse criticism of this text is that alternative complexing agents receive scant attention; a fuller comparison of EDTA with the other polyaminopolycarboxylic acids that have been recommended for various purposes would have been very useful.

Professor IRVING's translation is not only faithful to the original but also uncommonly fluent. English-speaking readers will find this text of particular importance, but its appearance should be welcomed by all, for it is certainly the most authoritative and up-to-date book on compleximetric titrations available in any language.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 50 (1970) 362

B. DOBINSON, W. HOFMANN AND B. P. STARK, *The Determination of Epoxide Groups*, Monographs in Organic Functional Group Analysis, Vol. 1, Pergamon Press, Oxford, 1969, xiii + 79 pp., price £2.10.

This book is the first in a series of monographs in organic functional group analysis and sets the authors of the succeeding volumes an excellent example. The first of the four chapters is an introduction to the epoxide group and describes the reactivities of the different epoxides to the various reagents used for their determination. The methods of analysis are considered more fully in chapters 2 and 3, chapter 2 being concerned with twelve different procedures of ring opening with hydrochloric or hydrobromic acids and chapter 3 dealing with other ring-opening reagents. Colorimetric and infra-red methods are also dealt with in this chapter. Only passing reference is made to instrumental techniques of end-point detection and none to automatic analysis. In the final chapter the authors choose the methods which they consider to be of most general applicability.

The writers of this little book, all of whom are employed in the resin industry, have not only provided a concise summary of epoxide chemistry but also a practical guide for the analyst concerned with the determination of epoxide groups.

L. H. RUDDLE (Welwyn Garden City)

Advances in Analytical Chemistry and Instrumentation. Vol. 7, Edited by C. N. REILLEY AND F. W. MCLAFFERTY, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1969, vi + 229 pp., price £5.50.

This seventh volume contains four review articles on widely differing subjects. The discussion of ultramicroanalysis with the microscope, by W. C. MCCRONE, is a timely reminder of the value of this much neglected technique. It is followed by an article on recent advances in Raman spectroscopy (26 pp.) by J. C. EVANS (written in 1966), and a comprehensive account of the production and radio-assay of tritium-labelled compounds (72 pp.) by J. K. LEE AND F. SCHMIDT-BLEEK. The final chapter on applications of kinetics to automated quantitative analysis (67 pp.) by H. L. PARDUE, is an excellent treatment of a topic that is difficult to discuss in a readable manner. The derivation of the kinetics and their subsequent treatment to make them suitable for automated systems is handled with great facility, and the discussion of the ways in which the various types of kinetic method (variable or fixed time, slope and signal-stat) have been automated is extremely interesting. The accuracy, precision and selectivity of kinetic methods when carried out automatically under optimized conditions is shown to be better than for many equilibrium procedures, which bodes well for the future development of analytical kinetic methods.

A. TOWNSHEND (Birmingham)

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PUBLICATIONS RECEIVED

BEHRENS-KLEY, *Microscopical Identification of Organic Compounds*, translated by R. E. STEVENS, Microscope Publications Ltd., Chicago, Ill. 60616, 1969, iv + 234 pp.

This is a translation of BEHRENS-KLEY'S *Organische Mikrochemische Analyse* published in 1922, which remains the only book to give a complete summary of the chemical microscopy of organic compounds. The translation is good and the book is well illustrated.

H. BENNETT AND W. G. HAWLEY, *The Accuracy of Industrial Ceramic Analysis*, The British Ceramic Research Association, Stoke-on-Trent, England, Special Publication No. 53, 1969, 60 pp., price 30 s.

Third Ceramic Chemist's Conference, British Ceramic Research Association, Stoke-on-Trent, England, Special Publication No. 62, 1969, 59 pp., price 40 s.

This booklet contains the proceedings of the Conference held in October, 1968, at B.C.R.A., Stoke-on-Trent, with full versions of 7 papers and discussions.

G. NEDEY, *Peintures et Vernis*, Le Point des Connaissances Actuelles No. 1348, Presses Universitaires de France, Paris, 1969, 128 pp.

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