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Completing Volume 52

Publication Schedule for 1971

In the interests of rapid publication it has been found necessary to schedule 5 volumes for appearance in 1971. Since monthly publication will be maintained, this implies that 2 of the volumes will each consist of three issues, while 3 of the volumes will each consist of only 2 issues. The following provisional schedule applies:

Vol. **53**, No. **1**	January 1971	
Vol. **53**, No. **2**	February 1971	**(completing Vol. 53)**
Vol. **54**, No. **1**	March 1971	
Vol. **54**, No. **2**	April 1971	
Vol. **54**, No. **3**	May 1971	**(completing Vol. 54)**
Vol. **55**, No. **1**	June 1971	
Vol. **55**, No. **2**	July 1971	**(completing Vol. 55)**
Vol. **56**, No. **1**	August 1971	
Vol. **56**, No. **2**	September 1971	
Vol. **56**, No. **3**	October 1971	**(completing Vol. 56)**
Vol. **57**, No. **1**	November 1971	
Vol. **57**, No. **2**	December 1971	**(completing Vol. 57)**

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GENERAL INFORMATION

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Papers will be published in English, French or German.

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Papers should be sent to:

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Coates Chemical Laboratories,
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Louisiana State University,
Baton Rouge 3,
La. 70803 (U.S.A.)

or to:

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Department of Chemistry,
The University,
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Birmingham B15 2TT (Great Britain)

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Fifty reprints will be supplied free of charge. Additional reprints (minimum 100) can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 52, No. 3, December 1970

THE AUTOMATION OF THERMAL ANALYSIS INSTRUMENTATION: DIFFERENTIAL THERMAL ANALYSIS

An automated DTA instrument is described which is capable of studying eight individual samples, each contained in a glass capillary tube, in a sequential manner. The samples are automatically introduced into the furnace, pyrolyzed to a preselected temperature limit, and then removed. After the furnace has been cooled back to room temperature, the cycle is repeated. Operation of the sample changing mechanism, furnace temperature programming, recording, etc. is completely automatic.

W. W. Wendlandt and W. S. Bradley,
Anal. Chim. Acta, 52 (1970) 397–403

THE USE OF ORGANIC SOLVENTS IN THE DETERMINATION OF PLATINUM BY ATOMIC ABSORPTION SPECTROSCOPY

Miscible and immiscible organic solvents are successfully applied in the atomic absorption determination of platinum with nitrous oxide–acetylene flames. A procedure is described which incorporates acetone solutions to increase the platinum sensitivity to 3 μg ml^{-1} for 1% absorption and the detection limit to 1 p.p.m. In another procedure, platinum is extracted into ethyl acetate which increases the sensitivity to 2.1 μg ml^{-1} for 1% absorption and the detection limit to 0.5 p.p.m. Interferences from noble metals and associated base metals are completely removed in both procedures.

A. E. Pitts and F. E. Beamish,
Anal. Chim. Acta, 52 (1970) 405–415

THE USE OF WATER-MISCIBLE ORGANIC SOLVENTS IN ATOMIC ABSORPTION SPECTROPHOTOMETRY

The use of water-miscible organic solvents in atomic absorption spectrophotometry is discussed with reference to the enhancement of analytical sensitivity and the reduction of interferences. Application to the determination of the elements Cu, Mn, Zn, Fe, Rb, Ca and Mg in fresh waters, plant materials, soils, biological tissues and some viscous inorganic materials is described.

V. K. Panday and A. K. Ganguly,
Anal. Chim. Acta, 52 (1970) 417–423

SUBMICRO METHODS OF ORGANIC ANALYSIS

by R. Belcher
Professor of Analytical Chemistry,
The University of Birmingham, Great Britain

6 × 9″, ix + 173 pages, 12 tables, 35 illus., 186 lit. refs., 1966, Dfl.27.50, 65s.

Contents: 1. Introduction. 2. The balance. 3. General apparatus. 4. The determination of nitrogen. 5. Carbon and hydrogen. 6. Chlorine. 7. Bromine and iodine. 8. Fluorine. 9. Sulphur. 10. Phosphorus and arsenic. 11. Carboxyl groups. 12. Organic bases in non-aqueous media. 13. Alkoxyl and N-methyl groups. 14. Acetyl groups. 15. The carbonyl group. 16. Olefinic unsaturation. 17. Oxidation with periodate. 18. The determination of nitro and nitroso groups. 19. Thiol groups. 20. The cryoscopic determination of molecular weight. Index.

TECHNIQUES OF OSCILLOGRAPHIC POLAROGRAPHY

Second Edition, completely revised and enlarged
by R. Kalvoda
Institute of Polarography, Czechoslovak Academy of
Sciences, Prague, Czechoslovakia
with a preface by Professor J. Heyrovský

6 × 9″, 214 pages, 3 tables, 90 illus., 263 lit. refs., 1965, Dfl. 30.00, 70s.

Contents: Preface (J. Heyrovský); Author's Preface; 1. Introduction. 2. Examples of application of the oscillopolarographic method. 3. Practical oscillopolarographic exercises. 4. Maintenance of apparatus and construction of auxiliary electrical circuits. Index.

TABLE OF META-STABLE TRANSITIONS FOR USE IN MASS SPECTROMETRY

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

9½ × 6½″, xix + 392 pages, 1965, Dfl. 50.00, £6.10.0.

These tables are intended to make it easy to determine the ionic reaction which gives rise to any meta-stable peak in a mass spectrometer, and will prove indispensable to any laboratory possessing this equipment. The introduction is given in English, German, French and Russian, to make the tables more generally useful.

STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Second International Symposium organized by the Chromatography
Group of the Czechoslovak Chemical Society, at Liblice
by K. Macek and I.M.Hais

7 × 10″, 358 pages, 69 tables, 135 illus., 494 lit. refs., 3 coloured plates, 1965, Dfl. 47.50, £5.15.0.

Contents: List of participants in the discussion. Introduction. Opening speech. I. Chromatography papers. II. Thin-layer materials. III. Stationary liquids and adsorbents in paper chromatography. IV. Stationary liquids and impregnations for thin layers. V. General problems of the stationary phase. Discussion. Closing remarks. Author index. Subject index.

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THE DETERMINATION OF TRACE AMOUNTS OF LEAD IN HIGH-ALLOY STEELS BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROSCOPY

A method is described for the determination of 0.001–0.01% lead in high-alloy steels by atomic absorption spectroscopy following solvent extraction. After sample dissolution, the bulk of the iron is removed by extraction with diisopropyl ether and residual traces of iron(III) are reduced with hydroxylammonium chloride. Lead is extracted as tetraiodoplumbate into methyl isobutyl ketone and the organic extract is sprayed into the flame. Iodine, which is liberated during the iodide extraction, particularly in the presence of copper, inhibits the extraction of lead, and the copper which is extracted also produces slight interference. Both the effects can be standardised by the addition of 0.012 g of copper to the aqueous solution before the iodide extraction in both the steel samples and the lead solutions for calibration.

M. E. HOFTON AND D. P. HUBBARD,
Anal. Chim. Acta, 52 (1970) 425–432

THE COULOMETRIC TITRATION OF SODIUM SECONAL AND SODIUM SANDOPTAL AND ITS APPLICATION TO THE ANALYSIS OF STANDARD BLOOD SERUM SAMPLES

Constant-current coulometry has been applied to the titration of the allylic barbituric acid derivatives, sodium seconal and sodium sandoptal. Electrogenerated bromine was employed as the titrant and biamperometry was used to detect the end-point. The effect of reaction time and excess bromine was evaluated, and optimum standard conditions were established. Quantitative bromination required an excess of bromine, hence a back-titration with standard arsenite was performed. Calibration curves were linear over the concentration range investigated, but changed slightly from day to day. The standard conditions were applied to the analysis of standard blood serum samples. Preliminary precipitation of protein was necessary, hence lower values than theoretical were obtained.

J. R. MONFORTE AND W. C. PURDY,
Anal. Chim. Acta, 52 (1970) 433–440

THE DETERMINATION OF MICROGRAM QUANTITIES OF MERCURY(II) AND SILVER(I) BY THERMOMETRIC TITRATION

By titration with standard potassium iodide silver(I) and mercury(II) can be determined in aqueous solution in the concentration range 1000–0.1 p.p.m. The end-point, which is detected thermometrically and recorded, is indicated by the heat liberated in the reaction between arsenic(III) and cerium(IV) which is catalysed by traces of iodide ion.

K. C. BURTON AND H. M. N. H. IRVING,
Anal. Chim. Acta, 52 (1970) 441–446

DIFFRACTION OF X-RAYS BY CHAIN MOLECULES

by B. K. VAINSHTEIN

Foreword by M. F. PERUTZ

6 x 9″, xiii + 414 pages, 3 tables, 258 illus., 256 lit.refs., Dfl. 65.00, £6.10.0, $23.50

Contents: 1. Principles of the theory of X-ray diffraction. 2. Structures of chain molecules and assembli 3. Diffraction by an isolated chain molecule. 4. Scattering intensity and structure of object. 5. Properti of the distribution and interference functions. 6. Diffraction by assemblies of parallel chain molecul 7. Diffraction by assemblies with nonparallel packing of chain molecules and by amorphous polymer Subject index.

INFRA RED INSTRUMENTATION AND TECHNIQUES

by A. E. MARTIN

5¼ x 8¼″, x + 180 pages, 13 tables, 94 illus., 86 lit.refs., 1966, Dfl. 32.50, 65s., $12.00

Contents: 1. Historical. 2. Modern infra-red spectrometers. 3. Miscellaneous instruments. 4. Interferometric spectrometers. 5. Accessories. 6. Experimental methods and techniques. Index.

ENERGY TRANSFER IN RADIATION PROCESSES

Chemical, Physical and Biological Aspects

Proceedings of the International Symposium held in Cardiff, 1965

edited by G. O. PHILLIPS

5¼ x 8¼″, xvi + 182 pages, 10 tables, 81 illus., 273 lit.refs., 1966, Dfl. 32.50, 65s., $12.00

Contents: Introductions to the sections by F. S. Dainton, G. F. J. Garlick and Tikvah Alper. Invited pape by E. J. Bowen, Jett C. Arthur, N. Riehl, R. Mason. Contributed papers.

MASS SPECTROMETRIC ANALYSIS OF SOLIDS

edited by A. J. AHEARN

5¼ x 8¼″, viii + 167 pages, 13 tables, 46 illus., 242 lit.refs., 1966, Dfl. 30.00, 60s., $10.75

Contents: 1. Introductory survey. 2. The production of ions from solids. 3. Photographic emulsions as io detectors in quantitative mass spectrography. 4. Analysis of special samples. 5. Mass spectrographic micr probe analysis. Subject index.

RADIOCHEMICAL SURVEY OF THE ELEMENTS

Principal characteristics and applications of the elements and their isotopes

by M. HAISSINSKY
and
J.-P. ADLOFF

6 x 9″, ix + 177 pages, 1965, Dfl. 32.50, 65s., $12.00

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

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DETERMINATION OF TRACE CONCENTRATIONS OF BARIUM EXTRACTED FROM AQUEOUS SYSTEMS

A sensitive and reliable method for the determination of barium in aqueous systems has been developed. The combination of the solvent extraction of the barium hexafluoroacetylacetonate into isoamyl acetate with subsequent determination by atomic absorption has increased by 50%, the best sensitivity previously attained. The proposed method presents a simple, rapid method of determining barium at concentrations as low as 0.015 μg ml^{-1} with an ultimate sensitivity of 0.005 μg ml^{-1} for 1% absorbance. The use of a high concentration of potassium ion in the aqueous system improves the sensitivity. The potassium is coextracted with the barium and acts to suppress the ionization and enhance the absorption of barium. Interference effects of 55 diverse ions were studied and their tolerance levels are summarized. No significant interferences were found.

L. Edelbeck and P. W. West,
Anal. Chim. Acta, 52 (1970) 447–453

THE COULOMETRIC GENERATION OF CHROMIUM(II) IN STRONGLY ACIDIC MEDIA

PART I. COULOMETRIC TITRATION OF TITANIUM(IV)

The stability of $CrBr_2(H_2O)_4^+$ was investigated in strong acid medium (1.5–6 *M*) as a function of acid type and bromide concentration; HCl, HBr, $HClO_4$ and H_2SO_4 were used. Chromium tribromide was shown to provide a suitable working solution for at least 3 days, for the coulometric generation of chromium(II). The reduction was also studied at the D.M.E. Chromium(II) catalysed the aquation process, the effect being greatest in sulphuric acid. Conditions for 100% generating efficiency of chromium(II) were established; the range of current density for $>99.9\%$ current efficiency increased in the order $HCl < HBr < HClO_4$. Polarographic and spectrophotometric techniques showed that $CrBr(H_2O)_5^{2+}$ is the species reduced at the mercury cathode. A direct coulometric determination of titanium(IV) with electrolytically generated chromium(II) is described. Amounts of *ca.* 1 and 0.5 mg were titrated; the standard deviation for 20 determinations was ± 7 μg.

C. Sheytanov and M. Neshkova,
Anal. Chim. Acta, 52 (1970) 455–464

A STUDY OF THE OPTIMAL CONDITIONS FOR POTENTIOMETRIC TITRATION OF FLUORIDE WITH LANTHANUM AND THORIUM IN UNBUFFERED MEDIA

Some of the difficulties encountered in the titration of fluoride with fluoride-selective electrodes and lanthanum and thorium titrants have been studied in unbuffered media. The solubility product of lanthanum fluoride decreases with time as the precipitate ages and this accounts for a drift of the potential towards decreasing fluoride activity after the end-point. The solubility product of lanthanum fluoride was determined to be $10^{-17.86}$ at 25.0° in 1 *M* potassium nitrate or 1 *M* sodium chloride and the β_1 value of $La^{3+} + F^- \rightarrow LaF^{2+}$ was found to be $10^{5.15}$ under the same conditions. In accurate titrations of fluoride, lanthanum is recommended for fluoride solutions stronger than 1 m*M*, with computer evaluation. Thorium is recommended as a titrant in the range 0.2–1 m*M* fluoride.

T. Eriksson and G. Johansson,
Anal. Chim. Acta, 52 (1970) 465–473

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 orde to present a still clearer picture of the multitudinous applications open to organic spo 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 tes 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 compare with 600 tests in 346 sections in the preceding edition.

An important feature is the inclusion of a large number of recently developed tests an 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 tha physical instrumentation is always superior to chemical methods for solving analytica problems. Each of the chapters presents instances of problems for which no solutions b physical means have yet been developed, or for which the rapid spot tests are equal o 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 certai types of organic compounds. 5. Identification of individual organic compounds. 6. Application of spot tests in th differentiation of isomers and homologous compounds. Determination of constitutions. 7. Application of spo 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

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

Bulletin de la Société Chimique de Franc

... 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, pharmaceutica chemists, and biochemists. Advanced students and research workers in analytical chemistry will find these tw volumes stimulating and helpful ...

Analytical Chemistry

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

Chemistry in Britain

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147E

IODINE MONOCHLORIDE AS AN OXIDIMETRIC REAGENT FOR THE DETERMINATION OF SOME WATER-INSOLUBLE IODIDES, SULPHIDES, XANTHATES AND DITHIOCARBAMATES AND SOME DIFFICULTLY OXIDIZABLE REDUCTANTS

Back-titration procedures with iodine monochloride as the oxidant in 5 *M* hydrochloric acid medium are described for the following reductants: iodides of copper(I), lead, thallium, silver, mercury(I) and mercury(II), and bismuth; sulphides of zinc, cadmium and manganese; ethylxanthates of potassium, zinc and copper; diethyldithiocarbamates of sodium, zinc and copper, sodium hypophosphite and sodium dithionate.

P. N. Krishnan Nambisan and C. G. Ramachandran Nair,
Anal. Chim. Acta, 52 (1970) 475–482

THE DETERMINATION OF SULPHATE IN SEA WATER BY MEANS OF PHOTOMETRIC TITRATION WITH HYDROCHLORIC ACID IN DIMETHYL SULPHOXIDE

The sulphate concentration in sea water has been determined by photometric titration to hydrogen sulphate in dimethyl sulphoxide solution with hydrochloric acid, using bromocresol green as indicator. The end-point is evaluated graphically and a complete titration can be performed in less than 15 min. Since borate, carbonate and hydrogen carbonate interfere, a separate determination of the alkalinity is necessary. The method can be used satisfactorily for sea water samples with a chlorinity of at least $2^{0}/_{00}$.

D. Jagner,
Anal. Chim. Acta, 52 (1970) 483–490

A RAPID SEMI-AUTOMATIC METHOD FOR THE DETERMINATION OF THE TOTAL HALIDE CONCENTRATION IN SEA WATER BY MEANS OF POTENTIOMETRIC TITRATION

A semi-automatic potentiometric titration of the total halide concentration in sea water with silver nitrate is described. The titration is followed with a silver electrode and the titration data, which are recorded directly on punched tape and typewriter, are evaluated by means of a computer program based on the Gran extrapolation method. The determinations have a precision of ± 0.02 % and, since many samples can be titrated simultaneously, the time for a single determination including evaluation and editing of titration data can be reduced to less than 5 min.

D. Jagner and K. Årén,
Anal. Chim. Acta, 52 (1970) 491–502

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 some 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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FLUORESCENCE AND METALLIC VALENCY STATES

PART IV. AROMATIC CARBOXYLIC ACIDS AS NEW FLUORESCENT DETECTION AGENTS FOR COPPER AND VANADIUM

Copper (20 p.p.b.) in solution is selectively and simply detected with aromatic carboxylic acids by observing, under the ultraviolet lamp, the fluorescence produced in the presence of reducing agents. Vanadium (0.2 p.p.m.) can also be detected, without interference from copper, if zinc amalgam is used as the reducing agent. Few ions interfere.

K. J. KOH AND D. E. RYAN,
Anal. Chim. Acta, 52 (1970) 503–506

GAS CHROMATOGRAPHIC DETERMINATION OF TRIMETHYLSILYLATED MONO- AND DISACCHARIDES IN SUGAR CANE JUICE

The gas chromatographic determination of the mono- and disaccharides in sugar cane juice is accomplished by drying the sample under reduced pressure and converting the common free sugars into their trimethylsilyl derivatives. Myoinositol was found to be a suitable internal standard for both the isothermal monosaccharide analysis and the isothermal disaccharide (sucrose) analysis. Accuracy is assessed to be within 5%.

L. E. VIDAURRETA, L. B. FOURNIER AND M. L. BURKS, JR.,
Anal. Chim. Acta, 52 (1970) 507–518

DESIGN AND EVALUATION OF A MICRORADIOMETRIC DETECTOR FOR COLUMN LIQUID CHROMATOGRAPHY

The theory of radiometric detection is discussed. An expression for the sensitivity is derived; peak-broadening owing to mixing phenomena in the feed line and the detector cell is described. The significance of the noise is discussed. The detector has been tested with respect to peak-broadening effects, sensitivity, linearity, precision and detection limit. The results demonstrate its excellent performance. It proves to be very suitable for high-speed column liquid chromatography.

A. M. VAN URK-SCHOEN AND J. F. K. HUBER,
Anal. Chim. Acta, 52 (1970) 519–527

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.

SEPARATION AND DETERMINATION OF TRACES OF METALLIC IMPURITIES IN SILVER HALIDES

A method for the enrichment and determination of elements present in trace amounts in high-purity silver halides is described. Concentrated solutions of potassium iodide are used as solvents for the samples. The elements determined are concentrated by solvent extraction: zinc, cadmium, lead, copper, cobalt and nickel as dithizonates, and iron, aluminium and manganese as oxinates. The complexes formed are then determined spectrophotometrically. The relative lower limits of detection are of the order of 1 p.p.m. with an accuracy better than 10%.

V. Concialini, P. Lanza and M. T. Lippolis,
Anal. Chim. Acta, 52 (1970) 529–535

BIPOTENTIOMETRY IN ORGANIC REDOX SYSTEMS

PART I. OXIDATION OF AROMATIC COMPOUNDS IN TRIFLUOROACETIC ACID

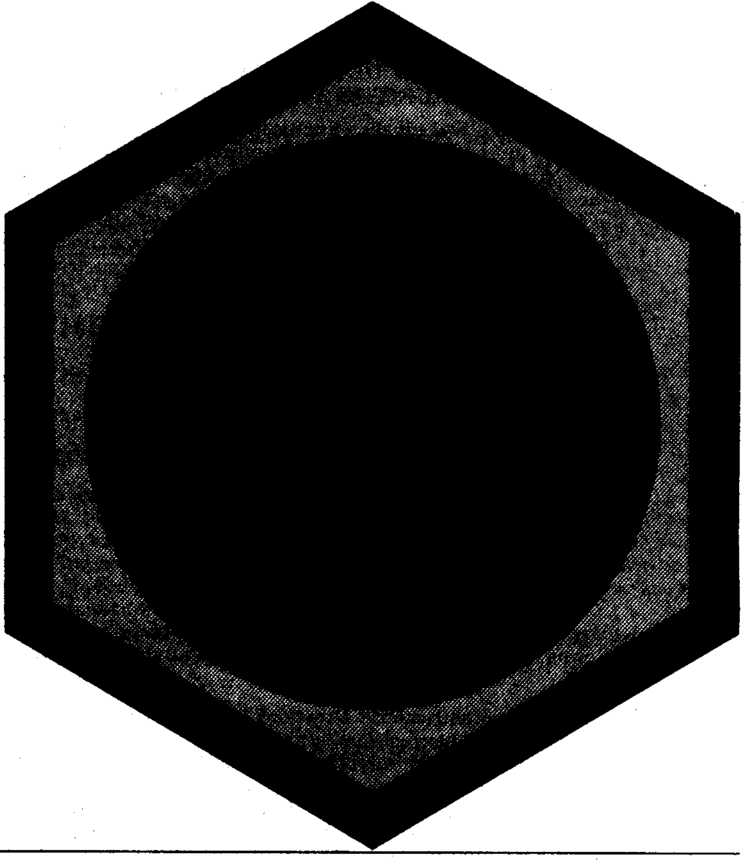
Bipotentiometric titrations of various polynuclear aromatic hydrocarbons, benzenes substituted with electron-donating groups, and π-excessive heteroaromatics in trifluoroacetic acid–dichloromethane with lead(IV) or cobalt(III) acetate solution resulted in novel titration curves. Optimum qualitative results were obtained with a 15-sec delay between additions of titrant. Each reagent increment usually resulted in the formation of a potential "saw-tooth", indicating formation and decay of reversible redox couples; the final titration curves had one or more potential minima regions before the end-point. Because of considerable differences in number, reversibility and stability of oxidation intermediates, no two aromatics of those tested gave identical curves. However, sufficient similarities existed to permit a system of curve classification and some degree of correlation. The technique is at present essentially a qualitative one. In almost all instances the titration curve for a given aromatic compound is characteristic somewhat in the manner of a spectrophotometric curve.

H. W. Yurow and S. Sass,
Anal. Chim. Acta, 52 (1970) 537–544

A COMPUTER METHOD FOR THE DETERMINATION OF THE FORMATION CONSTANTS OF COMPLEX IONS FROM SPECTROPHOTOMETRIC DATA

(Short Communication)

J. R. Siefker,
Anal. Chim. Acta, 52 (1970) 545–546



A CRITICAL ANALYSIS OF THE METHOD OF SUCCESSIVE DILUTIONS IN PHOTOMETRY

(Short Communication)

A. Shatkay,
Anal. Chim. Acta, 52 (1970) 547–550

SPECIFIC CATION-EXCHANGE SEPARATION OF NICKEL

(Short Communication)

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Interface Conversion for Polymer Coatings

Proceedings of the Symposium *held at* General Motors Research Laboratories, Warren, Michigan, October 2–3, 1967

Edited by

Philip Weiss

and

G. Dale Cheever

Polymers Department
General Motors Research Laboratories

"The symposium considered the substrate (metallic and nonmetallic) and how it may be treated or converted to make it an effective acceptor for a polymer coating. To cover interface conversion in greater depth than was possible in a two-day conference, papers on specific disciplines — such as zinc phosphate crystal formation, surfactant adsorption, and oxide nucleation — were submitted by invitation and are included as a part of the proceedings."

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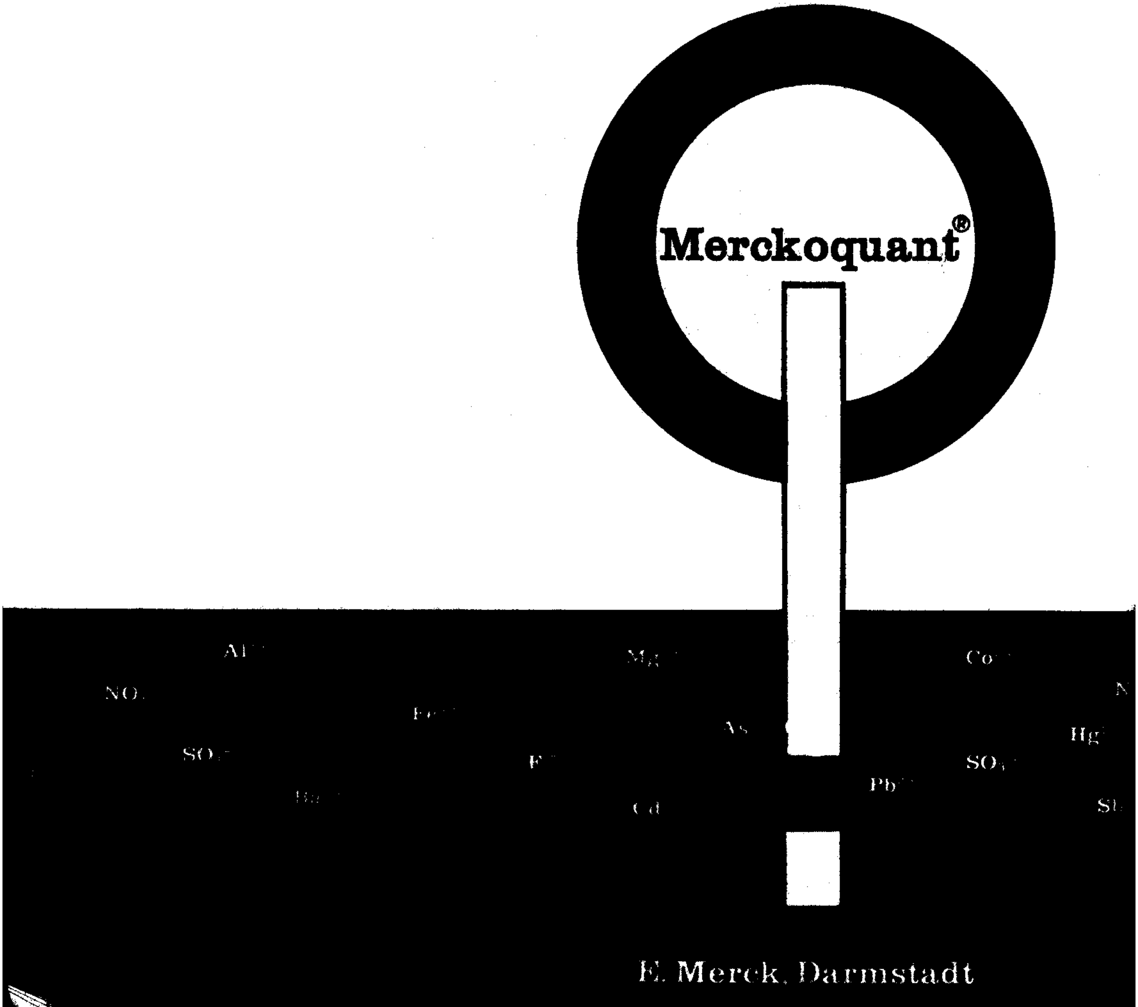
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THE AUTOMATION OF THERMAL ANALYSIS INSTRUMENTATION: DIFFERENTIAL THERMAL ANALYSIS

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Thermochemistry Laboratory, Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)

(Received July 21st, 1970)

The modern differential thermal analysis (DTA) instrument is derived from the two thermocouple design suggested by ROBERTS-AUSTEN[1] in 1899. Many instruments have been designed and constructed since that time, each slightly different in the design of the furnace, furnace programmer, recording equipment, sample holder geometry, and so on. SMOTHERS AND CHIANG[2] in 1958 described some 225 instruments located throughout the world. This list was deleted in the second edition[3] but the latter included a bibliography of some 4248 references to DTA literature, many of them describing the instrumentation employed by the investigators. Modern DTA equipment is adequately summarized in various textbooks[3-6], while specifications on commercially available instruments are described elsewhere[7].

Present-day instruments are capable of automatic operation in that after manually inserting the sample, the temperature rise is controlled by a furnace programmer which will turn off the instrument after a preselected temperature limit is attained. After cooling the furnace back to room temperature, the pyrolyzed sample is removed from the sample holder, a new sample is introduced, and the heating cycle repeated. In this paper, an automated DTA instrument which is capable of studying eight samples in a sequential manner is described. The samples are automatically introduced into the furnace, pyrolyzed to a preselected temperature limit, and then removed. After the furnace has been cooled back to room temperature, the cycle is repeated. Operation of the sample changing mechanism, furnace temperature rise and cooling, recording, and so on, is completely automatic.

EXPERIMENTAL

General instrument features

A line drawing of the sample changing mechanism, furnace and furnace platform is shown in Fig. 1.

The powdered samples are contained in glass capillary tubes, D, of 1.6–1.8 mm i.d. (Kimax No. 34050) which are placed in the circular sample holder plate, A. The aluminum sample holder plate is of 8.0 in diameter by 1/8 in thick and has provision for retaining eight glass capillary tubes. The glass tubes are held in their respective positions by means of small spring clips. The plate is rotated by a small synchronous electric motor (Hurst Type PCSM 1/2 r.p.m.) equipped with an electromagnetic clutch. The rotation of the plate by the motor is controlled by a lamp–slit–photocell arrangement. Adjacent to each sample holder position is a 0.50 × 0.06-in slit cut in the

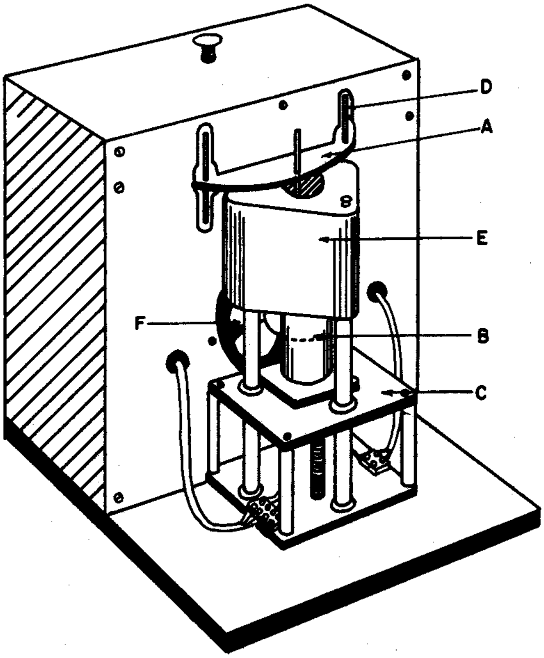

Fig. 1. General view of instrument sample changer, furnace, and furnace platform. (A) Sample holder plate; (B) furnace; (C) furnace platform assembly; (D) sample capillary tube; (E) furnace insulation; (F) cooling fan.

aluminum plate. Alignment of the plate slit between the lamp and photocell by the drive motor permits exact positioning of each capillary tube with the furnace cavity.

After the capillary tube is in position, the furnace platform, C, is raised so that the tube is positioned into the aluminum heat transfer sleeve, located on the sample thermojunction. Movement of the furnace platform is controlled by a reversible electric motor (Bodine Type KCI-S3R8, 140 r.p.m., geared down to 90 r.p.m.) con-

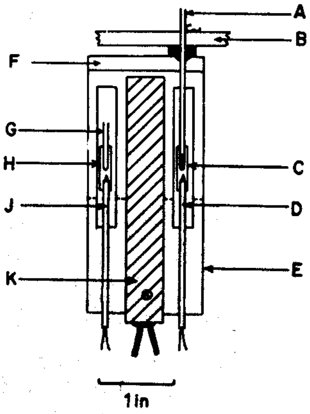

Fig. 2. Furnace and sample chamber. (A) Glass capillary tube for sample; (B) sample holder plate; (C) sample heat transfer sleeve; (D) sample thermocouple; (E) furnace block; (G) reference capillary tube; (H) reference heat transfer sleeve; (J) reference thermocouple; (K) heater cartridge.

nected to the platform by a screw-drive. Upper and lower limits of travel are controlled by two micro-switches. The furnace is insulated from the platform by a 0.25-in layer of Transite and while in the heating position, by a Marinite sleeve, E. Rotation interval for sample changing is 15 sec while it takes 50 sec to raise the furnace platform to the full upper limit.

After the sample has been heated to the upper temperature limit, the furnace is lowered, the sample holder plate rotates to a new position, and a cooling fan (Rotron muffin fan) is activated to direct air on the hot furnace. Cooling time for the furnace, from 450° to room temperature, takes about 20 min. After the furnace has been cooled to room temperature, the above cycle is repeated with a new sample.

Furnace and sample chamber

A schematic diagram of the furnace and sample chamber is shown in Fig. 2.

The cylindrical furnace, E, is of 1.5 in diameter and 3.3 in long, and is heated by a 210-W stainless-steel heater cartridge, K, (Hotwatt). The upper temperature limit of the furnace is about 500°. The sample and reference cavities are about 0.25 in diameter by 1.5 in long. Thermal contact between the sample and reference capillary tubes, A and G, is made by the aluminum heat transfer sleeves, C and H. The cylindrical sleeves are about 0.7 in long. The ends of the sleeves are drilled out so that the sample tube and the 1/16-in diameter ceramic insulator tube, D or J, fit closely within the sleeve. To minimize heat-leakage from the furnace to the sample holder plate, B, a transite cover, F, is used to enclose the top of the furnace.

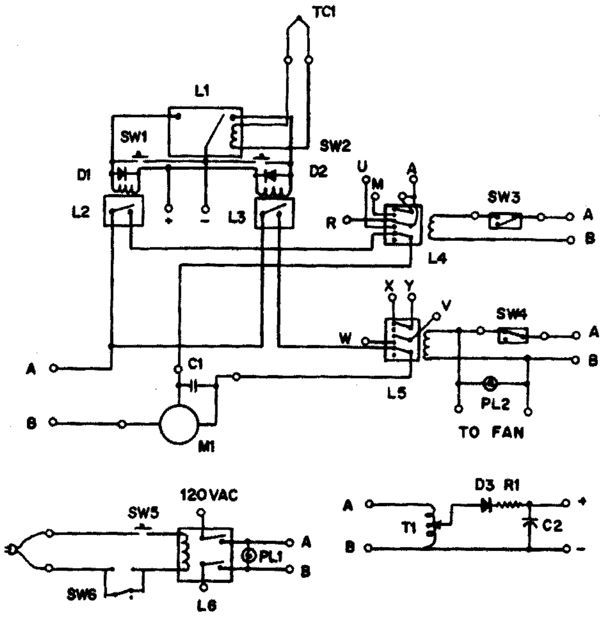

Fig. 3. Relay circuits. (L1) Meter relay, SPDT, Simpson Model 29XA, 0–50 mV; (L2 and L3) relay, SPST, 5 kΩ coil; (L4 and L5) relay, 3PDT, 120 VAC coil; (L6) latching relay, DPDT, 120 VAC coil; (C1) capacitor, 1 μfd; (C2) capacitor, 250 μfd, 25 V; (D1 and D2) diode, S93; (D3) diode, S93; (SW1, SW2, SW5) push-button switches; (SW3, SW4, SW6) micro-switches; (PL1 and PL2) pilot lamps; (M1) motor, Bodine, Type KCI-S3R8, 140 r.p.m.; (TC1) chromel–alumel thermocouple; (R1) resistor, 10 Ω, 0.5 W; (T1) variable voltage transformer, output about 13 VAC.

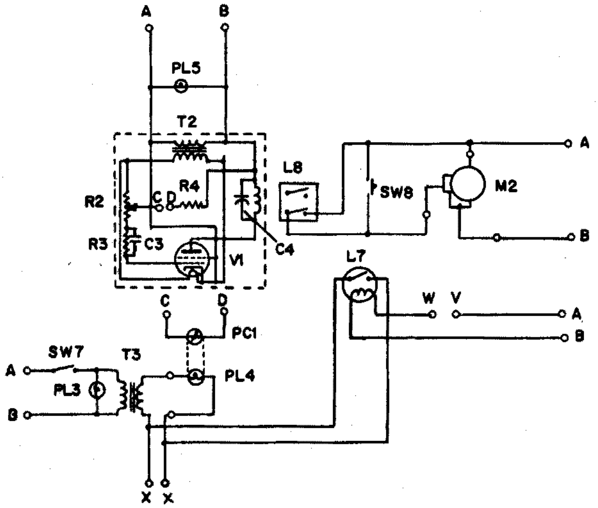

Fig. 4. Photocell and other circuits. (M2) Motor, Hurst, Type PCSM, 1/2 r.p.m.; (L7) relay, time-delay, Amperite, 115 NO5T, 5 sec delay, N.O.; (L8) relay, DPDT, 120 VAC coil; (T2 and T3) transformer, 6.3 VAC secondary; (R2) potentiometer, 500 kΩ, 3 W; (R3) resistor, 1 MΩ, 1/2 W; (R4) resistor, 100 kΩ, 1/2 W; (C3) capacitor, 500 $\mu\mu$F; (C4) capacitor, 8 mfd; (V1) 2D21 tube; (PC1) photocell, CL-602; (SW7) switch, SPST; (SW8) push-button switch; (PL3, PL4, PL5) pilot lamps.

Relay and other circuits

The relay and other circuits for the control of the sample holder plate and furnace platform assembly are shown in Figs. 3 and 4.

The low temperature limit contact of the meter relay, L1, activates the furnace platform motor, M1. Pushbutton switches, SW1 and SW2, permit manual control of the motor if so desired. The upper and lower limits of platform travel are controlled by the micro-switches, SW3 and SW4, which activate the two 3PDT relays, L4 and L5, respectively. The upper relay, L4, also activates the furnace programmer. The lower relay, L5, when closed, activates the time-delay relay, L8, and the photocell circuit[8,9].

When the temperature of the furnace reaches the upper preselected temperature limit of the meter relay, the furnace platform motor is activated and the platform lowered until it contacts the lower micro-switch. The latter then controls the positioning of a new sample and also turns on the furnace cooling fan. All power to the various circuits is through latching relay, L1. A micro-switch, SW6, is mounted in the sample holder plate to shut off the instrument after the eighth sample is run.

A schematic diagram of the instrument components and the furnace programmer is shown in Fig. 5.

The ΔT voltage from the differential thermocouples, TC2 and TC3, is amplified by a Leeds and Northrup microvolt d.c. amplifier, Model No. 9835-B, and is recorded on one channel of a Varian Model G-22 strip-chart potentiometric recorder. The sample temperature, as detected by thermocouple TC3 and the 0° reference junction thermocouple TC4, is recorded on the other channel. A chart-speed of 6 in h^{-1} was employed on all of the heating runs.

The furnace temperature programmer is similar to that previously described[10].

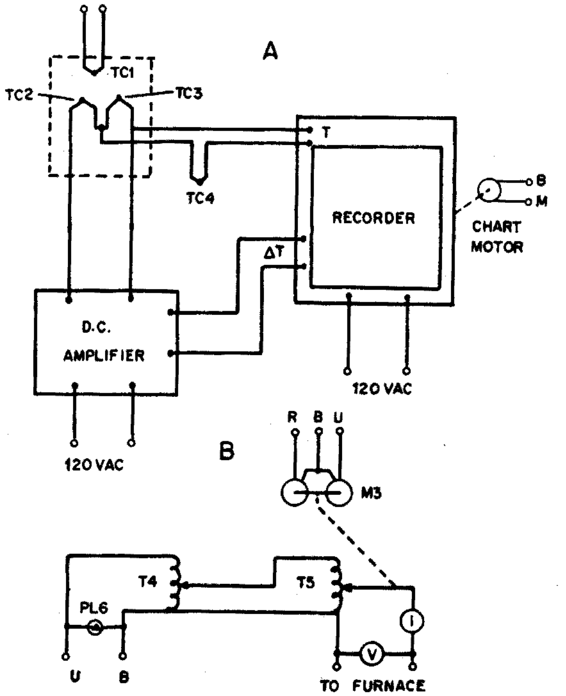

Fig. 5. (A) Schematic diagram of DTA components; (B) schematic diagram of furnace programmer. (TC2, TC3, TC4) Chromel-alumel thermocouples; (M3) motor, dual; (T4 and T5) transformer, variable voltage, Ohmite, Model No. VT3N; (PL6) pilot lamp; voltmeter, Simpson, 0–150 VAC; ammeter, Simpson, 0–5 A a.c.

Movement of the contact wiper arm of transformer T5 is controlled by a dual-speed motor unit, Bristol Type 42. The drive motor speed is 0.5 r.p.h. while the reset motor is 0.5 r.p.m. The reset limit of the wiper arm is controlled by a micro-switch connected in series with the reset motor. Variable furnace heating rates can be obtained by varying the output voltage from transformer T4. A 120 V output gives a furnace heating rate of about 7° min^{-1}; 90 V gives a heating rate of 4° min^{-1}.

Procedure

The procedure for a run consists of weighing out the samples into the eight glass capillary tubes. Sample sizes usually ranged in weight from 1 to 8 mg. The glass capillary tubes are placed in the sample holder plate, a convenient ΔT range is selected on the amplifier, and the meter relay is activated by movement of the lower temperature contact. Operation of the instrument is then completely automatic. All eight samples are heated in a sequential manner and after the eighth sample is run, the instrument shuts off all power to the various components via the latching relay.

RESULTS AND DISCUSSION

Two sequential runs of copper(II) sulfate pentahydrate samples are shown by the DTA curves in Fig. 6. The DTA curve and the temperature of the sample are shown

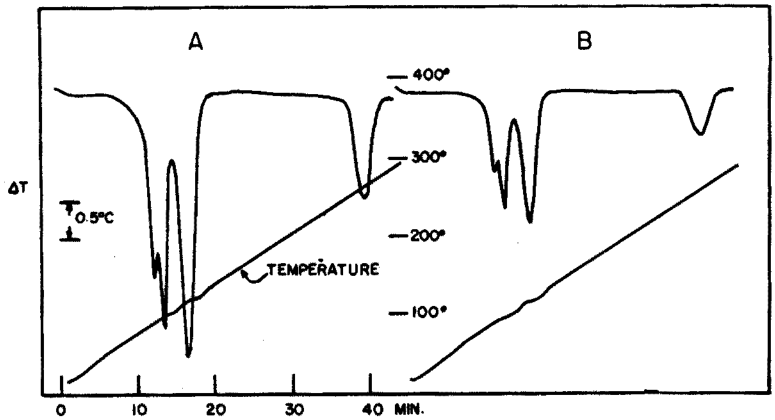

Fig. 6. DTA curves of two samples of $CuSO_4 \cdot 5H_2O$. Sample A, 5.72 mg; Sample B, 3.32 mg.

by the two curves for samples A and B. The only difference in the samples is their weight. The curves show the dehydration reactions very clearly. The first shoulder peak indicates the evolution of liquid water by the reaction,

$$CuSO_4 \cdot 5H_2O\ (s) \rightarrow CuSO_4 \cdot 3H_2O\ (s) + 2H_2O\ (l) \quad (1)$$

while the second endothermic peak is due to the vaporization of the liquid water[11]. The formation of the monohydrate is indicated by the third endothermic peak, as shown by the reaction,

$$CuSO_4 \cdot 3H_2O\ (s) \rightarrow CuSO_4 \cdot H_2O\ (s) + 2H_2O\ (g) \quad (2)$$

The fourth endothermic peak is caused by the dehydration of the monohydrate, according to,

$$CuSO_4 \cdot H_2O\ (s) \rightarrow CuSO_4\ (s) + H_2O\ (g) \quad (3)$$

A large number of inorganic salt hydrates have been studied by the automated instrument. The convenient size of the recorded curve permits the chart paper to be cut to fit a E-Z sort punched card and hence filed for easy reference at some future date. The instrument should find a wide use for routine DTA examination of a large number of samples, both inorganic and organic. The automated features of the instrument should permit convenient computer interfacing so that reaction temperatures, peak areas, and so on, can be easily calculated or tabulated.

The financial support of this work by the U.S. Air Force, Office of Scientific Research, through Grant No. 69–1620 is gratefully acknowledged. Many of the mechanical aspects of the instrument were designed and built by Mr. RALPH MARTIN. The Sun Oil Co. is acknowledged by W. S. B. for a scholarship.

SUMMARY

An automated DTA instrument is described which is capable of studying eight individual samples, each contained in a glass capillary tube, in a sequential manner. The samples are automatically introduced into the furnace, pyrolyzed to a preselected

temperature limit, and then removed. After the furnace has been cooled back to room temperature, the cycle is repeated. Operation of the sample changing mechanism, furnace temperature programming, recording, etc. is completely automatic.

RÉSUMÉ

On décrit un appareil automatique pour l'analyse thermique différentielle, capable d'examiner huit échantillons à la suite. Les substances à analyser sont introduites automatiquement dans le four, pyrolysées à une température préalablement fixée et évacuées. Après refroidissement du four, le cycle se répète. Les manipulations de l'échantillon, la programmation de la température du four, l'enregistrement, etc. sont entièrement automatiques.

ZUSAMMENFASSUNG

Es wird ein automatisiertes DTA-Gerät beschrieben, mit dem aufeinanderfolgend acht einzelne, jede für sich in einem Glaskapillarrohr befindliche Proben untersucht werden können. Die Proben werden automatisch in den Ofen eingeführt, bis zu einer vorgewählten Temperaturgrenze pyrolysiert und dann entfernt. Nachdem der Ofen auf Raumtemperatur abgekühlt ist, wird der Cyclus wiederholt. Probenwechsel, Ofentemperatursteuerung, Aufzeichnung, etc. erfolgen völlig automatisch.

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THE USE OF ORGANIC SOLVENTS IN THE DETERMINATION OF PLATINUM BY ATOMIC ABSORPTION SPECTROSCOPY

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(Received July 20th, 1970)

The determination of platinum by atomic absorption spectroscopy has been reported in a number of papers[1-9]. Recently, new procedures were recommended for both air–acetylene and nitrous oxide–acetylene flames[10,11].

The use of organic solvents has had an important impact on the atomic absorption method. Large increases in the analytical sensitivity of many elements have been obtained either by addition of miscible solvents to aqueous solutions or by the solvent extraction of the elements into an immiscible solvent layer before their determination[12-14].

Up to now, the determination of platinum by atomic absorption with organic solvents has received little consideration. VAN RENSBURG AND ZEEMAN[7] tried various organic–aqueous solutions with acetone and alcohols up to butanol in propane–butane–air flames. Only acetone and methanol nebulized satisfactorily and they found that best results were obtained when the percentage of acetone or methanol was as high as possible. The detection limit for platinum was improved from 0.30 to 0.21 p.p.m. in 95% acetone using an ultrasonic nebulizer. ZEEMAN AND BRINK[6] determined platinum in 95% acetone solutions using a non-absorbing reference line of Pt 304.2 nm in propane–butane–air flames. They found interferences from gold, base metals and precious metals when determining platinum.

MULFORD[15] described a general solvent extraction system in which the non-specific reagent, ammonium pyrrolidine-dithiocarbamate, was used to form chelates with many metals including platinum, followed by solvent extraction into methyl isobutyl ketone. Atomic absorption determinations were later done on the organic extract; platinum was extracted at a pH of 3 in this system.

The initial work with miscible solvents is of limited value since little information is provided which would be useful in many practical applications. For instance, a 95% acetone solution would render constituents of concentrated solutions of base metals and precious metals insoluble. More information of how various solvent–aqueous solutions affect the platinum sensitivity would be helpful. In addition, there is little information concerning the extent of interferences that may be encountered when these solvents are used. Since most cations and anions interfere with the platinum determination in aqueous solutions[10], a further study of these interferences with miscible solvents is essential.

Although the platinum sensitivity may be increased by using miscible solvents, in some cases, the increased sensitivity is counterbalanced by the extra dilution imposed by adding the organic solvent. Clearly, a suitable solvent extraction system in which platinum is completely extracted into an immiscible solvent layer would have several further advantages. The determination of platinum in the organic phase would enhance the sensitivity by a factor of 3 or more and secondly, platinum in large aqueous volumes could be concentrated into a small volume of the organic phase thus increasing the detection limit. An ideal solvent extraction system would selectively isolate platinum quantitatively in a solvent layer which is preferably free from coextracted ions and which has suitable burning characteristics in the flame.

In this paper, the feasibility of determining platinum by atomic absorption with various miscible solvents in air–acetylene and nitrous oxide–acetylene flames is studied in detail. The solvent extraction of platinum into ethyl acetate, which was described by AYRES AND MEYER[16], is investigated and eventually applied in a sensitive atomic absorption method for platinum with the nitrous oxide–acetylene flame.

EXPERIMENTAL

Apparatus

The Techtron 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, a 5-cm Techtron AB 50 nitrous oxide–acetylene burner and calibrated Gilmont flowmeters for air, acetylene and nitrous oxide.

Reagents

The preparation of standard stock solutions of platinum, gold, rhodium, iridium and ruthenium was described in an earlier paper[10]. Lanthanum chloride solutions were prepared by dissolving high-purity lanthanum(III) oxide in a minimum amount of hydrochloric acid. All the cations used for interference studies were chloride salts or complex chloro anions.

A fresh tin(II) chloride solution, 1.0 *M* in tin(II) chloride and 3.5 *M* in hydrochloric acid, was prepared from reagent-grade tin(II) chloride dihydrate. After the salt was dissolved in hydrochloric acid and diluted to volume, the solution was filtered through a double layer of Whatman no. 42 filter paper and stored under a layer of xylene to protect it from atmospheric oxidation.

Miscible solvents

Platinum was determined by atomic absorption spectroscopy in organic solvent–aqueous hydrochloric acid solutions of five readily available miscible solvents; these included acetone, methanol, ethanol, propanol and 1,4-dioxane. Solutions of standard platinic acid with various solvent compositions (% by volume) were prepared for each solvent and the absorbances of these solutions in air–acetylene and nitrous oxide–acetylene flames were measured. By comparing these absorbances with that of a standard aqueous solution of platinum (0.1 *M* hydrochloric acid), relative enhancements in sensitivity of the platinum determination were obtained.

Since organic solvents act as a fuel when aspirated into the burner, the acetylene fuel flow had to be lowered and strictly monitored in order to compensate for the organic solvent present in the solution and to maintain reproducible flame conditions. In the air–acetylene flame, the acetylene flow was lowered until the characteristic, clear, blue, oxidizing flame was obtained. With the nitrous oxide–acetylene flame, the oxidizing flame was established by the first appearance of the "red feather". Solvent blanks were necessary for each solvent and for every solvent–hydrochloric acid composition in order to ascertain the necessary fuel conditions and to zero the recorder. Other instrumental parameters previously recommended for both flames[10,11] were adhered to since the platinum determination was still most sensitive with the same burner heights, slit widths and lamp currents when organic solvents were used. The only exception was the air–acetylene burner height which was adjusted to 0.5 cm rather than 0.1 cm; this corresponded to the region immediately above the interconal gases.

Falconbridge precious metal concentrate samples which were treated and used in previous work[10] were again analyzed with a new procedure incorporating acetone as the miscible solvent. Aliquots of the samples taken for analysis were reduced in volume by evaporation on a steam bath and subsequently diluted with acetone to give a 60% acetone (by volume) solution. Larger proportions of acetone could not be used because they rendered the concentrated ore constituents insoluble. Enough lanthanum chloride was added to each sample to give a concentration of 2000 p.p.m. in the final solution.

Immiscible solvents

The solvent extraction of trichlorostannate(II) complexes of platinum into ethyl acetate and the analysis of the ethyl acetate extracts for platinum with the nitrous oxide–acetylene flame were studied. The influence of precious metals and commonly occurring cations on the extraction procedure and on the determination were also investigated.

The extraction procedure described by AYRES AND MEYER[16] was strictly followed. A definite quantity of standard platinum solution together with 5 ml of concentrated hydrochloric acid, 12.5 ml of 20% ammonium chloride solution (to prevent cloudiness in the extraction layers) and 10 ml of 1.0 *M* tin(II) chloride were added to a 75-ml separatory funnel; the solution was diluted to a final volume of 50 ml with doubly distilled water. A 15-ml aliquot of ethyl acetate was added to the separatory funnel and the contents were shaken thoroughly. After separation of the layers, the ethyl acetate extract was transferred to a volumetric flask. The extraction procedure was repeated with a second aliquot of ethyl acetate to ensure the complete extraction of platinum. The combined extract was diluted to volume in the volumetric flask with ethyl acetate ready for aspiration into the nitrous oxide–acetylene flame. Platinum was determined in the ethyl acetate solution by using the same procedure outlined for miscible solvents. The acetylene flow was adjusted to 2.0 l min^{-1} when the ethyl acetate was aspirated into the flame; other instrumental parameters were the same.

RESULTS AND DISCUSSION

Determination of platinum in miscible solvents

The procedure described above was applied to the determination of platinum in methanol, ethanol, propanol, acetone and 1,4-dioxane with solvent–hydrochloric acid (0.1 *M*) compositions of 20%, 40%, 60% and 80% by volume. Table I shows the results of this study in air–acetylene and nitrous oxide–acetylene flames; all the

TABLE I

DETERMINATION OF PLATINUM WITH MISCIBLE SOLVENTS IN AIR–ACETYLENE AND NITROUS OXIDE–ACETYLENE FLAMES

Solvent	*Organic solvent (% by volume)*	*Air–acetylene flame*[a,b]		*Nitrous oxide–acetylene flame*[a,c]	
		Fuel flow (l min^{-1})	*Absorbance*	*Fuel flow (l min^{-1})*	*Absorbance*
Aqueous	0	1.25	0.124	3.00	0.030
Methanol	20	1.25	0.124	3.00	0.027
Methanol	40	1.12	0.123	2.87	0.031
Methanol	60	1.00	0.140	2.75	0.037
Methanol	80	0.87	0.184	2.62	0.051
Ethanol	20	1.25	0.112	3.00	0.028
Ethanol	40	1.12	0.097	3.00	0.027
Ethanol	60	1.12	0.108	2.87	0.030
Ethanol	80	1.00	0.140	2.87	0.039
Propanol	20	1.25	0.122	3.00	0.033
Propanol	40	1.12	0.112	2.87	0.030
Propanol	60	1.00	0.113	2.75	0.030
Propanol	80	0.87	0.126	2.62	0.036
Acetone	20	1.00	0.136	3.00	0.029
Acetone	40	0.75	0.138	2.75	0.031
Acetone	60	0.50	0.173	2.50	0.048
Acetone	80	0.50	0.268	2.50	0.068
1,4-Dioxane	20	1.25	0.124	2.87	0.031
1,4-Dioxane	40	1.25	0.118	2.75	0.031
1,4-Dioxane	60	1.00	0.122	2.62	0.033
1,4-Dioxane	80	0.87	0.149	2.50	0.041

[a] Concentration of platinum in all cases was 50 p.p.m. and aqueous solutions were 0.1 *M* in hydrochloric acid.

[b] Instrumental parameters: burner height = 0.5 cm, lamp current = 10 mA, slit width = 150 μm, air flow rate = 6 l min^{-1}, scale expansion = × 1.

[c] Instrumental parameters: burner height = 1 cm, lamp current = 10 mA, slit width = 150 μm, nitrous oxide flow rate = 4.5 l min^{-1}, scale expansion = × 5.

recorded absorbances were for 50-p.p.m. platinum solutions. Additional measurements, which are not tabulated, were made for platinum solutions ranging in concentration from 10 p.p.m. to 50 p.p.m. with an 80% organic solvent composition. This established that Beer's law was obeyed for platinum in all solvents and in both flames.

With all five solvents, the platinum sensitivity was increased when the highest organic solvent composition of 80% was used. Acetone and methanol were the most efficient and they enhanced the platinum absorbance by factors of 2.2 and 1.5, respectively, in air–acetylene flames. Similar factors of 2.3 and 1.6 were obtained in nitrous oxide–acetylene flames. Solutions with a high composition of acetone or methanol (*i.e.* 80% by volume) had lower viscosities, lower surface tensions and higher vapour pressures than those of ethanol, propanol and 1,4-dioxane[17] and therefore larger amounts of analyte reached the flame.

Acetone was selected as the most useful solvent since it had the best enhancement of sensitivity. The effects of different burner parameters on the platinum determination in acetone solutions are shown in Table II. In air–acetylene flames, the

TABLE II

THE EFFECT OF DIFFERENT BURNER PARAMETERS ON THE ABSORBANCE OF 50-p.p.m. PLATINUM SOLUTIONS IN 80% ACETONE SOLUTIONS

Air–acetylene flames[a]	*Acetylene flow rate (l min^{-1})*		
Burner height (cm)	*1.25*	*1.00*	*0.50*
0.1	0.022	0.041	0.143
0.3	0.063	0.120	0.260
0.5	0.077	0.117	0.268
1.0	Too noisy	0.139	0.268

Nitrous oxide–acetylene flames[b]	*Acetylene flow rate (l min^{-1})*		
Burner height (cm)	*3.0*	*2.5*	*2.0*
0.5	0.045	0.056	0.067
1.0	0.048	0.066	0.068
1.5	0.051	0.063	0.063

[a] Air flow rate = 6 l min^{-1}.
[b] Nitrous oxide flow rate = 4.5 l min^{-1}

best sensitivity was obtained with burner heights between 0.3 and 1.0 cm (this corresponds to the region immediately above the interconal gases) and the lowest acetylene flow rate of 0.50 l min^{-1}; the flame was extinguished with any further reductions of the acetylene flow. In nitrous oxide–acetylene flames, the sensitivity was best at a burner height of 1.0 cm and the lowest possible acetylene flow rate of 2.0 l min^{-1}.

Interferences. Before these better sensitivities become analytically useful, several questions must be answered. Does the use of solvents such as acetone reduce the interferences which occur in air–acetylene flames? If not, does the addition of lanthanum chloride effectively eliminate these interferences? Do nitrous oxide–acetylene flames remove possible interferences in organic solvents?

To answer these questions, the interference effects of some selected cations on platinum solutions were studied in both air–acetylene and nitrous oxide–acetylene flames; these cations included Na(I), Fe(III), Cu(II), Ni(II), Al(III), Cr(III), Au(III), Pd(II), Rh(III), Ir(III) and Ru(IV). Acetone was used as the organic solvent. Three different types of experiments were conducted.

1. The absorbances of 40 p.p.m. platinum in dilute hydrochloric acid solutions (0.1 *M*) were measured with different concentrations of concomitant added.

2. The absorbances of 40 p.p.m. platinum in acetone–hydrochloric acid solutions (80% acetone by volume) were measured with the same concentrations of concomitant added. This enabled a comparison of the interference effects in the two types of solutions.

3. The absorbances of 40 p.p.m. platinum in acetone–hydrochloric acid solutions (80% acetone by volume) containing 2000 p.p.m. of lanthanum chloride were measured using the same concomitant concentrations. From this last experiment, it could be determined if lanthanum chloride was efficient in removing possible interferences.

In the nitrous oxide–acetylene flames, only the latter two experiments were attempted since it has already been established that these flames eliminated all interferences in aqueous solutions[11].

Table III summarizes the results. The interferences in the hydrochloric acid

TABLE III

EFFECTIVE CATIONIC INTERFERENCES ON THE PLATINUM ABSORBANCE (40 p.p.m.) IN ACETONE SOLUTIONS

(A. Air–acetylene flame. Burner height = 0.5 cm, lamp current = 10 mA, slit width = 0.49 nm, air flow rate = 6 l $\min^{-1}$, acetylene flow rate (aqueous) = 1.5 l $\min^{-1}$ or (acetone) = 0.50 l $\min^{-1}$, scale expansion = ×1.
B. Nitrous oxide–acetylene flame. Burner height = 1.0 cm, lamp current = 10 mA, nitrous oxide flow rate = 4.5 l $\min^{-1}$, acetylene flow rate (acetone) = 2.50 l $\min^{-1}$, scale expansion = ×5.
C. Nitrous oxide–acetylene flame. Burner height = 2.0 cm; other parameters as in B.
Aqueous solutions were 0.1 *M* in hydrochloric acid)

Concn. of concomitant (p.p.m.)	*Solvent composition*	*Concn. $LaCl_3$ (p.p.m.)*	*Concomitant*										
			Na(I)	*Fe(III)*	*Cu(II)*	*Ni(II)*	*Al(III)*	*Cr(III)*	*Au(III)*	*Pd(II)*	*Rh(III)*	*Ir(III)*	*Ru(IV)*
A. Stand.	Aqueous	—	0.094	0.094	0.094	0.094	0.094	0.094	0.094	0.094	0.094	0.094	0.094
50	Aqueous	—	0.041	0.079	0.026	0.083	0.032	0.045	0.091	0.077	0.044	0.049	0.043
250	Aqueous	—	0.047	0.065	0.025	0.046	0.030	0.050	0.089[a]	0.046[a]	0.036[a]	0.046[a]	0.046[a]
Stand.	80 % acetone	—	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214
50	80 % acetone		0.045	0.167	0.052	0.210	0.036	0.064	0.207	0.199	0.072	0.074	0.048
250	80 % acetone		0.066	0.122	0.037	0.095	0.031	0.064	0.204[a]	0.161[a]	0.042[a]	0.057[a]	0.031[a]
Stand	80 % acetone	2000	0.188	0.188	0.188	0.188	0.188	0.188	0.188	0.188	0.188	0.188	0.188
50	80 % acetone	2000	0.204	0.177	0.154	0.196	0.191	0.171	0.190	0.187	0.175	0.133	0.128
250	80 % acetone	2000	0.196	0.146	0.092	0.193	0.127	0.102	0.184[a]	0.185[a]	0.156[a]	0.088[a]	0.083[a]
B. Stand.	80 % acetone	—	0.054	0.054	0.054	0.054	0.054	0.054	0.054	0.054	0.054	0.054	0.054
50	80 % acetone	—	0.054	0.055	0.054	0.054	0.054	0.055	0.053	0.055	0.050	0.046	0.048
250	80 % acetone	—	0.055	0.054	0.054	0.054	0.055	0.055	0.054[a]	0.055[a]	0.046[a]	0.041[a]	0.045[a]
Stand.	80 % acetone	2000	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055
50	80 % acetone	2000	0.054	0.055	0.055	0.054	0.056	0.056	0.056	0.054	0.054	0.055	0.055
250	80 % acetone	2000	0.055	0.055	0.054	0.055	0.056	0.057	0.056[a]	0.054[a]	0.055[a]	0.056[a]	0.055[a]
C. Stand.	80 % acetone	—	—	—	—	—	—	—	—	—	0.050	0.050	0.050
50	80 % acetone	—	—	—	—	—	—	—	—	—	0.050	0.048	0.048
200	80 % acetone	—	—	—	—	—	—	—	—	—	0.048	0.047	0.046

[a] Concentration of concomitant: 200 p.p.m.

solutions in the air–acetylene flame were similar in magnitude with those observed in a previous paper[10]. The interferences in 80% acetone solvent were similar to those in the aqueous solutions with the exceptions of Na(I), Cr(III), Al(III), Rh(III), Ir(III) and Ru(IV), for which the interferences were worse. The reduction in sensitivity caused by these interferences was similar in all regions of the flame. At higher burner heights of 1.0 cm and 1.5 cm, the effect of interferences was slightly less, but not significantly less. This would be expected, since non-volatile platinum compounds would have a longer time to dissociate. The addition of lanthanum chloride reduced the interferences but did not completely eliminate them. From these results, it was concluded that the use of acetone to enhance the platinum sensitivity in air–acetylene flames was not practical with the one exception of determining platinum in simple solutions which contained only platinic acid.

On the other hand, the use of acetone in nitrous oxide–acetylene flames was successful with the added advantage of doubling the normal sensitivity. The interferences observed with the air–acetylene flames were completely eliminated with the exceptions of Rh(III), Ir(III) and Ru(IV). These three interferences were removed by either adding lanthanum chloride to the 80% acetone solution or by measuring the absorbance at a burner height of 2.0 cm rather than 1.0 cm. It should be emphasized here that burner heights below 1.0 cm should be avoided because various other cations begin to interfere slightly.

Since the Falconbridge precious metal concentrate contains large concentrations of precious metals including rhodium, iridium and ruthenium, several samples were analyzed with the new procedure described above. Platinum determinations in the nitrous oxide–acetylene flame yielded a mean value of 1.21% ± 0.06% (platinum) which agreed with previous determinations (see Table IV).

TABLE IV

DETERMINATION OF PLATINUM IN A PRECIOUS METAL CONCENTRATE IN A 60% ACETONE SOLUTION IN A NITROUS OXIDE–ACETYLENE FLAME

Weight of sample (g)	*Pt found (μg)*	*% Pt*	*Deviation from mean (%)*
0.2210	2753	1.24	+ 0.03
0.2208	2507	1.14	− 0.07
0.2436	2750	1.13	− 0.08
0.2089	2510	1.21	0.00
0.2349	3122	1.33	+ 0.12
	Mean value	1.21 % ± 0.06	
ZACHARIASEN AND BEAMISH[19]		1.21 %	
Falconbridge Nickel Mines Ltd.		1.36 %	

Conclusions. The addition of miscible solvents to platinum solutions generally enhances the sensitivity of the atomic absorption method. Acetone is the most efficient of the miscible solvents examined and in nitrous oxide–acetylene flames, an 80% acetone solution increases the platinum sensitivity from 7.0 μg ml^{-1} for 1% absorption to a value of 3 μg ml^{-1} for 1% absorption and lowers the detection limit from 2 p.p.m. to 1 p.p.m. Air–acetylene flames have limited use in this application because of the restrictions imposed by the interferences which cannot be eliminated entirely. However, platinum is easily determined in acetone solutions by means of the nitrous oxide–acetylene flame with complete removal of interferences. This is an important improvement over the aqueous determination, because it makes the nitrous oxide flame more competitive with the air–acetylene one which has normally been used for aqueous solutions.

Determination of platinum in immiscible solvents

Platinum in the form of *cis* and *trans* $[PtCl_2(SnCl_3)_2]^{2-}$, was completely extracted from hydrochloric acid solutions into the ethyl acetate layer; these isomers are the major species known to exist in solution under the given experimental conditions[18]. Beer's law was obeyed for platinum concentrations up to 50 p.p.m. in the ethyl acetate layer (see Table V). The platinum sensitivity was increased to 2.1 μg ml^{-1} for 1% absorption and the detection limit lowered to 0.5 p.p.m. By comparing these values with those obtained from previous methods with nitrous oxide–acetylene flames (Table VI), it was apparent that this extraction procedure with an immiscible solvent provided the best sensitivity and detection limit. This was due to the favourable physical properties of ethyl acetate such as a low viscosity and a high vapour pressure; in addition, it was possible to aspirate a solution which had an organic solvent composition of close to 100%.

TABLE V

DETERMINATION OF PLATINUM IN ETHYL ACETATE EXTRACTS WITH NITROUS OXIDE–ACETYLENE FLAMES[a]

Volume ratio aqueous : organic	*Concn. of Pt (p.p.m.) (aqueous layer)*	*Concn. of Pt (p.p.m.) (ethyl acetate layer)*	*Absorbance*
1:1	5	5	0.011
1:1	10	10	0.023
1:1	15	15	0.034
1:1	20	20	0.044
1:1	50	50	0.102
2:1	25	50	0.105
5:1	10	50	0.102

[a] Scale expansion × 5.

TABLE VI

A COMPARISON OF SENSITIVITIES AND DETECTION LIMITS IN NITROUS OXIDE–ACETYLENE FLAMES

Solution composition	*Sensitivity*[a]	*Detection limit (p.p.m.)*
0.1 *M* Hydrochloric acid[10]	7.0	2.0
80 % Acetone–20 % hydrochloric acid (0.1 *M*)	3.0	1.0
100% Ethyl acetate	2.1	0.5

[a] μg ml^{-1} for 1% absorption.

By varying the volume of ethyl acetate, platinum in large volumes of aqueous solutions could be concentrated into smaller volumes of organic solvent. Platinum was efficiently extracted with aqueous-to-solvent volume ratios of 2:1 and 5:1. This effectively reduced the detection limit to 0.1 p.p.m. for aqueous solutions and made this procedure the most sensitive of all the atomic absorption methods developed for platinum.

Interferences. The extraction and determination procedure was applied to a number of solutions containing standard platinic acid and various concomitants including Rh(III), Ir(III), Ru(IV), Pd(II), Au(III), Fe(III), Cu(II), Ni(II), Cr(III), Na(I) and Ca(II). The results are tabulated in Table VII. Rh(III), Ir(III) and Pd(II) were partially extracted with platinum into the ethyl acetate layer; however, they did not interfere with the platinum determination.

TABLE VII

DETERMINATION OF PLATINUM IN ETHYL ACETATE EXTRACTS OF AQUEOUS SOLUTIONS CONTAINING OTHER CONCOMITANTS[a]

Concomitant	*Concn. of concomitant (p.p.m.) (aqueous layer)*	*Concn. of Pt (p.p.m.) (ethyl acetate layer)*	*Absorbance*
Standard	—	20	0.044
Rh(III)	50	20	0.046
	200	20	0.044
Ir(III)	50	20	0.044
	200	20	0.043
Ru(IV)	50	20	0.044
	200	20	0.044
Pd(II)	50	20	0.045
	200	20	0.044
Au(III)[b]	50	20	0.044
	200	20	0.045
Fe(III)	250	20	0.046
	1000	20	0.043
Cu(II)	250	20	0.043
	1000	20	0.044
Ni(II)	250	20	0.044
	1000	20	0.046
Cr(III)	250	20	0.045
	1000	20	0.045
Na(I)	250	20	0.044
	1000	20	0.045
Ca(II)	250	20	0.045
	1000	20	0.045

[a] Original aqueous solution contained platinum and concomitant with concentration indicated in the Table.

[b] Au(III) was initially extracted from the aqueous layer with ether.

Gold(III) formed a dark brown colour in tin(II) chloride solutions which was partially co-extracted with platinum. A dark precipitate gradually formed in the ethyl acetate layer. It appeared as though the gold was slowly reduced to the metal. The exact chemistry of these reactions was not clear; presumably, gold formed a trichlorostannate(II) complex which was not stable in ethyl acetate. This difficulty was avoided by preliminary treatment of platinum solutions containing gold. Before the usual extraction procedure was applied, gold in the form of chloroauric acid was quantitatively separated by extraction into ether.

The other concomitants which included Ru(IV), Fe(III), Cu(II), Ni(II), Cr(III), Na(I) and Ca(II) were not extracted into ethyl acetate and did not interfere with the platinum determinations.

Conclusions. The quantitative extraction of platinum from solutions of tin(II) chloride furnishes a rapid method of isolating platinum from many other elements. The ethyl acetate extract improves the platinum sensitivity in nitrous oxide–acetylene flames over the previous platinum determinations in dilute hydrochloric acid[11] and miscible solvent–hydrochloric acid solutions. By concentration of platinum into the organic phase, the effective detection limit of aqueous solutions can be lowered to 0.1 p.p.m.; for this reason, this is the most sensitive atomic absorption procedure for platinum yet developed. The practical concentration range is 0.5–50 p.p.m. for aqueous platinum solutions.

The corresponding spectrophotometric method[16] which uses the same reagents and procedure has an optimum concentration range of 3–25 p.p.m. The co-extraction of rhodium, iridium and palladium constitutes a serious limitation on the spectrophotometric determination. The atomic absorption method removes these limitations and is therefore a superior analytical method.

The platinum determination in air–acetylene flames has a practical range of 1–100 p.p.m.; the method is useful to analysts who are not equipped for the nitrous oxide flames and who wish to do sensitive, direct determinations on aqueous solutions.

On the other hand, the practical concentration ranges with nitrous oxide–acetylene flames are 4–200 p.p.m. for direct aqueous determinations, 2–100 p.p.m. for 80% acetone solutions and 0.5–50 p.p.m. with solvent extraction into ethyl acetate. The nitrous oxide flame is preferred because it has a wider range of application and removes many uncertainties with regard to interferences, especially if large concentrations of other precious metals are present.

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SUMMARY

Miscible and immiscible organic solvents are successfully applied in the atomic absorption determination of platinum with nitrous oxide–acetylene flames. A procedure is described which incorporates acetone solutions to increase the platinum sensitivity to 3 μg ml^{-1} for 1% absorption and the detection limit to 1 p.p.m. In another procedure, platinum is extracted into ethyl acetate which increases the sensitivity to 2.1 μg ml^{-1} for 1% absorption and the detection limit to 0.5 p.p.m. Interferences from noble metals and associated base metals are completely removed in both procedures.

RÉSUMÉ

Des solvants organiques miscibles et non miscibles ont été employés avec succès pour le dosage du platine par absorption atomique, avec des flammes oxyde nitreux–acétylène. On décrit une méthode utilisant l'acétone, et qui permet d'obtenir une sensibilité de 3 μg ml^{-1} de platine, pour 1% d'absorption et une limite de détection de 1 p.p.m. On décrit un autre procédé, avec extraction du platine dans l'acétate d'éthyle: sensibilité 2.1 μg ml^{-1} pour 1% d'absorption et limite de détection de 0.5 p.p.m. Les interférences d'avec les métaux nobles et d'autres métaux de base sont totalement éliminées dans les deux méthodes.

ZUSAMMENFASSUNG

Bei der Atomabsorptionsbestimmung von Platin mit Lachgas–Acetylen-Flammen werden mischbare und unmischbare organische Lösungsmittel mit Erfolg angewendet. Bei dem einen beschriebenen Verfahren wird durch die Verwendung von Acetonlösungen die Empfindlichkeit des Platins auf 3 μg ml^{-1} für 1% Absorption und die Nachweisgrenze auf 1 p.p.m. verbessert. Bei einem anderen Verfahren wird Platin mit Äthylacetat extrahiert. Dies ergibt eine Empfindlichkeit von 2.1 μg ml^{-1} für 1% Absorption und eine Nachweisgrenze von 0.5 p.p.m. Störungen durch Edelmetalle und begleitende unedle Metalle werden bei beiden Verfahren vollständig beseitigt.

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THE USE OF WATER-MISCIBLE ORGANIC SOLVENTS IN ATOMIC ABSORPTION SPECTROPHOTOMETRY

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The enhancement of the absorption signal of an element obtained through the use of organic solvents in the sample solution is well known[1-6] and is believed to arise, among other factors, because of an increase in the proportion of finer droplets[3,4,7]. Although WILLIS[8] has pointed out that chemical interferences are usually expected to be a function of droplet size, the effectiveness of organic solvents in reducing many of these interferences did not receive much attention until recently[9-11]. The purpose of the work described here was to study the use of some water-miscible organic solvents for reducing chemical interferences in addition to increasing analytical sensitivities by atomic absorption methods. The work is presented in three parts.

Enhancement studies

Methanol, ethanol and acetone mixed in different proportions with aqueous solutions of various elements were investigated for relative enhancements by the solvents. The enhancement is defined as the ratio of the absorbance of a given concentration of an element in the medium containing the organic solvent to that obtained in water.

Interferences in different matrices

Interference effects observed in the determination of the elements Cu, Mn, Fe, Zn, Rb, Ca and Mg in samples of fresh waters, soil extracts and plant materials were compared with those obtained by the addition of an organic solvent to the sample solutions.

Applications

The above elements were determined in different types of material and in viscous substances, *e.g.* phosphoric acid and phosphorus oxychloride, after suitable dilution with acetone and the use of appropriate flames.

EXPERIMENTAL

Reagents

AnalaR grade solvents and distilled deionized water were used for solution and dilution. Stock solutions of the respective elements were prepared by dissolving AnalaR grade materials in 5% hydrochloric acid.

Absorbance measurements

Absorbance measurements in the air–acetylene flame were carried out with a Perkin–Elmer 303 atomic absorption spectrophotometer unless otherwise stated. Calcium and magnesium were also determined in the nitrous oxide–acetylene flame, by means of a Techtron AA-4 instrument with an AB-52 burner. Data on gas flow rates are given in Table I.

TABLE I

DATA ON THE VARIOUS GAS FLOW RATES USED FOR AQUEOUS AND 50% ACETONE–WATER SOLUTIONS

Instrument	*Atomizing system*	*Gas composition*	*Gas flows (l min^{-1})*			
			Aqueous soln.		*50% Acetone–water soln.*	
			Oxidant	*Fuel*	*Oxidant*	*Fuel*
Perkin–Elmer 303	Premix with standard nebulizer	Air–C_2H_2	22.0	3.4	18.0	2.0
Techtron AA-4	Premix with standard Techtron nebulizer and AB-51 burner	Air–C_2H_2	9.0	1.4	9.0	1.0
Techtron AA-4	AB-52 burner	N_2O–C_2H_2	8.5	4.2	8.5	4.0

It was observed during these measurements that absorption by the flame in presence of an organic solvent depended strongly on the part of the flame intercepting the light beam. All measurements were therefore carried out with the burner so adjusted that absorption by the flame on aspirating a pure organic solvent was a minimum.

Methods

Enhancement studies. A stock solution of the element under study was diluted with the organic solvent–water mixtures to obtain different concentrations of the element with varying proportions of organic solvent. The absorbance of each solution was then measured to obtain relative enhancements by the different solvents.

Interferences in various matrices. Solutions of the matrices were obtained as described under RECOMMENDED PROCEDURES. To investigate the interferences in the determination of an element the following procedure was adopted.

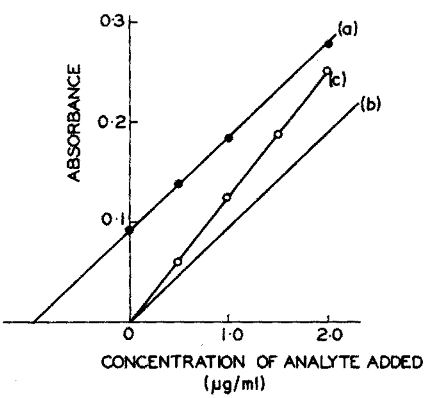
The absorbance–concentration curve of the analyte alone was obtained for a given solvent mixture, and then the corresponding curve obtained by adding known amounts of the analyte to a solution of the matrix in the same solvent mixture. The ratio of the slopes of these curves represented a measure of the interference (Fig. 1).

Applications. The determination of various elements was carried out in different types of material by obtaining absorbance–concentration curves for the respective matrices as described and reading off these. For the determination of elements in viscous materials, *e.g.* phosphoric acid, it was found necessary to dilute the samples in the ratio 1:4 with acetone.

RESULTS AND DISCUSSION

Enhancement studies

The effects of solvent composition on absorbance in an air–acetylene flame are shown in Table II. The general trend is towards greater enhancement with increased volume percent of the organic solvent, the effect being most pronounced with acetone. The solvent concentration effect is least in the case of zinc and most in the case of rubidium. The enhancements obtained for the elements copper, manganese, calcium, magnesium and iron are nearly equal for a given organic solvent mixture. It will also be observed that the enhancement decreases somewhat with increase in concentration of the analyte for each of the solvent–water mixtures. This results in non-linearity of the absorbance curves in the presence of organic solvents, particularly at higher volume percentages of the latter in the mixtures. An organic solvent concentration of 50% was found to be optimum for making use of the enhancement effect with slight loss in linearity of the absorbance–concentration curves. The observed enhancement may be attributed to the fact that with organic solvents a greater volume of solution reaches the flame per unit time than with water[3] and also to the finer drop-size in the spray. The non-linearity observed at higher concentrations of the analyte for a given solvent composition would appear to be due to a decrease in the degree of dispersion at these concentrations. These observations are in agreement with those of WILLIS[8], that particle size in the flame plays a major role in determining the atomization efficiency. Support for this view was also found in the observation that the use of a Techtron spray chamber with a glass bead (used for selecting finer droplets) did not produce very appreciable enhancements. However, if the glass bead was removed,



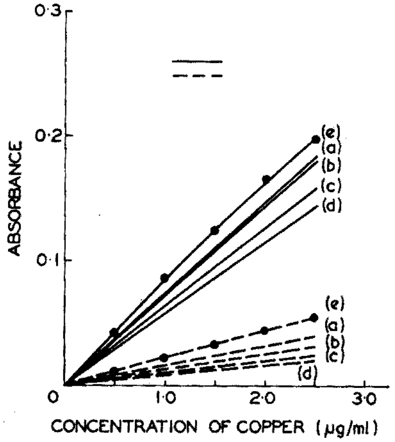


Fig. 1. Procedure for obtaining a working curve for the sample matrix: (a) standard addition plot for the matrix, (b) working curve for the matrix obtained by drawing a parallel to (a), (c) absorbance–concentration curve in simple medium. Relative interference = ratio of the slopes of (b) and (c).

Fig. 2. Working curves for copper in different matrices: (- - - -) aqueous solution, (——) 50% acetone–water mixtures. (a) Water sample matrix, (b) soil leach matrix, (c) plant material matrix, (d) body tissue matrix, (e) simple medium containing only analyte.

TABLE II

ENHANCEMENT IN ATOMIC ABSORPTION FOR Cu, Mn, Fe, Zn AND Rb WITH VARIOUS ORGANIC SOLVENTS IN THE AIR–C_2H_2 FLAME

Element	*Concn. in final soln.* ($\mu g\ ml^{-1}$)	*Organic solvent*	*Enhancement*[a] *Vol. % of organic solvent* 20	40	50	80
Cu						
324.7 nm	2	Methanol	1.3	1.45	1.5	2.1
	5		1.3	1.4	1.5	2.0
	2	Ethanol	1.4	1.7	1.8	2.0
	5		1.4	1.5	1.7	1.95
	2	Acetone	1.55	2.85	4.2	5.4
	5		1.5	2.7	3.6	5.2
Mn						
279.5 nm	2	Methanol	1.2	1.45	1.6	2.2
	5		1.2	1.45	1.6	2.1
	2	Ethanol	1.5	1.6	1.7	2.1
	5		1.4	1.5	1.7	2.0
	2	Acetone	1.55	2.95	4.2	5.45
	5		1.5	2.9	3.7	5.15
Fe						
248.3 nm	2	Methanol	1.3	1.5	1.9	2.3
	5		1.3	1.5	1.8	2.2
	2	Ethanol	1.4	1.6	1.8	2.3
	5		1.4	1.5	1.7	2.1
	2	Acetone	1.6	2.5	2.8	4.9
	5		1.6	2.5	2.6	4.8
Zn						
213.8 nm	2	Methanol	1.5	1.7	1.9	1.9
	5		1.5	1.7	1.8	1.8
	2	Ethanol	1.4	1.5	1.7	—
	5		1.4	1.4	1.7	1.8
	2	Acetone	1.7	2.5	2.6	3.3
	5		1.6	2.4	2.3	3.2
Rb						
780.0 nm	2	Methanol	1.35	1.6	2.8	5.0
	5		1.35	1.5	2.7	4.8
	2	Ethanol	1.6	2.1	2.3	3.9
	5		1.55	1.9	2.2	3.8
	2	Acetone	1.9	3.8	4.8	6.1
	5		1.8	3.2	3.8	5.4
Ca						
422.7 nm	2	Methanol	2.3	1.45	1.8	2.3
	5		2.28	1.45	1.8	2.2
	2	Ethanol	1.3	1.5	1.7	2.2
	5		1.3	1.5	1.7	2.1
	2	Acetone	1.6	2.45	2.7	4.8
	5		1.6	2.4	2.65	4.8
Mg						
285.2 nm	2	Methanol	1.3	1.5	1.8	2.25
	5		1.3	1.45	1.8	2.2
	2	Ethanol	1.35	1.5	1.8	2.3
	5		1.35	1.5	1.75	2.2
	2	Acetone	1.6	2.5	2.8	4.8
	5		1.6	2.5	2.7	4.75

[a] Enhancement is expressed as the ratio of absorbance in the organic solvent mixture to that obtained in water for the same concentration of the analyte.

TABLE III

RELATIVE INTERFERENCES OBTAINED IN THE DETERMINATION OF VARIOUS ELEMENTS IN AQUEOUS AND IN 50% ACETONE SOLUTIONS

Element	*Relative interference*[a]							
	Fresh water		*Soil*		*Plant material*		*Biological tissue*	
	Aq.	*50% org.*	*Aq.*	*50% org.*	*Aq.*	*50% org.*	*Aq.*	*50% org.*
Cu	0.7 –0.75	0.88–0.95	0.6 –0.8	0.85–0.90	0.50–0.70	0.70–0.80	0.45–0.7	0.70–0.85
Mn	0.6 –0.7	0.95–0.98	0.65–0.8	0.95–0.98	0.6 –0.7	0.72–0.85	0.5 –0.7	0.70–0.85
Zn	0.7 –0.8	0.90–0.95	0.7 –0.8	0.85–0.9	0.5 –0.6	0.65–0.75	0.65–0.7	0.92–0.96
Rb	0.7 –0.9	0.95–1.0	0.65–0.8	0.85–0.9	0.45–0.8	0.75–0.92	0.7 –0.8	0.88–0.95
Fe	0.7 –0.85	0.95–1.0	0.8 –0.9	0.95–1.0	0.7 –0.8	0.85–0.95	0.7 –0.8	0.9 –0.98
Ca (Air–C_2H_2	0.6 –0.8	0.85–0.95	0.8 –0.9	0.95–0.98	0.80–0.9	0.82–0.95	0.75–0.85	0.90–0.95
(N_2O–C_2H_2	0.9 –0.95	0.92–1.0			0.85–0.95	0.90–1.0		
Mg (Air–C_2H_2	0.85–0.9	0.95–0.98	0.8 –0.9	0.92–0.95	0.75–0.9	0.90–0.98	0.75–0.95	0.90–0.98
(N_2O–C_2H_2	0.9 –1.0	0.95–1.0			0.85–0.9	0.95–1.0		

[a] Defined as $\dfrac{\text{Slope of absorbance–concentration plot observed in matrix}}{\text{Slope of absorbance–concentration plot observed in simple medium}}$

very marked enhancements were observed with organic solvent mixtures. Higher enhancement in the case of rubidium may be ascribed to a decrease in the extent of ionization*.

Interferences in various matrices

Figure 2 shows typical absorbance–concentration plots for copper in various matrices in aqueous solutions and in 50% acetone–water mixtures. The interference in a given medium is defined as the ratio of the slope of the absorbance–concentration plot for the analyte in the sample matrix to that for the analyte alone.

The results in Table III show that interferences can be reduced by the use of organic solvents and by a high-temperature flame.

It is not possible at this stage to comment on the mechanisms by which the organic solvents tend to diminish these interferences although it seems that the basic reason may be the formation of smaller particles which can decompose more quickly and to a higher degree than the coarser ones.

RECOMMENDED PROCEDURES

The samples are brought into solution by the following sample preparation procedures.

Fresh waters

Take 1 l of the filtered sample in a beaker, acidify with 2 ml of hydrochloric acid and evaporate to about 100 ml. If silica appears, filter and transfer the residue to a platinum dish. Add a few drops of hydrochloric acid followed by hydrofluoric acid

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* Measurements by the sodium line reversal method showed that the air–acetylene flame temperature dropped by 100–150° when 50% acetone solutions were aspirated compared to aqueous ones.

and evaporate to remove the silica. Add 2 ml of hydrochloric acid and combine with the filtrate. Transfer to a 100-ml volumetric flask and make up to volume.

Soils

Select a representative soil sample, thoroughly mix, grind finely and dry at 110° in an electrically heated oven. Leach 1.0 g of the dried sample with 20-ml aliquots of the extractant (*N* ammonium chloride) and make up to 100 ml with water.

Plant material and body tissue

Oven-dry about 2.0 g of the sample, add 0.5 ml of hydrochloric acid and ash the dried material in a muffle furnace at 450°. Add 0.25 ml of hydrochloric acid again and make up to 100 ml with water.

The absorbance–concentration curves for the sample matrix in 50% acetone–water mixtures are obtained as follows.

Take four 10-ml aliquots of the sample in 25-ml beakers and add 0, 5, 10, 20 μg of the analyte respectively to each. Evaporate to reduce the volume and mix thoroughly. Transfer to a graduated flask and make up the volume to 10 ml with water. Add 10 ml of acetone, mix well and transfer to stoppered flasks. Measure the absorbance of each and plot against the amount added. Obtain the result by interpolation.

Phosphoric acid and phosphorus oxychloride

Take four 5-ml aliquots of the sample in 25-ml volumetric flasks. To each add 1 ml containing a known concentration of the analyte. Make up the volume with acetone. Measure the absorbance of each and construct the calibration curve. Determine the concentration in the sample by interpolation.

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SUMMARY

The use of water-miscible organic solvents in atomic absorption spectrophotometry is discussed with reference to the enhancement of analytical sensitivity and the reduction of interferences. Application to the determination of the elements Cu, Mn, Zn, Fe, Rb, Ca and Mg in fresh waters, plant materials, soils, biological tissues and some viscous inorganic materials is described.

RÉSUMÉ

On examine les possibilités d'utilisation de solvants organiques miscibles à l'eau, pour améliorer la sensibilité et réduire les interférences en spectrophotométrie par absorption atomique. On décrit un dosage des éléments Cu, Mn, Zn, Fe, Rb, Ca et Mg dans les eaux naturelles, les plantes, les sols, les tissus biologiques et certains produits inorganiques visqueux.

ZUSAMMENFASSUNG

Es wird die Verwendung mit Wasser mischbarer organischer Lösungsmittel für die Atomabsorptionsspektrophotometrie im Hinblick auf die Verbesserung der analytischen Empfindlichkeit und die Verringerung von Störungen erörtert. Die Anwendung auf die Bestimmung der Elemente Cu, Mn, Zn, Fe, Rb, Ca und Mg in Süsswasser, Pflanzen, Böden, biologischen Geweben und einigen viskosen anorganischen Stoffen wird beschrieben.

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THE DETERMINATION OF TRACE AMOUNTS OF LEAD IN HIGH-ALLOY STEELS BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROSCOPY

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SCHOLES[1] has reviewed the application of atomic absorption spectroscopy (a.a.s.) to the determination of elements, including lead, in steels. There are few problems in the determination of lead at the 0.005% level and above in cast iron, mild and low-alloy steels. However, large amounts of chromium and nickel, as present in high-alloy steel, interfere[2,3]. The interferences are difficult to interpret and therefore a preliminary solvent extraction stage is necessary for the determination of lead in high-alloy steels.

CHAKRABARTI *et al.*[4] extracted lead as the tetraiodoplumbate ion, into methyl isopropyl ketone in the determination of trace amounts of lead in water by a.a.s. DAGNALL AND WEST[5] have studied the extractions of lead oxinate and lead diethyldithiocarbamate into methyl isobutyl ketone (hexone) and determined lead by a.a.s. in some commercially available products such as chocolate samples, beer and gasoline. WEST *et al.*[6] have also determined trace amounts of lead in steels, brass and bronze alloys after extraction of tetraiodoplumbate into hexone. In the case of steel samples they found it necessary to remove iron by preliminary solvent extraction. They found that a 5–6-fold increase in sensitivity was obtained on spraying the hexone layer into the flame after iodide extraction of the lead and noted no interference from 1000-fold molar amounts of several cations including iron(III), chromium(III) and copper(II). However, most of the samples analysed were mild steels.

It was thought, at first, that a method for the determination of trace amounts of lead in high-alloy steels should be straightforward after prior removal of the iron and subsequent extraction of lead as its iodo complex into hexone. On examination of the method, however, small amounts of iron(III) and copper(II) produced an appreciable interference, in conflict with the findings of WEST *et al.*[6]. This is attributed mainly to the formation of iodine which inhibits the extraction of lead. The percentage extraction of lead, however, becomes constant above a certain amount of liberated iodine. Copper, extracted into the hexone layer, shows slight interference with the lead absorbance, quite apart from the effect of liberating iodine and consequent inhibition of the lead extraction. This interference, however, also becomes constant above a certain amount of copper. The method proposed here to overcome these difficulties involves adding a constant amount of copper both to the steel solutions and to the calibration solutions before extraction into hexone. The effects of copper and liberated iodine are then constant between the steel samples and the calibration solutions. Although the method involves two solvent extraction procedures it is still very much quicker than the standard dithizone method[7] and the results obtained for the determination of lead in eight high-alloy steels are considered perfectly satisfactory.

EXPERIMENTAL

Apparatus

A Unicam SP 90 atomic absorption spectrophotometer and a lead hollow cathode lamp were used.

Standard instrumental conditions

Air–propane (used for studies in aqueous solution).

Wavelength	217.0 nm	Air	pressure	30 p.s.i.
Slit width	0.10 mm		flow	5 l min^{-1}
Burner height	1.4 cm	Propane	pressure	10 p.s.i.
Lamp current	6 mA		flow	0.4 l min^{-1}

Air–acetylene (used for studies in organic phase after solvent extraction).

Wavelength	217.0 nm	Air	pressure	30 p.s.i.
Slit width	0.10 mm		flow	5 l min^{-1}
Burner height	0.4 cm	Acetylene	pressure	10 p.s.i.
Lamp current	6 mA		flow	0.6 l min^{-1}

Reagents

All the reagents used were of analytical-reagent grade.

Standard lead solution (100 p.p.m.). Dissolve 0.1599 g of AnalaR anhydrous lead nitrate in distilled water and make up to 1 l with water. Store in a polythene bottle.

Standard copper solution (0.24% w/v). Dissolve 0.24 g of copper foil in the minimum volume of 50% (v/v) nitric acid with gentle heating. Add 10 ml of concentrated hydrochloric acid, evaporate to dryness and bake until all nitrous fumes have been evolved. Cool and dissolve the residue in 25 ml of distilled water. Transfer to a 100-ml graduated flask and dilute to the mark with water. Store in a polythene bottle.

Analysis of high-alloy steels

Dissolve 2.00 g of the alloy in 25 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid. Evaporate the solution to dryness and bake until all nitrous fumes have been evolved. Cool and dissolve the residue in 25 ml of 8 *M* hydrochloric acid with a minimum of boiling. Transfer to a 125-ml separating funnel, add 50 ml of diisopropyl ether and shake for 1 min. Allow the layers to separate and run the lower aqueous layer into a beaker. Wash the organic layer with three 2-ml portions of 8 *M* hydrochloric acid and add the washings to the beaker. Evaporate the solution in the beaker to dryness, and redissolve the salts in 25 ml of distilled water with gentle warming. Add 15 ml of 50% (v/v) hydrochloric acid and 10 ml of 6% (w/v) hydroxylammonium chloride. Simmer gently for a few minutes and remove from the hot plate. Allow to cool and add a further 10 ml of 6% (w/v) hydroxylammonium chloride.

Transfer to a 250-ml separating funnel and make up to about 135 ml with distilled water. Add 5 ml of standard copper solution and 10 ml of 43% (w/v) potassium iodide solution. Pipette 20 ml of hexone into the funnel, shake for 1 min and allow the layers to separate. Discard the aqueous layer and run the hexone layer into a beaker containing 0.25–0.5 g of anhydrous sodium sulphate. Filter the hexone solution through a Whatman 541 filter paper into a stoppered polythene bottle and spray into the flame. Read off the lead content from the calibration graph.

Preparation of calibration graph. From a burette transfer 0, 2, 4, 6, 8, 10 ml of 10-p.p.m. lead solution (prepared by appropriate dilution of the standard lead solution) into separate 250-ml separating funnels. Dilute each to about 120 ml with distilled water and add 15 ml of 50% (v/v) hydrochloric acid. Add 5 ml of standard copper solution and 10 ml of 43% (w/v) potassium iodide solution, and continue as described above. The calibration graph is linear from 0 to 5 p.p.m. lead in the hexone layer.

RESULTS AND DISCUSSION

Preliminary investigations in aqueous solution

An air–propane flame was found to be more sensitive than an air–acetylene flame. Optimum sensitivity (1% absorption) in the former flame was 0.28 p.p.m. lead compared with 0.43 p.p.m. in the latter flame. In both flames the resonance line at 217.0 nm was found to be more sensitive than the one at 283.3 nm.

All of the following information in this section was obtained with the air–propane flame for the resonance line at 217.0 nm. All solutions contained 5 p.p.m. lead. Both a 5000-fold amount of chromium and a 3000-fold amount of nickel increased the absorbance of a 5-p.p.m. lead solution. In addition, solutions with these high concentrations of chromium and nickel gave positive absorbances even in the absence of lead. The "blank" absorbances were inconsistent and difficult to interpret. These results are in agreement with those of other workers[2,3] for an air–acetylene flame.

Organic solvents are well known to enhance the absorbance of many elements in atomic absorption spectroscopy[8]. It was thought that the use of an aqueous organic solution, in addition to increasing the sensitivity of the method, might possibly eliminate the interference of chromium and nickel. Although enhancement was observed, the effect was far less marked than with some other elements. A solution containing 20% (v/v) n-propanol enhanced the absorbance by a factor of 1.6 relative to aqueous solution. This was the largest enhancement found in a study of the effects of 0–60% (v/v) methanol, ethanol, n- and iso-propanol. This limited enhancement for lead has been observed by several other workers[4,5,9]. Both chromium (5000-fold amount) and nickel (3000-fold amount) gave severe positive interference in 20% (v/v) n-propanol. In addition, as with the results in aqueous solution, positive absorbances were obtained even in the absence of lead.

It became obvious, at this stage, that to determine lead in high-alloy steels containing high concentrations of chromium and nickel, a preliminary solvent extraction stage, to isolate the lead, is necessary.

The extraction of lead as tetraiodoplumbate into methyl isobutyl ketone

On spraying the organic layer, after extraction of lead as tetraiodoplumbate into hexone, into the air–propane flame, the background noise became excessive. In an attempt to reduce this noise by lowering the propane flow rate, the flame simply "lifted off" the burner. The background noise, however, on spraying the extract into an air–acetylene flame, under the conditions described in the experimental section, was minimal. All subsequent work was carried out with the air–acetylene flame.

DAGNALL *et al.*[10], in a study of the determination of lead spectrophotometrically with 4-(2-pyridylazo)-resorcinol, established optimum conditions for the extraction of lead as its iodo complex into hexone, the results being more promising than extraction into methyl isopropyl ketone[11]. They found that optimum extraction was obtained from a solution which was 5% in hydrochloric acid and 7% in potassium iodide. By consideration of the absorbance of the hexone layer after extraction of lead, the optimum conditions obtained in the present work were from a solution which was 5% in hydrochloric acid and which contained 4 ml of saturated potassium iodide in a total aqueous volume of 150 ml; this amount of iodide is equivalent to 10 ml of 43% (w/v) potassium iodide solution as stated in the procedure. No further extraction was obtained after 1 minute of shaking. Some lead remained in the aqueous phase after a single shaking. Atomic absorption measurement of the hexone and aqueous layers after one, two and three extractions, indicated that only 82% of the lead was extracted after one extraction. This was consistently found to be the case. A hexone extract containing 4.1 p.p.m. lead gave an absorbance of 0.132 which corresponded to a sensitivity (1% absorption) of 0.14 p.p.m. This is approximately a 3-fold increase in sensitivity over aqueous solutions in the air–acetylene flame under optimum conditions.

Interference from chromium, nickel and iron

Assuming a 2-g sample weight, a steel containing 0.01% lead extracted into 20 ml of hexone gives a solution containing 10 p.p.m. lead (approximately, in view of the incomplete extraction). On addition of sufficient chromium and nickel to the aqueous solution to correspond to 25 and 20%, respectively, in steel, no interference on the lead absorbance was observed after the extraction procedure. This is to be expected as neither chromium nor nickel is extracted. However, on extracting a solution containing lead and iron(III) corresponding to 60% in steel, a severe depression of the absorbance was obtained and a red coloration of the hexone layer was observed. Iron(II), however, produced no such red colour and no interference. In view of the large amounts of iron(III) present in the aqueous solution after steel dissolution, a preliminary separation of iron was deemed necessary.

The solvent extraction separation of iron from hydrochloric acid solution is well documented[12,13]. No detailed investigations were carried out but a single shaking of a solution, 8 *M* in hydrochloric acid, with diisopropyl ether proved to be satisfactory for the removal of most of the iron. A trace of iron(III) remained in the aqueous phase after the extraction which caused depression of the lead absorbance in the hexone layer after iodide extraction. However, the addition of hydroxylammonium chloride reduced the iron(III) to iron(II) and no interference then occurred.

Interference from other elements

The interference of other elements found in minor amounts in steels was then investigated. As in the study of the interferences of chromium, nickel and iron, a number of other elements, in amounts corresponding to their maximum possible concentration in steel, were added to a solution of lead and extracted into hexone after addition of hydroxylammonium chloride. The lead content of the hexone layer in this study was 5 p.p.m. (actually 4.1 p.p.m., in view of 82% extraction). This corresponds to 0.005% lead in steel based on a 2-g sample weight after extraction into 20 ml of hexone. The concentration (equivalent percentage in steel) of each element studied is given in parenthesis after the element. There was no interference from manganese (10%), aluminium (10%), molybdenum (5%), cobalt (2%), vanadium (2%), niobium (2%), titanium (1%), boron (1%), sulphur (0.5%) and phosphorus (0.5%). Interference was considered to have occurred if the lead absorbance altered by more than ±4% from its value in the absence of interferent. This is considered a satisfactory precision for lead in the region of 0.005% in steel.

Copper(II), however, produced severe depression of the lead absorbance (Fig. 1). As in the case of iron(III), on extraction of copper(II) into hexone a red colour was observed in the organic extract. This was thought to be due to liberated iodine, according to the reaction:

$$2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI + I_2$$

Attempts to prevent the interference of copper by addition of ethylenediaminetetraacetic acid were unsuccessful.

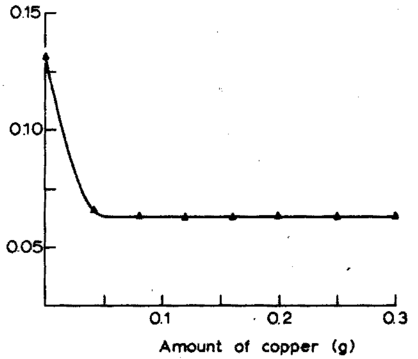

Fig. 1. Effect of copper in the aqueous phase on the lead absorbance after extraction into methyl isobutyl ketone.

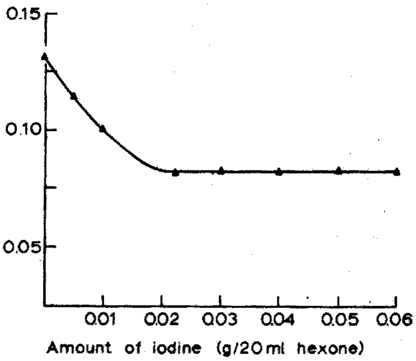

Fig. 2. Effect of iodine in the methyl isobutyl ketone layer on the lead absorbance after extraction.

Interference of iodine

The partition coefficient of iodine between hexone and water is very high; no iodine could be detected spectrophotometrically in the aqueous phase after shaking with hexone. The effect of extracting lead into hexone containing various amounts of added iodine is shown in Fig. 2. The similarity with the effect of copper (Fig. 1) was noted. In an attempt to elucidate whether the interference of iodine was spectral, chemical or otherwise, lead was extracted into 20 ml of hexone and increasing volumes of a solution of iodine in hexone were added to the organic extract each time. The volume was adjusted to 25 ml with hexone in each case, the solutions containing 3.3 p.p.m. lead and 0–0.1 g iodine per 25 ml of hexone. None of the solutions showed any variation in absorbance. In other words iodine, liberated in the presence of copper, must inhibit the extraction since iodine itself does not interfere with the lead absorbance. This was shown to be the case by examination of the aqueous phase after extraction of lead with hexone containing increasing amounts of iodine. The amount of lead remaining in the aqueous phase increased as the amount of iodine increased.

The amounts of iodine liberated on extraction of lead plus varying amounts of copper, were determined spectrophotometrically, and the equation proposed earlier was confirmed. The "flame" absorbances obtained, however, on extracting lead plus added copper (Fig. 1) were consistently found to be lower than those obtained on extracting lead into hexone containing iodine (Fig. 2). It is assumed that copper extracted into hexone interfered slightly with the lead absorbance. The effect shown in Fig. 1, therefore, is explained in the following way. Copper present in the aqueous solution, before extraction with hexone, liberates iodine which inhibits the extraction of lead. The percentage extraction of lead, however, becomes constant above *ca.* 0.024 g of iodine liberated in the 20 ml of hexone. The copper which is extracted into hexone[14] causes a slight depression of the absorbance. This interference also becomes constant above a certain level of copper (in view of the parallel nature of the plateaux of Figs. 1 and 2). It is estimated that the effect of copper becomes constant above 0.01 g present in the aqueous solution before extraction. The solution to this problem is obvious. One needs to ensure that the amount of copper present in both the sample and the calibration solutions, before extraction, is such that on extraction, the amount of iodine liberated falls on the plateau of Fig. 1. The amount of copper must also exceed 0.01 g, since up to this amount copper interferes with the lead absorbance. These conditions are achieved by adding 5 ml of the standard copper solution (equivalent to 0.012 g of copper) to the aqueous solution before the final extraction.

On extracting steels without the added copper, 0.02–0.03 g of iodine was consistently found in the hexone layer. All of this cannot have been formed from the

TABLE I

RESULTS FOR THE DETERMINATION OF LEAD IN HIGH-ALLOY STEELS BY ATOMIC ABSORPTION SPECTROSCOPY

Alloy		*Lead content*		
		Dithizone method[a] (%)	*A.a.s.*[b] (%)	*A.a.s.*[c] (%)
1[d]	0.20% Cu	0.0025	0.0025	0.0025
2[d]		0.0045	0.0040	0.0045
3	9% Ni, 18% Cr, 0.25% Cu	0.0015	0.0015	0.0015
4		0.0035	0.0035	0.0035
5		0.0030	0.0025	0.0025
6		0.0025	0.0025	0.0025
7		0.0035	0.0035	0.0030
8	11% Ni, 18% Cr, 0.20% Cu	0.0015	0.0015	0.0015
9		0.0055	0.0055	0.0060
10		0.0007	0.0003	0.0005

[a] Values quoted by the British Steel Corporation.
[b] Values obtained by the recommended procedure.
[c] Values obtained by calibration with B.C.S.334 (containing 0.10% copper) with lead additions. No copper was added to either the steel samples or calibration solutions before extraction in this case.
[d] Low-alloy steels.

copper present in the steels (normally of the order of 0.25%). The total amount of iodine liberated from the steels with added copper, however, never exceeded 0.06 g and hence falls on the plateau. It is suggested that in analysing steels with high copper contents, care should be exercised in calibrating the method.

Application to high-alloy steels

Results for the determination of lead in eight high-alloy steels by the proposed procedure are shown in Table I. The analyses of two low-alloy steels are also included. The values obtained by reference to a calibration curve prepared from B.C.S.334 (containing 0.10% copper) with lead additions are also shown. No copper was added to the steel samples in this case. The results are considered satisfactory and the method, although involving two solvent extraction stages, is considerably shorter than the standard dithizone method.

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SUMMARY

A method is described for the determination of 0.001–0.01% lead in high-alloy steels by atomic absorption spectroscopy following solvent extraction. After sample dissolution, the bulk of the iron is removed by extraction with diisopropyl ether and residual traces of iron(III) are reduced with hydroxylammonium chloride. Lead is extracted as tetraiodoplumbate into methyl isobutyl ketone and the organic extract is sprayed into the flame. Iodine, which is liberated during the iodide extraction, particularly in the presence of copper, inhibits the extraction of lead, and the copper which is extracted also produces slight interference. Both the effects can be standardised by the addition of 0.012 g of copper to the aqueous solution before the iodide extraction in both the steel samples and the lead solutions for calibration.

RÉSUMÉ

On décrit une méthode pour le dosage de 0.001 à 0.01% de plomb dans les aciers, par spectroscopie par absorption atomique, après extraction dans un solvant. Après dissolution de l'échantillon, le fer est éliminé par extraction avec l'éther diisopropylique; les traces de fer(III) résiduelles sont réduites par le chlorhydrate d'hydroxylamine. Le plomb est extrait comme tétraiodoplombate dans la méthylisobutylcétone; l'extrait organique est vaporisé dans la flamme. L'iode formé, spécialement en présence de cuivre, gêne l'extraction du plomb; le cuivre qui est extrait produit également une légère interférence.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von 0.001–0.01% Blei in hochlegierten Stählen durch Atomabsorptionsspektroskopie nach vorhergehender Solventextraktion beschrieben. Nach Auflösung der Probe wird die Hauptmenge Eisen durch Extraktion

mit Diisopropyläther entfernt, die restlichen Eisen(III)-Spuren werden mit Hydroxylammoniumchlorid reduziert. Blei wird als Tetrajodoplumbat mit Methylisobutylketon extrahiert und der organische Extrakt direkt in die Flamme gesprüht. Jod, das während der Jodidextraktion besonders in Gegenwart von Kupfer freigesetzt wird, beeinträchtigt die Bleiextraktion; auch das extrahierte Kupfer stört etwas. Beide Effekte können dadurch standardisiert werden, dass die wässrige Lösung vor der Jodidextraktion sowohl bei den Stahlproben als auch bei den Blei-Eichlösungen mit 0.012 g Kupfer versetzt wird.

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THE COULOMETRIC TITRATION OF SODIUM SECONAL AND SODIUM SANDOPTAL AND ITS APPLICATION TO THE ANALYSIS OF STANDARD BLOOD SERUM SAMPLES*

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Several coulometric methods for the determination of olefins by titration with electrogenerated bromine have been described in the literature[1-4]. The bromine usually is generated at a platinum anode from an acidic solution of bromide ions. Several methods of end-point detection are available and have been employed.

At least one reference to the coulometric titration of sodium seconal with electrogenerated bromine has appeared in the literature[5]. These workers found that the reaction proceeded too slowly to be measured directly; therefore a residual titration with standard arsenite was performed. The generating solution consisted of potassium bromide and sulfuric acid, and the end-point was detected amperometrically. This titration has not been applied to sodium sandoptal nor to biological materials.

The present paper describes a detailed investigation of the reaction between electrogenerated bromine and these two allylic barbituric acid derivatives, and the applicability of this titration to the analysis of standard blood serum samples.

EXPERIMENTAL

Apparatus

All coulometric measurements were made with a Microcoulometric Quantalyser Model 6 (ChrisFeld Precision Instruments, Beltsville, Md.). The current output of this instrument was calibrated by measurement of the potential drop across a 100-Ω, 0.1% precision resistor with a Leeds and Northrup 8687 Potentiometer.

Several titration cells were investigated for titrations with electrogenerated bromine. The cell that was eventually selected was a 30-ml beaker with a platinum-foil electrode (1 cm^2, E. H. Sargent Co.) as generating anode. A small piece of platinum wire served as the cathode and was isolated from the titration cell by means of a glass tube constructed of "thirsty glass" (porous Vycor, Corning Glass Works, Corning, N.Y.). A small volume of potassium nitrate solution was employed as catholyte.

The biamperometric end-point detection system was used by imposing a potential difference of 200 mV across two identical platinum-wire electrodes. The entire electrode assembly was contained in a rubber stopper which rested on top of the titration vessel. The titration solution was agitated by means of a magnetic stirring bar.

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The potential across the indicating electrodes was supplied by a Sargent Model XV Polarograph. All biamperometric end-points were determined by recording the changes in current on this polarograph. The titration curve obtained was the reverse-L type, and the end-point was taken as the current reading 0.4 μA above the base line.

Reagents

All chemicals were reagent grade whenever possible, and were employed without further purification. The solution employed for generating bromine consisted of 1.0 *M* sodium bromide and 0.2 *M* sulfuric acid.

Procedures

Standard solutions. The barbiturates were weighed out as the sodium salt and diluted to volume in a volumetric flask with distilled water. Generating solution (15 ml) was added to the titration cell by means of a polyethylene Measure-Matic Dispenser (E.H. Sargent Co.). The standard solution of the barbiturate as the sodium salt was added next by means of a calibrated microliter pipet and titrated.

Analysis of blood serum samples–standard u.v. spectrophotometric procedure without protein precipitation[6,7]. To exactly 1.00 ml of blood serum was added 4.0 ml of pH 6.1 phosphate buffer. Chloroform (35 ml) was added and the mixture was shaken for 1 min in a 60-ml separatory funnel fitted with a Teflon stopcock. The chloroform layer was filtered through Whatman No. 41 filter paper and then extracted with 5.0 ml of 0.45 *N* sodium hydroxide. The sodium hydroxide layer was collected and centrifuged. Two 2.0-ml portions of the centrifuged sodium hydroxide extract were pipetted into two 10-ml Erlenmeyer flasks. To one portion was added 0.5 ml of 16% (w/v) ammonium chloride, and to the other was added 0.5 ml of 0.45 *N* sodium hydroxide. The difference in absorbance of these two solutions was measured at 260 nm with the ammonium chloride portion in the reference beam and the sodium hydroxide portion in the sample beam.

A standard calibration curve was prepared in the following manner. Different volumes of a standard aqueous solution of the sodium salt of the barbiturate were added to a 5.0-ml volumetric flask and diluted to the mark with 0.45 *N* sodium hydroxide. Two 2.0-ml portions of this solution were pipetted into two 10-ml Erlenmeyer flasks. To one flask was added 0.5 ml of 16% ammonium chloride, and to the other was added 0.5 ml of 0.45 *N* sodium hydroxide. The difference in absorbance of these two solutions was measured at 260 nm, and this figure was plotted against the concentration (mg%) of the standard solution.

Analysis of blood serum samples–standard u.v. spectrophotometric procedure with protein precipitation[6–8]. To 1.00 ml of blood serum was added 7.0 ml of distilled water, 1.0 ml of 0.33 *M* sulfuric acid, and 1.0 ml of 10% (w/v) sodium tungstate solution. The mixture was shaken vigorously and centrifuged. A 5.0-ml aliquot of the clear supernate was taken and extracted with 35 ml of chloroform. The remainder of the procedure was identical to the u.v. procedure without protein precipitation.

Analysis of blood serum samples—coulometric. To 1.00 ml of blood serum was added 7.0 ml of distilled water, 1.0 ml of 0.33 *M* sulfuric acid, and 1.0 ml of 10% sodium tungstate solution. The mixture was shaken vigorously and centrifuged. A 5.0-ml aliquot of the clear supernate was extracted with 35 ml of chloroform. The chloroform extract was filtered through Whatman No. 41 filter paper and extracted with 5.0 ml of 0.45 N sodium hydroxide. The alkaline extract was acidified with 0.5 ml of 6 M hydrochloric acid and extracted with 30 ml of chloroform. The chloroform extract was added to a 30-ml beaker and evaporated to dryness under nitrogen at 80°. The residue was dissolved in 15 ml of generating solution (1.0 M sodium bromide and 0.2 M sulfuric acid). *Ca.* 0.6 μeq of bromine was generated coulometrically. The bromine was allowed to react for 1 min at room temperature and then 25 μl of a standard 0.05 M arsenic(III) solution was added. The residual arsenic(III) was titrated with generated bromine and the end-point determined biamperometrically. The bromine was generated at a current of 0.2895 mA which is equivalent to 0.003 μeq $\sec^{-1}$. The end-point was taken as the current reading 0.4 μA above the baseline. A blank was determined by treating 1.0 ml of distilled water as above, except that only 0.3 μeq of excess bromine was generated. The net number of μeq was obtained by substracting the number of μeq required for the blank from the number of μeq required for the sample.

Standard solutions of the sodium salts of the barbiturates were determined by pipetting a standard solution into 15 ml of generating solution and proceeding as described above, with the generation of bromine and back-titration. A plot of the number of μeq found *versus* the number of μeq added was prepared from the titration of the standard solutions; the number of μeq found in the serum sample was determined by comparing the net titration time with the standard calibration curve. The concentrations of the individual barbiturates were calculated as follows.

$$\text{Sodium seconal (F.W. 260.2): mg\%} = \frac{\mu\text{eq (Graph)} \cdot 0.130\ \text{mg}/\mu\text{eq} \cdot 100}{0.500\ \text{ml}}$$

$$\text{Sodium sandoptal (F.W. 246.2): mg\%} = \frac{\mu\text{eq (Graph)} \cdot 0.123\ \text{mg}/\mu\text{eq} \cdot 100}{0.500\ \text{ml}}$$

RESULTS AND DISCUSSION

Preliminary studies of the reaction between generated bromine and allylic barbiturates showed that a direct coulometric titration was not possible. The reaction proceeds too slowly at room temperature and, therefore, cannot be followed directly. For this reason a residual titration employing standard arsenite was investigated in detail.

Current efficiency

The current efficiency of the generation of bromine was studied according to the directions of LINGANE[9]. This procedure involves the direct titration of a known quantity of standard arsenite solution. Then the equivalent of approximately 90–95% of this titration value is generated in the absence of the arsenite. Next the arsenite is added and the titration is completed. The ratio of the first titration time divided by the second titration time, multiplied by 100, is equal to the current efficiency. Hopefully, this number is very close to 100%; however, if a calibration curve is employed in the actual analysis, current efficiencies less than 100% are acceptable.

This procedure was applied to three different types of titration cell, a standard Cotlove cell, a weighing bottle, and a 30-ml beaker. The volume of generating solution was 3.0 ml for the Cotlove cell and 6.0 and 7.0 ml for the weighing bottle and 30-ml beaker, respectively. The current efficiency was *ca.* 96% in the Cotlove cell and 93–94% in the other two cells. The fact that the current efficiency is less than 100% is attributed to the volatilization of the generated bromine. Although the current efficiency was slightly higher in the Cotlove cell, the 30-ml beaker was selected as the standard titration cell since it was the most practical for the analysis of blood serum samples.

The effect of reaction time

Since it is necessary to perform a residual titration when allylic barbiturates are reacted with generated bromine, the effect of reaction time was investigated. The data obtained for sodium seconal are shown in Table I and the data for sodium sandoptal in Table II.

It is seen from these data that the effect of reaction time is very similar for both compounds. The reaction is virtually complete as soon as excess of bromine has

TABLE I

EFFECT OF REACTION TIME ON THE COULOMETRIC TITRATION OF SODIUM SECONAL

(10% excess bromine generated; generation rate, 0.003 μeq sec^{-1}; indicator potential, 200 mV; current sensitivity, 0.006 μA mm^{-1}; generating solution, 1.0 M NaBr, 0.2 M H_2SO_4)

Time (min)	*µg Added*	*µg Found*	*Average*
0	30.01	34.1 35.1	34.6 ± 0.5
1	30.01	37.5 35.4	36.5 ± 1.0
3	30.01	39.8 40.6	40.2 ± 0.4
5	30.01	44.2 43.3	43.7 ± 0.5

TABLE II

EFFECT OF REACTION TIME ON THE COULOMETRIC TITRATION OF SODIUM SANDOPTAL

(Conditions as given in Table I)

Time (min)	*µg Added*	*µg Found*	*Average*
0	76.70	80.2 81.0	80.6 ± 0.4
1	76.70	82.1 82.7	82.4 ± 0.3
3	76.70	83.6 85.2	84.4 ± 0.7
5	76.70	85.8 85.8	85.8 ± 0.0

been generated. As reaction times are increased, more bromine is consumed. This observation probably is due to the volatilization of bromine and the occurrence of secondary side reactions.

The effect of excess bromine

Another factor that could affect the results of a residual titration is the amount of excess titrant generated. Various amounts of bromine were generated and were allowed to react with sodium seconal and sodium sandoptal for a specified period of time. The results for sodium seconal are shown in Table III and those for sodium sandoptal in Table IV.

TABLE III

EFFECT OF EXCESS BROMINE ON THE COULOMETRIC TITRATION OF SODIUM SECONAL

(Conditions as in Table I; reaction time, 1 min)

% *Excess bromine*	*µg Added*	*µg Found*	*Average*
20	30.01	30.8 31.0	30.9 ± 0.1
90	30.01	34.2 33.8	34.0 ± 0.2
150	30.01	37.3 35.8	36.5 ± 0.4

TABLE IV

EFFECT OF EXCESS BROMINE ON THE COULOMETRIC TITRATION OF SODIUM SANDOPTAL

(Conditions as in Table III)

% *Excess bromine*	*µg Added*	*µg Found*	*Average*
30	47.64	50.3 50.2	50.3 ± 0.05
70	47.64	56.0 56.1	56.1 ± 0.05
120	47.64	62.9 65.1	64.0 ± 1.1

In both cases the amount of barbiturate found was directly related to the amount of excess bromine generated. This observation probably is due to the occurrence of secondary substitution reactions in addition to the reaction of bromine with the allylic bond of the barbiturate. This would consume more bromine than would be required for the simple addition reaction across the double bond, and therefore would indicate a higher barbiturate concentration than is actually present.

Standard conditions

The conditions that were empirically selected were a reaction time of 1 min and a generation of 0.6 μeq of bromine. The 1-min reaction time was selected because all of the bromine was shown to have reacted within this time period, and the amount reacted was not very different from that reacted at zero time. Therefore, a slight error in the measurement of reaction time would not result in a large error in the measurement of the amount of bromine consumed. The generation of 0.6 μeq of bromine was selected because this could accommodate both therapeutic and toxicological levels of these barbiturates.

The standard conditions described above were examined at several barbiturate levels and on several days to verify the linearity of the titration. For barbiturate levels from 6 to 60 μg, agreement with standard solutions from day to day was within 2 μg. Daily calibration curves were reasonably linear but changed slightly from day to day. It was observed also that the calibration curves were always elevated above the origin. This is to be expected, however, since the number of microequivalents of the barbiturate found is always higher than the theoretical value.

It was also apparent from the data that the amount of barbiturate found differed from the theoretical value to a larger extent at the lower concentration levels. This is due to the fact that the per cent bromine in excess is very large at these low barbiturate levels, and secondary reactions and volatilization of bromine are favored. Even though this is the case, a straight line may be drawn through the points without much difficulty. For the analysis of unknown quantities of an allylic barbiturate, the recommended procedure is to prepare a calibration curve on each day that an analysis is to be performed.

Analysis of standard blood serum samples

Since barbiturates are not normal constituents of blood serum, it was necessary to prepare standard blood serum samples containing these compounds. This was accomplished by adding known quantities of a standard barbiturate solution (as the sodium salt) to clinical control sera (Versatol, Warner-Chilcott, Morris Plains, N.J.). After agitation, the samples were treated as normal blood serum samples.

A protein precipitation step usually is not employed in the analysis of barbiturates in blood serum. The chloroform extraction is selective, and the small amount of protein extracted does not interfere with the ultraviolet spectrophotometric measurement.

In the case of the coulometric procedure, however, preliminary studies showed that a protein precipitation was necessary. The times obtained for the blank titration when a protein precipitation was not performed were very large indicating that considerable amounts of bromine-titratable material were present. When a protein precipitation was performed, the blank values obtained with blood serum samples were identical to those obtained with a distilled water blank.

Tungstic acid was the only precipitating reagent for proteins investigated in this study. This reagent was prepared as described by HENRY[8], and provided a filtrate with a pH of *ca.* 4. Other reagents commonly employed for protein precipitation provide a filtrate with either a more acid pH, or a neutral to basic pH which possibly would not permit extraction of the barbiturate into the organic phase.

Recovery studies with the tungstic acid protein precipitation were performed. This was done by analyzing a standard blood serum sample which was taken through the protein precipitation procedure and comparing its u.v. absorbance with a standard aqueous solution which was analyzed in an identical manner. The results showed that the recovery of sodium seconal was approximately 81% and the recovery of sodium sandoptal was approximately 88%. These data show that apparently some of the barbiturate is lost in the protein precipitation step, presumably owing to coprecipitation with the protein. The recovery of sodium sandoptal is significantly higher than that of sodium seconal, which is somewhat surprising since these two compounds are very similar in structure.

The results of the analyses of standard blood serum samples are shown in Table V. The ultraviolet procedure does not include a protein precipitation, and these results agree very well with the theoretical values. In the case of the coulometric analyses, most of the values obtained are lower than the theoretical and ultraviolet spectrophotometric values. These coulometric results parallel the results obtained in the u.v. recovery experiments employing the tungstic acid protein precipitating agent: the coulometric results are usually lower than theory and the coulometric results for sodium sandoptal are usually higher than for sodium seconal. The higher values obtained for sodium sandoptal at the lower concentrations are probably due to the fact that the amount of bromine in excess is very high at these low levels.

TABLE V

ANALYSIS OF STANDARD BLOOD SERUM SAMPLES FOR SODIUM SECONAL AND SODIUM SANDOPTAL

mg% Theory	*mg% Found u.v.*	*mg % Found coulometric*
Sodium seconal		
5.00	5.1 ± 0.1 (2)[a]	4.0 ± 0.2 (4)[a]
3.00	3.0 ± 0.1 (2)	2.1 ± 0.4 (5)
1.50	1.8 ± 0.5 (2)	1.3 ± 0.1 (3)
0.75	—	0.67 ± 0.13 (4)
Sodium sandoptal		
5.00	4.9 ± 0.1 (2)	4.8 ± 0.3 (4)
3.00	3.2 ± 0.2 (2)	3.1 ± 0.4 (5)
1.50	1.5 ± 0.1 (2)	2.1 ± 0.4 (3)
0.75	—	1.3 ± 0.3 (3)

[a] Number of determinations.

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SUMMARY

Constant-current coulometry has been applied to the titration of the allylic barbituric acid derivatives, sodium seconal and sodium sandoptal. Electrogenerated bromine was employed as the titrant and biamperometry was used to detect the end-point. The effect of reaction time and excess bromine was evaluated, and optimum standard conditions were established. Quantitative bromination required an excess of bromine, hence a back-titration with standard arsenite was performed. Calibration curves were linear over the concentration range investigated, but changed slightly from day to day. The standard conditions were applied to the analysis of standard blood serum samples. Preliminary precipitation of protein was necessary, hence lower values than theoretical were obtained.

RÉSUMÉ

La coulométrie à courant constant est appliquée au titrage de dérivés allyliques de l'acide barbiturique, sodium seconal et sodium sandoptal. Le brome électrogéneré est utilisé comme titrant; la biampérométrie permet de déceler le point final. On examine l'influence du brome en excès et de la durée de réaction. Les conditions standards optima sont établies, et appliquées à l'analyse d'échantillons de sérum sanguin; une précipitation préliminaire des protéines est nécessaire.

ZUSAMMENFASSUNG

Die Allylbarbitursäure-Derivate Natriumseconal und Natriumsandoptal sind coulometrisch bei konstantem Strom titriert worden. Elektrochemisch erzeugtes Brom diente als Titrationsmittel; der Endpunkt wurde biamperometrisch bestimmt. Der Einfluss von Reaktionszeit und Bromüberschuss wurde ermittelt; die optimalen Standardbedingungen wurden festgelegt. Die quantitative Bromierung erforderte einen Überschuss an Brom; deshalb wurde eine Rücktitration mit Standard-Arsenit durchgeführt. Die Eichkurven waren im untersuchten Konzentrationsbereich linear, änderten sich aber etwas von Tag zu Tag. Die Standardbedingungen wurden auf die Analyse von Standard-Blutserumproben angewendet. Es war notwendig, das Protein vorher zu fällen; deshalb wurden niedrigere als die theoretischen Werte erhalten.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF MERCURY(II) AND SILVER(I) BY THERMOMETRIC TITRATION

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In recent years thermometric titrimetry has been used for the determination of many inorganic and organic substances[1] but very few publications deal with the estimation of microgram quantities of material in solution. The use of a catalytic end-point in titrations where the presence of a slight excess of titrant catalyses the actual indicator reaction has already been reported[2]. For example, iodide ions catalyse the oxidation of arsenic(III) by cerium(IV). This has been used for the determination of iodide, and indirectly of mercury(III) and silver(I), by following the kinetics of the As(III)–Ce(IV) reaction spectrophotometrically[3–5], and a titration procedure with a potentiometric end-point has been used by WEISZ AND KLOCKOW[6] for the determination of milligram quantities of mercury(II) in aqueous solution.

The present paper describes a procedure for determining mercury(II) and silver(I) in the range 1000–0.1 p.p.m. by means of this catalytic end-point with thermometric detection. To some extent the results have been anticipated in a recent paper by WEISZ, KISS AND KLOCKOW[7] who used a similar procedure for samples mainly in the range 50–500 μg. The basic procedure is as follows. A stirred solution of the sample containing silver or mercury(II) ions and a fixed amount of As(III)–Ce(IV) indicator solution is titrated with standard potassium iodide solution. Immediately after the end-point, the excess of iodide ion catalyses the indicator reaction and the rise in temperature is detected by a thermistor probe in a Wheatstone bridge circuit. By using a mechanically driven syringe burette to deliver the titrant at a constant rate and by displaying the out-of-balance signal from the bridge circuit on a chart recorder, after suitable filtering and amplification, the procedure can be made semiautomatic.

EXPERIMENTAL

Solutions

All solutions were made up in deionised water and all chemicals were of AnalaR grade.

Cerium(IV) solution (*ca.* 0.1 *M*) was prepared by dissolving ceric ammonium nitrate (54.8 g) in *ca.* 1 *M* sulphuric acid and making up to 1 l.

Arsenic(III) solution (*ca.* 0.1 *M*) was prepared by dissolving arsenic(III) oxide (9.8 g) in water (300 ml) containing sodium hydroxide (71 g), neutralizing with dilute sulphuric acid and making up to 1 l.

A stock $9.883 \cdot 10^{-3}$ *M* solution of potassium iodide was prepared from the salt dried at 150° for 12 h. Other solutions ($9.883 \cdot 10^{-4}$, $\cdot 10^{-5}$ and $\cdot 10^{-6}$) were prepared by dilution.

Mercury(II) chloride solution ($4.947 \cdot 10^{-4}$ M) was prepared by dissolving mercury(II) chloride (0.1343 g) in 0.1 M hydrochloric acid and making up to 1 l with distilled water. The standard solution of silver nitrate was obtained by dissolving the pure material (0.1700 g) in water and making up to 1 l.

More dilute solutions containing known amounts of mercury or silver were made up each day as required by dilution in glassware specially treated to minimise the adsorption of metal ions on the surface. This was done by first cleaning the glassware with hot chromic acid and then with nitric acid (50% v/v); after thorough washing with deionized water, it was dried overnight in an oven, then treated with a solution of dichlorosilane in benzene and dried[8].

Apparatus

The titration cell consisted of a flat-bottomed cylindrical glass vessel of height 9 cm and diameter 5 cm having a capacity of 75 ml. This was totally enclosed in a polystyrene block and carried a polystyrene lid with apertures for the thermistor and the inlet tube for the titrant. The solution was stirred magnetically. The thermistor (Type STC/F23) had a resistance of 2000 ohms at room temperature which changed by *ca.* 3.1 % per degree. The response of the thermistor to temperature changes was sensed by incorporating it as one arm of a Wheatstone bridge circuit. The out-of-balance signal was filtered and amplified and fed into a chart recorder (Bryans, Model 2700). The response of the system to temperature changes was evaluated by titrating 25 ml of 0.015 M calcium ions with 0.5 M EDTA. Taking $\Delta H = -5.7$ kcal mole^{-1} for the complexation reaction at 20–25° [9,10], it was found that full-scale deflections were obtained for temperature changes of 0.2, 0.1 and 0.05° at the three sensitivities used.

A syringe burette was constructed using a synchronous motor to drive a 2.5-ml Hamilton precision syringe through a gearbox which enabled different rates of delivery to be preselected. The titrant entered the titration cell through Teflon tubing which terminated in a glass tube drawn out to a fine point. Some slight variation was found over long periods of time but consistent results were obtained during any one week. Some typical results are shown in Table I.

TABLE I

CALIBRATION OF SYRINGE BURETTE

Running time (sec)	400	280	320	380
Wt. solution delivered (g)	0.396	0.276	0.313	0.374
Weight per min (g min^{-1})	0.0594	0.0592	0.0593	0.0596

Procedure

Measured portions (5–5.5 ml each) of the cerium(IV), arsenic(III) and 3 M sulphuric acid solutions were added (measuring cylinder) to the titration cell and after the sample containing silver or mercury had been added, the polystyrene lid and thermistor were replaced and the magnetic stirrer started. The bridge was then balanced and the recorder started to check for any signal drift. After the system had stabilized (1–2 min), any excess of titrant was carefully wiped off the glass tip of the titrant delivery tube and this was inserted into the cell so that the end was just immersed in the solution. The syringe burette motor was then started: this caused a "blip" on the recorder trace conveniently marking the start of the titration.

At the end-point the excess of iodide ion catalyses the As(III)–Ce(IV) reaction and a rise of temperature ensues. This was slow at first, especially for concentrations of potassium iodide lower than 10^{-3} *M*, but it gradually accelerated. When an appreciable temperature rise had occurred (about 30 sec after the true end-point), the syringe burette motor was switched off. The As(III)–Ce(IV) reaction then proceeded at a steady rate and a linear portion was obtained on the temperature–time recorder tracing (Fig. 1).

Extrapolation of the linear portions of the trace on either side of the true end-point yields an incorrect but reproducible end-point which lags behind the true end-point by an amount determined by the concentration of the potassium iodide in the titrant and by the rate at which it enters the reaction mixture. However, these two factors are easily kept constant so that reproducible calibration curves of time (or travel of chart paper in cm) against the concentration of metal taken (in μg) could readily be prepared. This procedure was found to be more convenient and satisfactory than attempting to locate the true end-point which occurs just before the first rise in temperature is observed. This initial rise of temperature becomes particularly difficult to detect with sample concentrations less than 10 p.p.m.

RESULTS AND DISCUSSION

Stability of the recorder signal

Some difficulty was experienced at first from noise generated by the magnetic stirrer motor and from the mains: this was later filtered out by inserting a simple R-C circuit immediately before the input to the recorder. With the sensitivities commonly used (*viz.* 0.2 or 0.1° full scale for titrations down to 1 p.p.m. and 0.05° for titrations at the 0.1-p.p.m. level), the signal was found to be practically noise-free so that the extrapolations needed to locate the end-point (*cf.* Fig. 1) could be carried out accurately and reproducibly.

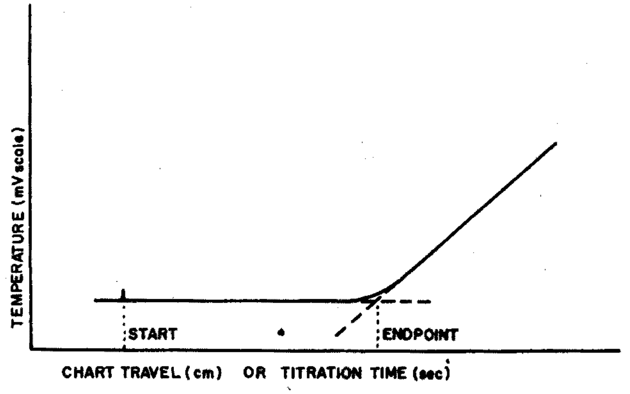

Fig. 1. Thermometric titration curve.

Indicator reagent solutions

Random variations in the results for mercury and silver at the 0.1-p.p.m. level were encountered initially and found to be due to traces of contaminants in the A.R.-grade cerium and arsenic solutions. The amount of each component in the Ce(IV)–As(III)–H_2SO_4 indicator solution was therefore varied systematically to identify the source of the errors. Graphs of chart travel (cm) against ml of each reagent had the following slopes: As(III) 0.5 cm ml^{-1} and Ce(IV) 0.3 cm ml^{-1}. Since measurements of chart travel were carried out to the nearest 0.1 cm, it follows that for titrations of silver(I) or mercury(II) at the 0.1-p.p.m. level, any random errors caused by impurities in the indicator solution will be negligible provided that the components are measured out to ± 0.1 ml. The A.R. sulphuric acid appeared to contain no contaminant.

Calibration graphs

Calibration graphs were prepared for each metal and for each of four ranges (1000–100, 100–10, 10–1, 1–0.1 p.p.m.) with a solution of titrant ten times as concentrated as the sample solution (1–10 ml). Each titration was repeated at least four times to check reproducibility. The plot of time taken (or chart travel) against μg of metal taken gave an almost linear relationship in each case but only when titrations were

TABLE II

TITRATION OF SILVER NITRATE WITH POTASSIUM IODIDE

Ag^+ taken (μg)	*Ag^+ found (μg)*	*Ag^+ taken (μg)*	*Ag^+ found (μg)*	*Ag^+ taken (μg)*	*Ag^+ found (μg)*
Titrant: $9.883 \cdot 10^{-3}$ M KI[a]		*Titrant: $9.883 \cdot 10^{-4}$ M KI*[a]		*Titrant: $9.883 \cdot 10^{-5}$ M KI*[b]	
215.8	216.4 ± 2.0[c]	21.58	21.3 ± 0.4[c]	2.16	2.10 ± 0.04[c]
323.7	322.7 ± 0.0	43.16	43.2 ± 0.6	5.40	5.42 ± 0.02
413.6	431.6 ± 2.0	53.95	53.7 ± 0.4	7.55	7.58 ± 0.03
539.5	539.5 ± 4.0	75.53	75.5 ± 0.6		
646.5	646.5 ± 1.0	107.9	108.2 ± 0.6		
755.3	755.3 ± 4.0				
1079	1080 ± 4.0				

[a] Sensitivity: 0.2° for full-scale deflection.
[b] Sensitivity: 0.1° for full-scale deflection.
[c] Standard deviation ± σ based on 5 determinations.

TABLE III

TITRATION OF MERCURY(II) CHLORIDE WITH POTASSIUM IODIDE

Hg^{2+} taken (μg)	*Found (μg)*	*Hg^{2+} taken (μg)*	*Found (μg)*
Titrant: $9.883 \cdot 10^{-5}$ M KI[a]		*Titrant: $9.883 \cdot 10^{-6}$ KI*[b]	
1.998	2.03 ± 0.03[c]	0.200	0.198 ± 0.003[c]
2.997	3.00 ± 0.05	0.400	0.395 ± 0.005
5.00	5.00 ± 0.01	0.500	0.497 ± 0.005
6.994	6.92 ± 0.05	0.699	0.704 ± 0.005
9.991	9.97 ± 0.02		

[a] Sensitivity 0.1° for full-scale deflection.
[b] Sensitivity 0.05° for full-scale deflection.
[c] Standard deviation ± σ based on five determinations.

carried out with 10^{-2} *M* potassium iodide, where the temperature rise at the end-point was most rapid, did the plot pass through the origin.

Analysis of samples

Typical results are summarized in Tables II and III. Difficulty was encountered with samples containing 0.1 p.p.m. of silver because of adsorption on the walls of glass vessels. Even so, reproducible results could be obtained with measurements carried out consecutively over short intervals: over a full day there was a steady decrease in the titres for silver(I).

Interfering ions

Of the common ions only cyanide, thiocyanate, sulphide and thiosulphate were found to interfere. With silver(I), equivalent concentrations of chloride and bromide did not affect the titration results although larger excesses certainly diminished the titre.

When tetraphenylborate ions were added, the determination of silver(I) was unaffected whereas that for mercury(II) was reduced (*e.g.* from 25 cm to 1.5 cm). However, the possibility of using this anion as a masking agent for the selective determination of silver(I) in the presence of mercury(II) was not realised in tests with synthetic mixtures.

Clearly the procedure is satisfactory for silver(I) and mercury(II) in concentrations down to 0.1 p.p.m. The precision varies from 0.3% or better for 1000–100 p.p.m. down to 1% or better for 100–0.1 p.p.m. Relatively simple and inexpensive apparatus is needed.

One of us (K.C.B.) gratefully acknowledges a Fellowship from Imperial Chemical Industries Ltd.

SUMMARY

By titration with standard potassium iodide silver(I) and mercury(II) can be determined in aqueous solution in the concentration range 1000–0.1 p.p.m. The end-point, which is detected thermometrically and recorded, is indicated by the heat liberated in the reaction between arsenic(III) and cerium(IV) which is catalysed by traces of iodide ion.

RÉSUMÉ

Il est possible de doser argent(I) et mercure(II) par titrage à l'aide d'iodure de potassium standard, en solution aqueuse, à des concentrations allant de 1000 à 0.1 p.p.m. Le point final, détecté thermométriquement et enregistré, est indiqué par la chaleur libérée dans la réaction entre arsenic(III) et cérium(IV), catalysée par des traces d'iodure.

ZUSAMMENFASSUNG

Durch Titration mit Standard-Kaliumjodid können Silber(I) und Quecksil-

ber(II) in wässriger Lösung im Konzentrationsbereich 1000–0.1 p.p.m. bestimmt werden. Spuren Jodidionen katalysieren die Reaktion zwischen Arsen(III) und Cer(IV). Die hierbei freiwerdende Wärme zeigt den Endpunkt an, der thermometrisch ermittelt und aufgezeichnet wird.

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DETERMINATION OF TRACE CONCENTRATIONS OF BARIUM EXTRACTED FROM AQUEOUS SYSTEMS

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Soluble barium salts are known to be toxic, both when ingested into the system and when external exposure occurs. They are irritating to the skin and mucous membrane and may produce dermatitis and marked bronchial irritation. They stimulate smooth, striated, and cardiac muscles and may produce abdominal pains, muscle twitching, and cardiac dysfunction[1]. Recent studies have disclosed the presence of soluble barium in the environment. It has been detected[2] in the exhausts from moving vehicles in New York, Cincinnati, Washington, Chicago, and Los Angeles, although no quantitative data are available from these samples. A barium-base additive has been used to suppress smoke emission from vehicles burning Diesel fuel and small amounts of soluble barium have been found in the exhaust from these vehicles[3]. Barium polysulfide has been used as a fungicide and its presence on fruit has been reported by KROLLER[4]. In a study completed by KOPP AND KRAMER[5] in 1967, of 1400 surveillance samples, the presence of soluble barium in the surface waters of the United States was confirmed and its concentration was found to average 43 μg l^{-1}. These isolated studies indicate the presence of a potentially harmful contaminant in the environment.

The methods for the microdetermination of barium currently used include the spectrophotometric method of BUDESINSKY *et al.*[6] who used sulphonazo-III as a barium-selective reagent. Emission spectroscopy has been used by WILSKA[7], CARDELL[8], GRABOWSKI AND UNICE[9], GOLEB *et al.*[10], and KOPP AND KRAMER[5]. For the low concentrations of barium found in natural waters, 0.012–0.063 μg ml^{-1}, TUREKIAN AND BOLTER[11] recommend isotope dilution mass spectrometry or neutron activation as the only acceptable methods. These require time-consuming sample preparations and sophisticated equipment and techniques.

For simplicity, selectivity, and accuracy, atomic absorption spectrophotometry excels any of the above-mentioned methods. The greatest sensitivity using atomic absorption for the determination of barium was achieved by WILLIS *et al.*[12] who used a nitrous oxide–acetylene flame. Through the use of potassium, they suppressed the ionization of barium which is normally enhanced by the relatively high temperature of the nitrous oxide–acetylene flame. They achieved a sensitivity of 0.3 μg ml^{-1} for 1% absorption.

Greater sensitivities for metal determinations have been achieved by the use of extraction into suitable organic solvents followed by atomic absorption measurements.

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The use of an organic solvent aspirated into the flame greatly enhances the absorption signal. An important factor in the enhancement is the effect of concentrating a metal from the aqueous phase into the organic phase by the use of a chelating reagent. Furthermore, such procedures serve to eliminate interferences from matrix effects.

Although methods for the determination of many of the metals have been established which use solvent extraction followed by atomic absorption, none has been proposed previously for barium. This report does present a method for the trace determination of barium in aqueous systems which achieves optimum sensitivity and reliability through a combination of solvent extraction and atomic absorption measurements.

EXPERIMENTAL

Reagents and solutions

Hexafluoroacetylacetone (1 M). 34.9 ml (52.0 g) were diluted to 250 ml with isoamyl acetate. The reagent (Columbia Organic Chemicals, Inc.) was used without purification. It is highly volatile and irritating to the respiratory tract and adequate ventilation should be provided in areas where it is used.

Buffer (pH 10.6). 55 ml of 2 *M* ammonium acetate were added to 500 ml of 2 *M* ammonia solution.

Ionization buffer (10 mg K^+ ml^{-1}). 25.0 g of potassium acetate were dissolved in water and diluted to 1 l.

Barium standard (1.00 mg Ba^{2+} ml^{-1}). 1.90 g of reagent-grade barium nitrate was dissolved in water and diluted to 1 l.

Interference cations and anions. Stock solutions containing 10 mg of test ion per ml were used.

Apparatus

Perkin-Elmer 303-Atomic Absorption Spectrophotometer. The instrument was equipped with a Perkin-Elmer Recorder Readout and Texas Instruments-Servoriter II, a tri-flame laminar flow burner from Jarrell-Ash, Hoke fuel flow meter, a hollow-cathode lamp for barium, and an Osram lamp for potassium.

Procedure

Extraction. Transfer 200 ml of a solution containing from 5–300 μg barium to a 500-ml separatory funnel. Add 50 ml of the pH buffer and 30 ml of the ionization buffer. Add 5 ml of hexafluoroacetylacetone (HFA) solution and agitate the mixture for 1 min. Allow the phases to separate. When the HFA solution is added to the buffered solution, a transitory white smoke forms but does not interfere with the extraction.

Spectroscopy. The hollow-cathode lamp for barium was operated at 30 mA, which generated a signal with much less noise than the lower current recommended by the manufacturers of the lamp. A spectral slit width of 0.4 nm was used. A nitrous oxide–acetylene flame was used. The acetylene flow was adjusted while aspirating a solution into the flame so as to yield a maximum signal. On the Hoke flow meter, this was usually about 18 units for the acetylene flow and 9 units for the nitrous oxide flow. The specified ratio of fuel to nitrous oxide produced a red reaction zone, about

1.5 mm high. The height of the burner was adjusted so that the beam passed through the flame about 1.4 cm above the burner. A 5-min warm-up period was allowed after lighting the burner, since it was found that the signal increased progressively during that time.

Calibration curve. With the above chemical and spectroscopic procedure, the calibration curve was linear over a concentration of 0.015 to 1.00 μg ml^{-1}. The sensitivity measured from the concentration in the aqueous phase, was 0.005 μg ml^{-1} for 1% absorption, based on a concentration factor of 60 for the extraction step. The detection limit, at 0.5% noise level was 0.005 μg ml^{-1} at a signal-to-noise ratio of 2:1.

RESULTS AND DISCUSSION

Chelating agent and solvent

Several reagents which had been used successfully in spectrophotometric or titrimetric determinations of barium were examined as possible ligands for a barium extraction system. Glyoxal bis-(2-hydroxyanil), eriochrome black T, sulphonazo III, and the dianilide of methylsulphonazo III were employed as chelating agents. Unfortunately, the extent of extraction of the resulting chelates, measured by the use of a barium isotope tracer, was never complete enough to warrant the further investigation of any of them for quantitative separations. Hexafluoroacetylacetone, however, was found to complex barium very efficiently, enabling its complete extraction from aqueous solutions. As little as 0.015 μg Ba^{2+} ml^{-1} can be completely extracted into the organic phase in a single extraction by the use of hexafluoroacetylacetone.

Methyl isobutyl ketone, butyl acetate, isoamyl acetate, or ethyl propionate may be used as the solvent for the extraction of the barium hexafluoroacetylacetonate complex. Although each gave complete separation of the chelate, isoamyl acetate was chosen as the preferred solvent because it enhanced the atomic absorption to a greater extent than any of the other solvents used.

Ionization suppression

MANNING AND DELGADO-CAPACHO[13] have demonstrated the necessity of using an alkali metal ion to suppress the ionization of barium in a nitrous oxide–acetylene flame. It was, therefore, desirable to develop a procedure that included potassium in the organic phase. Attempts to dissolve potassium tetraphenylboron in an organic solvent met with only partial success and were abandoned. Instead, potassium acetate was added to the aqueous phase, at a concentration of 1 mg ml^{-1}, and the recommended extraction of barium was completed. The absorption at the resonance line, 553.5 nm, was enhanced from 42% to 48%, while the absorption of the barium ion (455.4 nm) was suppressed from 78% to 54%. It was clearly evident that potassium was extracting into the organic phase and affecting the absorption signal. Further studies demonstrated that maximum suppression of the ionization of barium was achieved by using 1 mg ml^{-1} of potassium ion in the aqueous phase, and the presence or absence of sodium was found to be irrelevant at this concentration of potassium. The results of these studies are shown in Fig. 1. The recommended procedure provides a simple means for extracting and concentrating barium while at the same time providing a sufficient concentration of potassium to stabilize its ionization.

pH effects

The influence of pH upon the determination of barium was demonstrated by corollary studies. A series of extractions was made with barium-133 and a scintillation counter, while a parallel study was conducted with a stable barium isotope and atomic absorption measurements. From the tracer studies it was evident that barium was extracting completely through the pH range studied. Yet, the atomic absorption signal was found to be a function of the pH used for extraction. The extractions with the stable barium isotope were then repeated and the absorption of potassium was monitored at the potassium wavelength, 404.0 nm. As shown in Fig. 2, the barium absorption is influenced by the pH of the extraction system, through the effect of potassium.

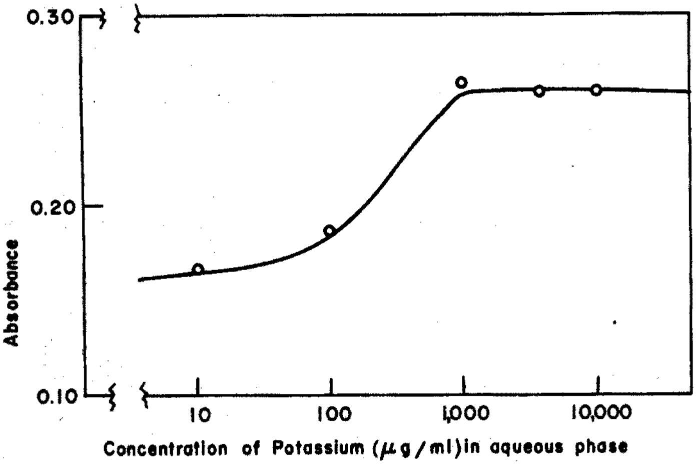

Fig. 1. Effect of potassium on barium absorption at 553.5 nm.

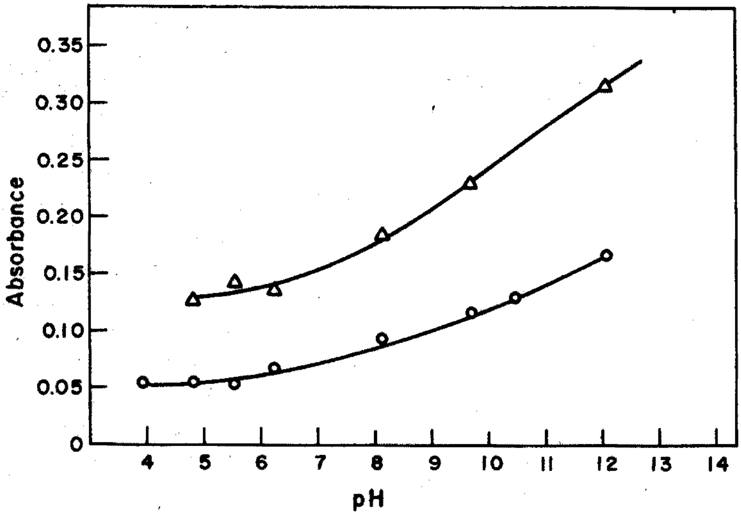

Fig. 2. Barium–potassium relationship *versus* pH. (△) Barium 553.5-nm line, (○) potassium 404.0-nm line.

Interferences

A thorough study was made of the effect of possible interference from 55 common anions or cations. Extractions were conducted according to the proposed procedure on solutions containing 0.1 μg ml^{-1} of barium and 10 μg ml^{-1} or 100 μg ml^{-1} of the interfering ion as suggested by WEST[14]. Table I summarizes the results of these tests. Most of the ions of interest can be tolerated at the higher concentration, but those of aluminum, lead, cobalt, iron and nickel significantly decreased the absorption of barium. With the exception of lead, all can be tolerated at 10 μg ml^{-1} concentration. However, in the presence of suitable masking reagents the interference from these ions can be suppressed as indicated in Table II. The presence of EDTA suppressed all response from barium.

TABLE I

INTERFERENCE STUDIES

Group	*No interferences at concentration of 100 μg ml^{-1}*	*No interferences at concentration of 10 μg ml^{-1}*
I	Li^+, Na^+, K^+, Cu^{2+}, Rb^+, Ag^+, Cs^+	
II	Zn^{2+}, Sr^{2+}, Cd^{2+}, Hg^+, Hg^{2+}	Mg^{2+}, Ca^{2+}, Be^{2+}
III	BO_2^-, $B_4O_7^{2-}$, Ce^{3+}	Al^{3+}
IV	CO_3^{2-}, SiO_3^{2-}, GeO_3^{2-}, Sn^{2+}	
V	NH_4^+, NH_2^-, NO_3^-, HPO_4^{2-}, VO_3^-, $HAsO_4^{2-}$, Bi^{3+}	
VI	S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, CrO_4^{2-}, SeO_3^{2-}, MoO_4^{2-}, TeO_2^{2-}	
VII	F^-, Cl^-, ClO_4^-, Br^-, BrO_3^-, I^-, IO_3^-	
VIII		Ni^{2+}, Co^{3+}
Miscellaneous:	CN^-, SCN^-, oxalate, malonate, tartrate, citrate, gluconate	

TABLE II

MASKING AGENTS

Cation	*Concentration (μg ml^{-1})*	*Masking agent*	*Concentration (μg ml^{-1})*
Al^{3+}	100	Gluconate	300
Pb^{2+}	100	Tartrate	100
Co^{3+}	100	Tartrate	100
Ni^{2+}	100	Cyanide	100
Fe^{3+}	50	Sodium diethyldithiocarbamate	0.03 *M*

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SUMMARY

A sensitive and reliable method for the determination of barium in aqueous systems has been developed. The combination of the solvent extraction of the barium hexafluoroacetylacetonate into isoamyl acetate with subsequent determination by atomic absorption has increased by 50%, the best sensitivity previously attained. The proposed method presents a simple, rapid method of determining barium at concentrations as low as 0.015 μg ml^{-1} with an ultimate sensitivity of 0.005 μg ml^{-1} for 1 % absorbance. The use of a high concentration of potassium ion in the aqueous system improves the sensitivity. The potassium is coextracted with the barium and acts to suppress the ionization and enhance the absorption of barium. Interference effects of 55 diverse ions were studied and their tolerance levels are summarized. No significant interferences were found.

RÉSUMÉ

On propose une méthode sensible pour le dosage du baryum. En procédant par extraction de l'hexafluoroacétylacétonate dans l'acétate isoamilique et dosage par absorption atomique, on augmente de 50% la meilleure sensibilité déjà atteinte. Cette méthode est simple, rapide et permet de doser le baryum jusqu'à des concentrations de 0.015 μg ml^{-1} avec une sensibilité de 0.005 μg ml^{-1} pour 1% d'absorption. La présence de potassium améliore la sensibilité; il est coextrait avec le baryum et tend à supprimer l'ionisation et augmenter l'absorption du baryum. On a examiné l'influence de 55 ions différents.

ZUSAMMENFASSUNG

Es ist eine empfindliche und zuverlässige Methode für die Bestimmung von Barium in wässrigen Systemen entwickelt worden. Das Barium wird als Hexafluoroacetylacetonat mit Isoamylacetat extrahiert und anschliessend durch Atomabsorption bestimmt. Die Empfindlichkeit ist durch diese Kombination um 50% besser als die beste früher erhaltene Empfindlichkeit. Nach der vorgeschlagenen Methode kann Barium einfach und schnell bei so niedrigen Konzentrationen wie 0.015 μg ml^{-1} mit einer Empfindlichkeit in der Messlösung von 0.005 μg ml^{-1} für 1% Absorption bestimmt werden. Die Anwendung hoher Konzentration an Kaliumionen im wässrigen System verbessert die Empfindlichkeit. Das Kalium wird zusammen mit Barium extrahiert und bewirkt eine Unterdrückung der Ionisation und Erhöhung der Absorption des Bariums. Die Störeffekte von 55 verschiedenen Ionen wurden untersucht und deren Toleranzkonzentrationen zusammengestellt. Wesentliche Störungen wurden nicht gefunden.

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THE COULOMETRIC GENERATION OF CHROMIUM(II) IN STRONGLY ACIDIC MEDIA

PART I. COULOMETRIC TITRATION OF TITANIUM(IV)

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Chromium(II) solutions are well established as excellent reagents for the determination of weak oxidants. Their advantages have long been appreciated[1] and the many available titrimetric methods for the determination of oxidants such as Ti^{4+}, Tl^{3+}, Sn^{4+}, Hg^{2+}, Bi^{3+}, etc., as well as in organic analysis, have been thoroughly reviewed[2,3]. All the analytical reactions of titanium(III) can be reproduced with chromium(II) but usually under less stringent conditions. However, this type of redox titrimetry has not been widely used in analytical practice because of the difficulties found in preparation and storage of standard solutions of chromium(II). From this point of view, the advantages conferred by the coulometric generation of this reagent are obvious, but the first investigations in this field were not encouraging[4,5]. BARD AND PETROPOULUS[6], having investigated the current efficiency for the reduction of hexaquochromium(III) chloride in saturated calcium chloride solution and of chromium(III) sulfate in 0.1 *M* potassium chloride, concluded that coulometric titration with chromium(II) was suitable only for the determination of oxygen. The difficulties in obtaining 100% current efficiency for the generation of chromium(II) arise from the negative E^0 value (−0.41 V *vs.* N.H.E.), as a result of which hydrogen ions and chromium(III) compete in strong acid medium (which is essential for most determinations). Accordingly, the papers quoted are limited to the determination of oxygen and copper(II) at pH 3–4. Nowadays, the most useful data on the reduction of chromium(III) complexes in various media are to be found in the polarographic literature[7–10]. AIKENS AND CARLITA[11] were the first to show the possibility of coulometric generation of chromium(II) in acidic medium from chromium(III) complexes, which are reduced at less negative potentials; these workers also indicated suitable conditions, under which the reduction of hydrogen ion has a high overpotential. Chromium(II) was generated in 1.5 *M* hydrochloric acid from chromium tribromide hexahydrate with 99.1% efficiency, determined by the titration of aromatic nitro compounds.

However, more extensive studies are needed for wider application of this mode of generation of chromium(II) to be considered reliable. The green modifications of chromium(III) halide, with the proved structure $CrX_2(H_2O)_4X \cdot 2H_2O$, are known to be thermodynamically unstable in aqueous solutions and are rapidly converted to their blue modifications, especially in the absence of acid (over about 30 min). The process is accompanied by a shift of the half-wave potential for the chromium(III) reduction from about −0.4 to −0.9 V *vs.* S.C.E., so that the current efficiency decreases far below 100% with time.

Accordingly, it is necessary to establish conditions such that chromium(II) is generated with efficiency greater than 99% in acid medium, without decreasing the advantages conveyed by the coulometric methods, *i.e.* simplicity, high precision and accuracy, sensitivity, and the possibility of repeatedly using the same working solution. In the present paper the limits in which $CrBr_2(H_2O)_4Br \cdot 2H_2O$ is applicable as catholyte for the reduction to chromium(II), are outlined, on the basis of the stability of the salt and of current efficiency as a function of the acidity and the type of medium used.

STABILITY OF $CrBr_2(H_2O)_4Br \cdot 2H_2O$ IN ACID MEDIUM

The stability of $CrBr_2(H_2O)_4^+$ in aqueous solution has been frequently investigated[12-17]; the rate constants of the two-step aquation processes have been calculated, and the dependence of the rate constant on the hydrogen ion concentration has been proved. Unfortunately, these kinetic measurements have been carried out only at pH 1.5. Attempts to use the given relationships when the acid concentration ranged from 1 *M* to 6 *M* in order to calculate $\tau_{\frac{1}{2}}$ failed. There is another contradiction, which arises in the comparison of the data for the rate constants, connected with the particular aquo-species, obtained either by potentiometric titration of outer-sphere or by polarographic techniques. In the former[12,13], the aquation process of $CrBr_2(H_2O)_4^+$ is shown to pass through $CrBr(H_2O)_5^{2+}$, where the conversion, $CrBr_2^+ \rightarrow CrBr^{2+}$, is fast ($\tau_{\frac{1}{2}}=3$ min), and through $CrBr(H_2O)_5^{2+} \rightarrow Cr(H_2O)_6^{3+}$, which is a considerably slower process ($\tau_{\frac{1}{2}}=182$ min) at 20°. In the analogous polarographic investigation, the wave at −0.52 V is ascribed to $CrBr_2(H_2O)_4^+$ and that at −0.89 V to $Cr(H_2O)_6^{3+}$, although the scheme of stepwise aquation of $CrBr_2(H_2O)_4^+$ is not rejected. The kinetics of the reaction, which shows a first-order conversion, excludes the simultaneous presence of two species responsible for the first polarographic wave. Data obtained[18] in polarographic reduction of $CrBr(H_2O)_5^{2+}$ indicate that $E_{\frac{1}{2}}$ is a function of bromide concentration, which is in good agreement with the results of IBARZ *et al.*[17]. This fact, in conjunction with the finding that the analogous reaction $CrCl_2^+ \rightarrow CrCl^{2+}$ takes place instantaneously[19-21] when chromium(II) is present, supports the supposition that the polarographic wave at −0.52 V may be considered as identifying $CrBr(H_2O)_5^{2+}$ rather than $CrBr_2(H_2O)_4^+$, which under the conditions of the polarographic experiment is of negligible concentration.

In the work discussed here, the stability of $CrBr_2(H_2O)_4^+$ was investigated in the acidity range from 1.5–6 *M*, depending on the kind of acid and on the concentration of bromide added as a supporting electrolyte. Four acids were used (hydrochloric, hydrobromic, sulphuric and perchloric acids), and sodium or potassium bromide was added in concentrations of 0, 10^{-2} or 10^{-1} *M*. In order to follow the process, the polarographic technique was chosen, as it most closely resembles the conditions of coulometry with a mercury cathode.

Experimental

Chromium tribromide hexahydrate (the green modification) was prepared from chromium trioxide and hydrobromic acid, twice as much as the stoichiometrically required quantity being added. A vacuum installation, supplied with an absorbent for bromine, which was richly evolved in the initial step of the reaction, was used. After the bromine had been eliminated, the excess of hydrobromic acid was distilled under vacuum until crystallization began. The recrystallized product was analysed for bromide gravimetrically with silver nitrate, for chromium iodimetrically, and for water by the Karl Fisher method. The results obtained (60.1% Br^-, 28% H_2O, 13.2% Cr) agree with those required for the formula $CrBr_3 \cdot 6H_2O$. Several repeated experiments were made with the same reagent supplied by Schuchardt, and the data coincided.

A spectrophotometric investigation of $2.5 \cdot 10^{-2}$ *M* chromium tribromide solution in concentrated, 3 *M* and 1.5 *M* acid showed that the maximum identifying $CrBr_2(H_2O)_4^+$ [10,22] disappeared in 30 min (when concentrated acid was used) and in 15 min (for 3 *M* acid), and that a new isosbestic point appeared, indicating that only two species were present in the solution. Since the first recording of the polarogram was made 15 min after dissolving the salt (because of the time needed for deaeration) the supposition that $CrBr(H_2O)_5^{2+}$ was the species responsible for the wave, was thus considered proved. This assumption formed the basis of earlier discussions[11] but no proof was given.

A recording polarograph (Radelkis OH-102, Hungary) was used. The polarograms, recorded 15 min after reagent dissolution, showed only one wave, the half-wave potential of which changed greatly depending on the acid used (Table I). The height of the plateau decreased with time and a new wave with $E_{1/2} = -0.90$ V appeared; this wave was only slightly dependent on the above-mentioned factors. The sum of the heights of the two waves remained constant. As the changes were slow in these strongly acidic media, polarograms were recorded periodically for a week; all experiments were done at 20 ± 0.1°. Because of the high acidities, it was impossible to achieve constant ionic strength, hence the data obtained were treated to calculate the value of $\tau_{1/2}$, which is the most convenient quantity for assessment of coulometric conditions. However, the data obtained (Table II), which are in contradiction with literature data, cannot be explained by the effect of the different ionic strength only.

Discussion

High acidity strongly stabilizes the $CrBr(H_2O)_5^{2+}$ species, as is obvious from Table II, except when sulphuric acid is used. The role of the anion is also clear. The

TABLE I

$-E_{1/2}$ VALUES FOR THE FIRST WAVE IN DIFFERENT MEDIA (*vs.* S.C.E.)

N	$HClO_4$	H_2SO_4	*HCl*	$HClO_4$[a]	H_2SO_4[b]	*HCl*[b]	$HClO_4$[c]	H_2SO_4[d]	*HCl*[d]	*HBr*[d]
1.5	0.42	0.39	0.56	0.43	0.42	0.56	0.47	0.49	0.60	0.56
2.0	0.42	0.39	0.57	0.43	0.41	0.58	0.48	0.49	0.61	0.54
3.0	0.42	0.40	0.60	0.43	0.42	0.60	0.49	0.49	0.63	0.56
4.0	0.42	0.41	0.61	0.43	0.42	0.61	—	0.51	0.64	0.56
5.0	—	—	0.62	0.42	—	0.62	—	—	0.64	0.56
6.0	0.41	0.41	—	—	0.42	—	0.49	0.51	—	—

[a] $5 \cdot 10^{-2}$ *M* NaBr added.
[b] $1 \cdot 10^{-2}$ *M* NaBr added.
[c] $5 \cdot 10^{-1}$ *M*NaBr added.
[d] $1 \cdot 10^{-1}$ *M* NaBr added.

TABLE II

THE VALUES FOR $\tau_{\frac{1}{2}}$ (IN h) WITH AND WITHOUT BROMIDE ADDED

N	H_2SO_4	*HCl*	*HBr*	$HClO_4$	H_2SO_4	*HCl*	$HClO_4$
NaBr	10^{-1} *M*	10^{-1} *M*	10^{-1} *M*	$5 \cdot 10^{-1}$ *M*	0	0	0
1.5	45	65	67	77	31	65	74
2.0	—	75	77	79	32	68	82
3.0	46	110	98	112	30	92	96
4.0	34	152	121	174	29	142	119
5.0	—	250	130	—	—	249	—
6.0	28	—	—	338	24	—	185

behaviour of the sulphuric acid systems may be explained by the opposing actions of the sulphate and hydrogen ions; as the acid concentration increases, the effect of the sulphate ion predominates. These data do not agree with the previously suggested independence of the rate constant from the supporting electrolyte[17], but the mechanism of the reaction may have been changed by the greatly increased acidity in the present experiments. Variation of the concentration of the supporting electrolyte did not greatly affect $\tau_{\frac{1}{2}}$; accordingly, its addition to the catholyte for coulometric titrations seems unnecessary. In conclusion, the data for $\tau_{\frac{1}{2}}$ show that chromium tribromide solutions in acidic media can be effectively used for at least 3 days in 1.5 *M* acid, and longer in 3 *M* acid. This fact removes the inconvenience of dealing with thermodynamically unstable salts.

The data in Table I show the strong dependence of $E_{\frac{1}{2}}$ on the acid used. The reduction occurs most easily in sulphuric or perchloric acid media these media providing a greater difference from the decomposition potential of the water. The data for $E_{\frac{1}{2}}$ in hydrochloric acid medium are in good agreement with earlier values[9] obtained for the reduction of $CrCl_2(H_2O)_4^{2+}$ above 3 *M* acidities. Analysis of the polarographic waves in hydrochloric and hydrobromic acids proved an irreversible reduction in the former and a reversible one in the latter; the irreversibility is due to a change in the mechanism of the electrochemical reduction, which has not yet been clarified, but does not involve conversion to the $CrCl(H_2O)_5^{2+}$-form.

CURRENT EFFICIENCY FOR THE $CrBr(H_2O)_5^{2+}$ REDUCTION

On the basis of the stability investigated above, and since chromium(II) is generally used as a reagent in solutions which contain 1.5–4 *M* acid[23], the current efficiency was determined in hydrochloric, hydrobromic and perchloric acids for this range. Sulphuric acid was excluded, because accumulation of chromium(II) in these solutions of chromium tribromide hexahydrate appears to result in very fast aquation.

Experimental

A potentiostat IP – 410B (Bulgaria) was used for the determination of current efficiency. The chromium tribromide concentration was $5 \cdot 10^{-2}$ *M* in all experiments. An hermetically sealed H-cell, similar to those described in the literature, was used. A mercury pool cathode (10 cm^2) and a cadmium rod anode were used. Before chromium

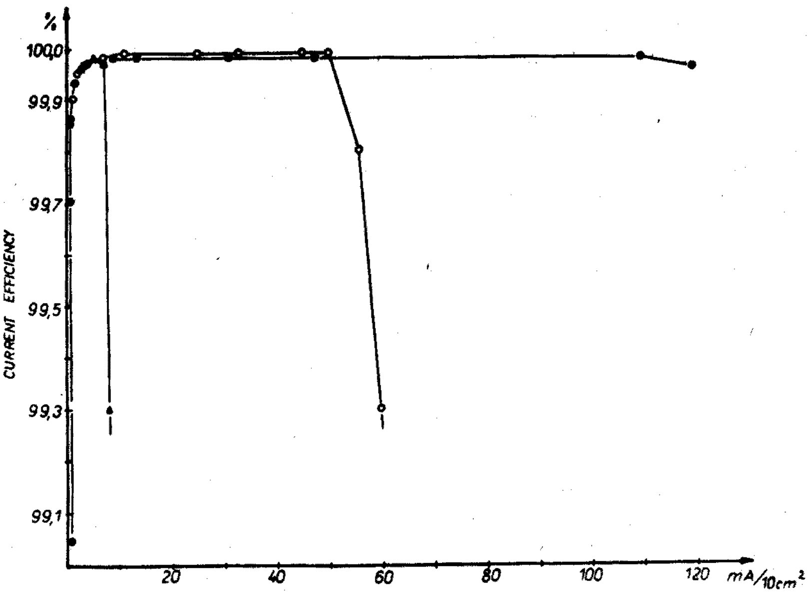

Fig. 1. Current efficiency in 1.5 *M* HBr (○), HCl (▲) and $HClO_4$ (●) solutions for $5 \cdot 10^{-2}$ *M* chromium tribromide.

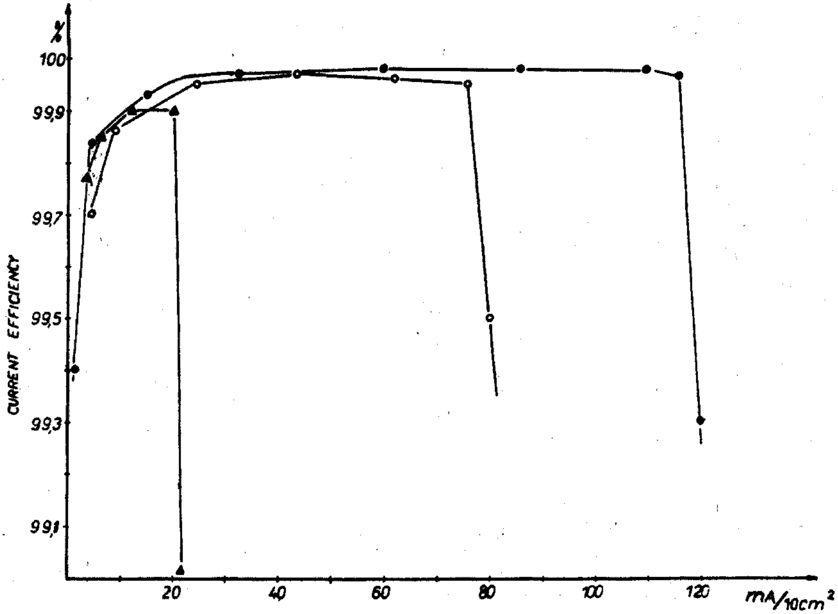

Fig. 2. Current efficiency in 3 *M* HBr (○), HCl (▲) and $HClO_4$ (●) solutions for $5 \cdot 10^{-2}$ *M* chromium tribromide.

tribromide was added, the acid solutions were cleaned electrolytically at −0.8 V till the current decreased to a constant value for at least 15 min. The solutions were deaerated by nitrogen, which had been passed through two scrubbers containing acidic

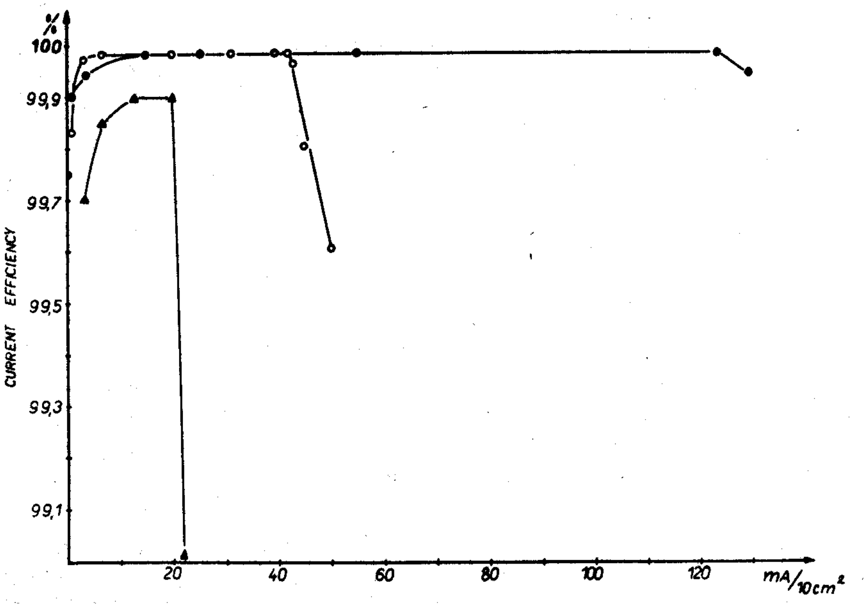

Fig. 3. Current efficiency in 4 M HBr (○), HCl (▲) and $HClO_4$ (●) solutions for $5\cdot 10^{-2}$ M chromium tribromide.

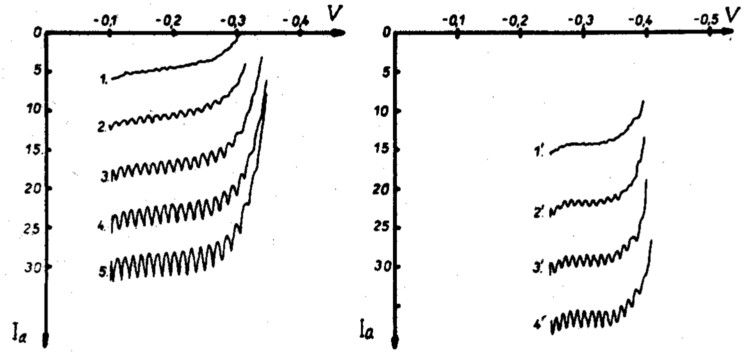

Fig. 4. Anodic waves of chromium(II) recorded in 3 M $HClO_4$ (1–5) and 3 M HBr (1'–4'), after generating for 1 min (1 and 1'), 2 min (2 and 2'), 3 min (3 and 3'), 4 min (4 and 4'), and 5 min (5). Generating current of 20 mA; sensitivity of recording, $6\cdot 10^{-8}$ A/div.

chromium(II) solution. The solutions were energetically stirred at a constant rate. The current–potential curves were plotted first for the supporting electrolyte (acid), and then for the chromium tribromide dissolved in the same acid. The current efficiency was then evaluated by Lingane's formula: $(i - i_{\text{res}})\cdot 100\% \cdot i^{-1}$ [23] and plotted against the current in mA (for a cathode area of 10 cm²). The results are shown in Figs. 1–3.

Results

The results of the potentiostatic experiments agree well with the conclusions drawn from the voltammetric curves. The range of current density at which chromium(II) can be generated with 99.9% efficiency increases in the direction HCl<

$HBr < HClO_4$ in 1.5 *M* acid solutions. When more concentrated acids are used, this general trend is maintained but the current efficiency for hydrochloric acid media decreases sharply, which is probably due to irreversible reduction.

The potentiostatic results were further confirmed by studying the anodic wave of chromium(II) formed by generating at a constant current of 10 or 20 mA. The cell arranged for potentiostatic experiments was used with the addition of a dropping mercury electrode and a saturated calomel electrode. A transistorized constant-current source, capable of maintaining currents from 10 to 40 mA, constant to about $\pm 0.01\%$, was used. The linear increase in the chromium(II) wave in the range from -0.1 to -0.4 V is shown in Fig. 4. These experiments showed that the D.M.E. is convenient for detection of end-points in the coulometric titration of oxidants with chromium(II). The shortening of the chromium(II) plateaux in hydrobromic acid is caused by the electrochemical dissolution of mercury, which begins at a more positive potential in that medium.

Several investigations have shown that the reaction $2Cr^{2+} + 2H^+ \rightarrow 2Cr^{3+} + H_2$ does not occur measurably in the absence of catalysts[24–26]. MEITES[26] has developed a controlled-potential coulometric determination of chromium(II) in 6 *M* hydrochloric acid. These results were confirmed in the present study; the decrease in the anodic wave was less than 1% in 15 min when nitrogen was bubbled through the solution. This decrease was shown to be caused by incompletely removed oxygen rather than by reaction with hydrogen ion. However, the D.M.E. was preferred as indicator electrode despite the advantages of biamperometric indication with two platinum electrodes, because platinum is known to catalyse the above reaction.

DIRECT COULOMETRIC TITRATION OF TITANIUM(IV) WITH ELECTROLYTICALLY GENERATED CHROMIUM(II)

The results discussed above were used in developing a method for the direct coulometric titration of titanium(IV). Titanium was chosen as a suitable example for the reducing power of chromium(II). Titanium(IV) in the presence of iron(III) has been determined by LINGANE[27] with an automatic potentiometric titrator with standard chromium(II) solution in 2 *M* sulphuric acid. SLOVAK[28,29] developed a coulometric determination of titanium(IV), based on reduction with excess of chromium(II), and titration of the titanium(III) formed with electrolytically generated iron(III).

Hydrobromic acid was chosen as the most suitable supporting electrolyte, because of the work of KARTUSHINSKAJA AND STROMBERG[30].

Experimental

Stock solutions of titanium(IV) were prepared by diluting a 3.6 *M* titanium(IV) solution in 7.4 *M* hydrochloric acid with 2 *M* sulphuric acid, to give a concentration of about 10^{-1} *M*; 1 ml of this solution corresponded to 11.5 mg Ti, determined gravimetrically.

The coulometric titration was performed in a hermetically sealed H-cell which contained a mercury pool cathode and was fitted with three conical ground sockets, for the indicator electrode, the S.C.E., and a micropipette, respectively. The micropipette made it possible to add successive quantities of the sample without opening the cell. Samples of about 0.1 ml were added with a precision of 0.3 µl. The cathodic compartment was purged with purified nitrogen (p. 459). A solution of 2 or 3 *M* hydrobromic acid which was *ca.* 0.1 *M* in chromium tribromide was used as catholyte, the total volume being kept to 16 ml. The bridge and the anode compartment, separated by sintered glass discs from the cathode, contained 1.5 *M* potassium bromide and 0.1 *M* hydrobromic acid. A cadmium rod was chosen as anode. The generating current, chosen from the controlled-potential data, was kept constant (9.95 mA) by the above-mentioned constant-current source. The catholyte was stirred vigorously by magnetic stirring. The solution in the cathodic compartment was pretitrated for about 2 min so that any oxidants present would be reduced. Amperometric end-point detection with a D.M.E. was used ($E = -0.28$ V) with the Radelkis polarograph. The time for generation of chromium(II) after the end-point was used as a correction for the following sample. The character of the curves is shown in Fig. 5. Several series containing 1.122 or 0.561 mg of titanium in volumes of 0.1 and 0.05 ml, respectively, were titrated.

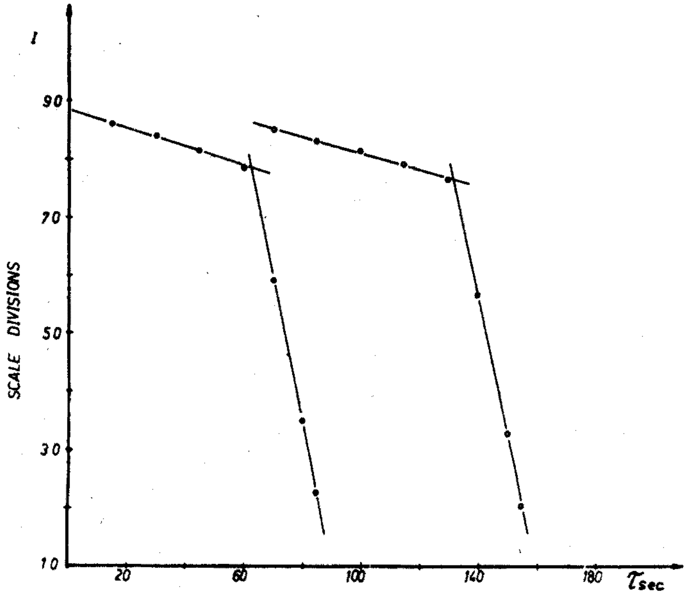

Fig. 5. Amperometric curves, obtained with D.M.E. indicator electrode at —0.28 V in the coulometric titration of titanium(IV) with chromium(II) in 2 *M* hydrobromic acid. Sensitivity 4 mA per scale division.

Results and discussion

The results of these titrations showed that the influence of titanium(IV) on the amperometric curve just before the end-point was considerably greater than expected[30]. A decrease in the hydrobromic acid concentration resulted in a shift of the polarographic wave for titanium(IV) to more negative values and in 2 *M* hydrobromic acid, the end-point could be determined with sufficient precision.

The mean result of 14 determinations for samples containing 1.122 mg of titanium was 1.121 ±0.005 mg (99.9% certainty); for 7 determinations of samples containing 0.561 mg, the mean result was 0.562±0.01 mg. The standard deviation, evaluated from 20 determinations, was ± 7 μg.

It was of interest to establish the form to which chromium(II) was reoxidized by titanium(IV)—$CrBr^{2+}$ (as was reasonable to suppose[19]) or $Cr(H_2O)^{3+}$. Accordingly, a polarogram of a $5 \cdot 10^{-2}$ *M* chromium tribromide solution as catholyte was recorded; titanium(IV) was then added in an amount previously estimated to correspond to ¼ of the recorded wave-height. Chromium(II) was generated and the titration was stopped 1 min before the calculated equivalence point so that any effect of chromium(II) would be avoided. The recorded polarographic wave showed a decrease equal to the predicted one, and a second wave appeared with a height equal to the decrease in the first step.

SUMMARY

The stability of $CrBr_2(H_2O)_4^+$ was investigated in strong acid medium (1.5–6 *M*) as a function of acid type and bromide concentration; HCl, HBr, $HClO_4$ and H_2SO_4 were used. Chromium tribromide was shown to provide a suitable working solution for at least 3 days, for the coulometric generation of chromium(II). The reduction was also studied at the D.M.E. Chromium(II) catalysed the aquation process, the effect being greatest in sulphuric acid. Conditions for 100% generating efficiency of chromium(II) were established; the range of current density for >99.9% current efficiency increased in the order $HCl < HBr < HClO_4$. Polarographic and spectrophotometric techniques showed that $CrBr(H_2O)_5^{2+}$ is the species reduced at the mercury cathode. A direct coulometric determination of titanium(IV) with electrolytically generated chromium(II) is described. Amounts of *ca.* 1 and 0.5 mg were titrated; the standard deviation for 20 determinations was ± 7 μg.

RÉSUMÉ

Une étude est effectuée sur la stabilité de $CrBr_2(H_2O)_4^+$ en milieu acide fort (1.5–6 *M*), en fonction du type d'acide et de la concentration en bromure. On propose une méthode coulométrique pour le dosage du titane(IV) à l'aide de chrome(II) formé électrochimiquement. Des quantités de titane de l'ordre de 1 à 0.5 mg ont pu être ainsi titrées; la déviation standard pour 20 dosages est de ± 7 μg.

ZUSAMMENFASSUNG

Es wurde die Stabilität von $CrBr_2(H_2O)_4^+$ in stark saurem Medium (1.5–6 *M*) als Funktion der Säureart (HCl, HBr, $HClO_4$ und H_2SO_4) und der Bromidkonzentration untersucht. Chromtribromid ergab eine geeignete Arbeitslösung für die coulometrische Erzeugung von Chrom(II) für wenigstens 3 Tage. Die Reduktion an einer tropfenden Quecksilberelektrode wurde ebenfalls untersucht. Chrom(II) katalysierte die Wasseranlagerung besonders in Schwefelsäure. Die Bedingungen für 100 %ige Ausbeute an Chrom(II) wurden festgestellt; der Stromdichtebereich für >99.9 %ige Stromausbeute nahm in der Reihenfolge $HCl < HBr < HClO_4$ zu. Polarographische und spektrophotometrische Verfahren ergaben, dass $CrBr(H_2O)_5^{2+}$ die an der Quecksilberelektrode reduzierte Spezies ist. Eine direkte coulometrische Bestimmung von Titan(IV) mit elektrolytisch erzeugtem Chrom(II) wird beschrieben. Es wurden Mengen von *ca.* 1 und 0.5 mg titriert; die Standardabweichung für 20 Bestimmungen war ± 7 μg.

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A STUDY OF THE OPTIMAL CONDITIONS FOR POTENTIOMETRIC TITRATION OF FLUORIDE WITH LANTHANUM AND THORIUM IN UNBUFFERED MEDIA

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The determination of fluoride has been much simplified with the introduction of fluoride-selective electrodes[1]. Determinations can be made either by direct potentiometry or by titration. LINGANE[2] described the potentiometric titration of fluoride with thorium(IV), lanthanum(III) and calcium(II) solutions and showed that fairly accurate results could be obtained if the titration was made to a specified potential rather than to the point of maximum deflection. These results were obtained in the range 7–80 mg of fluoride per 100 ml. LINGANE also studied the influence of buffers but arrived at a recommended titration procedure in unbuffered solutions. The properties of the electrode and the solubility product were further studied in a second paper[3]. Various applications to different analytical problems employing the principles outlined by LINGANE have appeared in the literature. Recently, ANFÄLT *et al.*[4] have applied computer calculation to the evaluation of potentiometric fluoride titrations with lanthanum(III) and thorium(IV). In two additional papers, ANFÄLT AND JAGNER[5,6] studied the mixed acetate and carboxylic acid complexes of lanthanum fluorides. They also varied the values of the stability constants in solutions without acetate until a good fit to an experimental curve was obtained. KNOECK[7] collected evidence to show the existence of complexes between lanthanum and nitrate.

The present study was undertaken in order to obtain more complete information about the equilibria present during a potentiometric fluoride titration. Such information may be extracted from kinetic measurements, from simultaneous accurate measurements of pH and pF and by a computer-fit of the results to a calculated curve.

EXPERIMENTAL

The titrations were made in a thermostatted plexiglass vessel adapted to a Penton top (Metrohm EA 615) which contained a fluoride electrode (Orion 94-09), a glass electrode, and a reference electrode (Radiometer K 401). All measurements were made at 25.0°. Titrant was added in increments from a motor-driven burette (Metrohm E 412). An electrode selector connected one electrode at a time to a digital voltmeter (Orion 801) via a follower (Analog Devices 801). A timing circuit operated the reed relays of the electrode switch and the print command of a serializer which was connected to an IBM-typewriter. The burette could also be operated by the timing circuit. In most of the slow titrations, additions of 0.1 ml were made at 6-min intervals and a reading of each electrode after 3-min intervals. All titrations were made in unbuffered solutions.

Kinetic measurements were made in the same vessel but the electrodes were connected to an operational amplifier potentiometer and a recorder with an overall stability better than 0.5 mV. In these experiments the titrant was added with a pipette.

The sodium fluoride (Merck Suprapur) was dried at 150°. Thorium nitrate (certified A.C.S.), lanthanum nitrate (Merck p.a.), and lanthanum chloride (Kebo puriss) solutions were standardized against EDTA with xylenol orange. The EDTA had been standardized against lead nitrate (Baker Analyzed).

Sodium chloride (Merck p.a.) and potassium nitrate (Baker Analyzed) were used. The contents of calcium and magnesium as R_2O_3 should be less than 0.005 %. Results obtained with potassium nitrate of lower purity were discarded.

RESULTS

Exploratory titrations showed that the fluoride activity changed with time after the addition of titrants, more especially after the equivalence point. In solutions containing only sodium fluoride and supporting electrolyte the stability of the potential reading of the electrode systems was very good and the response was fast. The time dependence was therefore ascribed to equilibrium changes in the thorium and lanthanum systems. In thorium solution a film was formed on the electrode, as reported elsewhere[8]. This film did not affect the equilibrium potential although it made the electrode response somewhat slower. By cleaning the electrode and repeating measurements in the same solution, it could be proved that the slow potential changes were caused by activity changes in the solution and not by film formation on the electrode. A porous plug at the end of the salt bridge of the reference electrode was blocked by the film and this affected the liquid junction potential by up to 20 mV. An open bridge was therefore used in all solutions containing thorium.

TABLE I

CONCENTRATION OF NaF IN TITRATION VESSEL

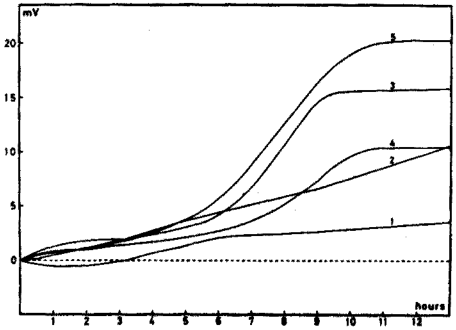
(All curves in Figs. 1–8 refer to this Table)

No.	*1*	*2*	*3*	*4*	*5*
mg NaF/50 ml	0.5039	2.520	12.60	62.99	126.0
Conc. NaF (*M*)	0.0002400	0.001200	0.006002	0.0300	0.06002

The kinetics of the equilibria between fluoride and thorium or lanthanum were studied for five different concentrations of NaF as specified in Table I. Measurements were made at 80 % and 135 % of the amount thorium and lanthanum required to give ThF_4 and LaF_3. Additions were made rapidly with a pipette, the solution was mixed and the recording was started. The results are shown in Figs. 1–4 in normalized form so that the potential 12 min after mixing is taken as zero. Repeated measurements were made on almost all the solutions and the results were highly reproducible.

The kinetics also influence the shape of a titration curve as shown in Figs.

5–8. Titrations were made at two different rates. Five different titrants were prepared so that titrations of the amounts of sodium fluoride specified in Table I always required the same volume. The fast titrations were made by adding a large increment and reading the electrodes at 3-min intervals so that the total titration time became 30–45 min. A slow titration always took 10 h; 0.1 ml was added every 6 min.



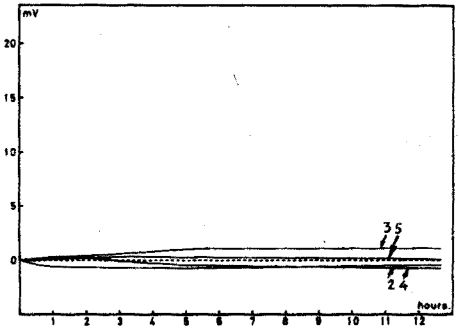
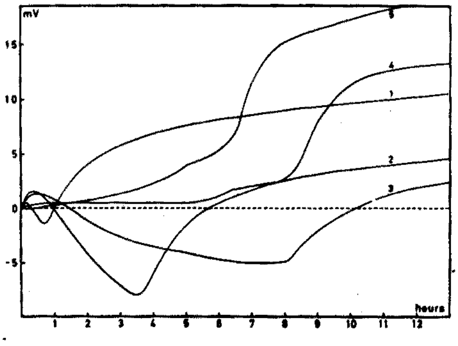


Fig. 1. Kinetic curves for thorium fluoride; 80% of the amount of thorium required to give ThF_4 was added and the recording was started at an arbitrary zero point 12 min after mixing.

Fig. 2. Kinetic curves for lanthanum fluoride; 80 % of the amount of lanthanum required to give LaF_3 was added and the recording was started at an arbitrary zero point 12 min after mixing.



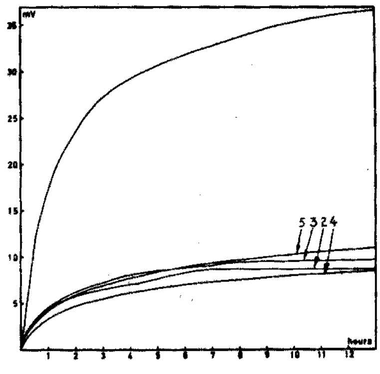
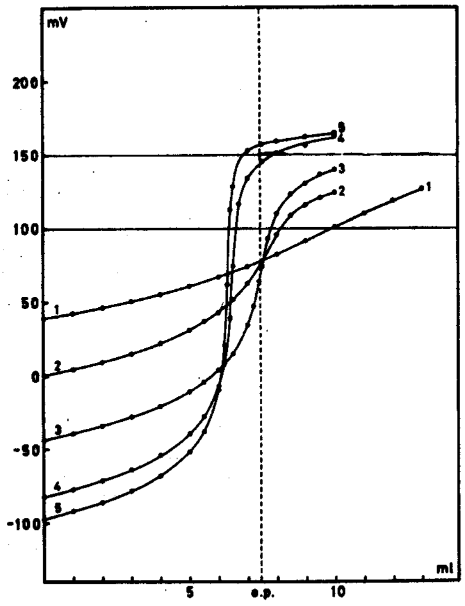


Fig. 3. Kinetic curves for thorium fluoride; 135% of the amount of thorium required to give ThF_4 was added and the recording was started at an arbitrary zero point 12 min after mixing.

Fig. 4. Kinetic curves for lanthanum fluoride; 135 % of the amount of lanthanum required to give LaF_3 was added and the recording was started at an arbitrary zero point 12 min after mixing.

Three titration rates are compared directly in Fig. 9, which shows that the potential in a titration with lanthanum is independent of titration rate in the first part of the titration curve but not in the last part. While lanthanum fluoride is a well-behaved system up to the vicinity of the end-point, the thorium fluoride system shows time-dependence even in this range.



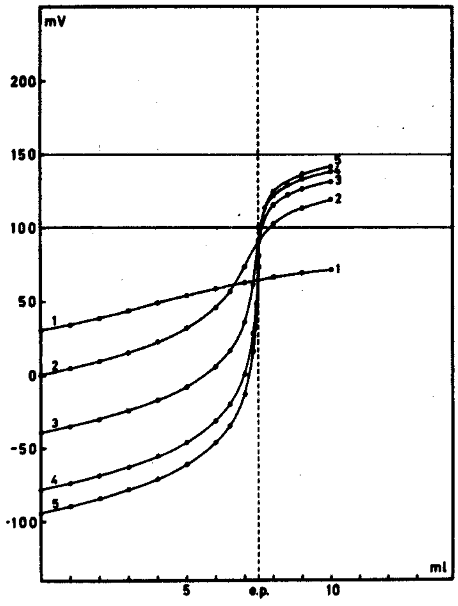
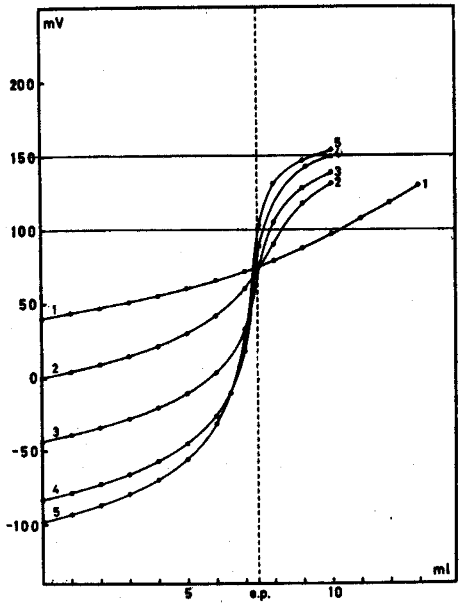


Fig. 5. Slow titration of NaF with thorium nitrate of the following concentration (M): (1) 0.0004034, (2) 0.002017, (3) 0.01009, (4) 0.05045, (5) 0.1009.

Fig. 6. Slow titration of NaF with lanthanum nitrate of the following concentration (M): (1) 0.0005358, (2) 0.002679, (3) 0.01339, (4) 0.06697, (5) 0.1339.



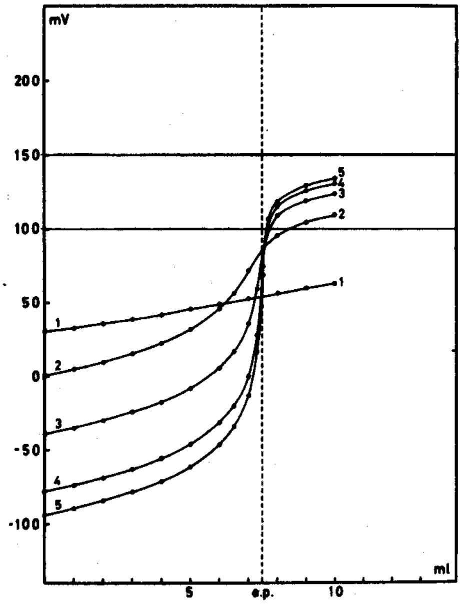


Fig. 7. Fast titration of NaF with thorium nitrate of the following concentration (M): (1) 0.0004034, (2) 0.002017, (3) 0.01009, (4) 0.05045, (5) 0.1009.

Fig. 8. Fast titration of NaF with lanthanum nitrate of the following concentration (M): (1) 0.0005358, (2) 0.002679, (3) 0.01339, (4) 0.06697, (5) 0.1339.

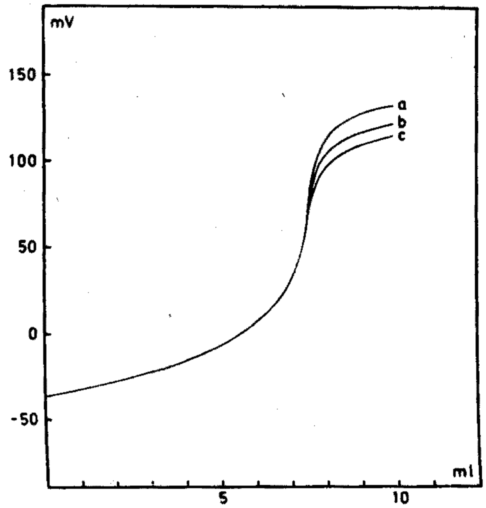


Fig. 9. Titration of 10.00 ml of 0.0300 M NaF+40.0 ml of water with 0.01308 M lanthanum nitrate at three different speeds. Total time for a titration: (a) 10 h, (b) 33 min, (c) 5 min 30 sec.

DISCUSSION

Lanthanum

ANFÄLT AND JAGNER[5] used a computer programme to fit their measurements to an equation containing the following constants:

$$La^{3+} + F^- \rightleftharpoons LaF^{2+} \qquad \beta_1 = 10^{5.1} \qquad (1)$$

$$La^{3+} + 2F^- \rightleftharpoons LaF_2^+ \qquad \beta_2 = 10^{5.56} \qquad (2)$$

$$LaF_3(s) \rightleftharpoons La^{3+} + 3F^- \qquad K_{s0} = 10^{-17.09} \qquad (3)$$

$$HF \rightleftharpoons H^+ + F^- \qquad K_1 = 10^{-3.28} \qquad (4)$$

and their measurements were made in 1 M sodium nitrate at 25°.

In order to ensure that equilibrium had been reached in the present work the constants were determined from a set of very slow titrations. In the light of the results shown in Fig. 4, readings of the potential after the end-point were made 12 h after the addition of an increment of titrant. In order to separate the complexation of lanthanum to nitrate and to fluoride, titrations were made in both 1 M sodium chloride and in 1 M potassium nitrate at 25.0°. The results were computer-fitted with $K_1 = 10^{-2.94}$, but in the pH range used, 6.0–4.5, the value of this constant is not of great importance. The slope in Nernst's equation was always set to −59.16 mV per decade and was checked by separate calibrations. The best fits were found for $\beta_1 = 10^{5.15}$, $\beta_2 = 10^{5.56}$ and $K_{s0} = 10^{-17.66}$ in both media. The results are shown in Table II. Two similar titrations, also shown in Table II, made during 10 h resulted in the same β_1 and β_2 values but gave K_{s0} values of $10^{-17.45}$ and $10^{-17.40}$. The value of K_{s0} obtained in a fitting procedure is very dependent on the fluoride electrode potential after the end-point and a lower value will result if the solution is allowed to reach equilibrium. The recording in Fig. 4 supports the belief that $K_{s0} = 10^{-17.66}$ represents an equilibrium value.

KNOECK[7] identified complexes of the type

$$La^{3+} + NO_3^- \rightleftharpoons LaNO_3^{2+} \tag{5}$$

and reported a value of $K_f = 30.0 \pm 4.0$ in chloride media. The results in Table II were calculated with $K_f = 0$ and the same values of β_1 and K_{s0} were obtained in both chloride and nitrate media. Calculation with $K_f = 30$ on the other hand results in poor fits. Lower values of β_1 and K_{s0} in nitrate media must also be assumed which indicates that KNOECK's value is too high. MATTERN[9] and KRISS AND SHEKA[10] report values of $K_f = 10^{-0.26}$ and $10^{0.25}$, respectively; the former are compatible with the results in Table II.

TABLE II

TOTAL FLUORIDE CONCENTRATION AND FITTED VALUE OF K_{s0} IN TITRATION WITH LANTHANUM

Medium (1 M)	*NaCl*	*KNO_3*	*KNO_3*	*KNO_3*
Titration time(h)	*70*	*65*	*10*	*10*
Titrant(ml)	*Total fluoride conc.·10^3 (corrected for dilution)*			
0	5.489	5.492	4.012	7.002
1	5.484	5.478	4.026	7.005
2	5.469	5.472	4.020	6.982
3	5.457	5.460	4.000	6.992
4	5.454	5.467	3.996	7.004
5	5.448	5.479	3.995	7.003
6	5.453	5.493	3.997	7.024
7	5.473	5.522	4.003	7.054
8	5.500	5.553	4.014	7.109
9	5.514	5.517	3.986	7.092
10	5.505	5.468	3.964	7.044
Mean	5.478	5.491	4.001	7.028
Taken	5.489	5.489	3.997	7.015
Equiv. point (ml)	7.93	7.93	8.30	8.30
K_{s0} fitted	$10^{-17.66}$	$10^{-17.66}$	$10^{-17.45}$	$10^{-17.40}$

LINGANE[3] discussed complex formation as an explanation of the disappearance of the turbidity after the end-point. He dismissed this possibility, assumed peptization and made calculations on the assumption that only reaction (3) takes place. He obtained a value of $K_{s0} = 10^{-17.92}$. His definition of constant potential was less rigorous than in this work and further there was a variation of the ionic strength during the titration.

In this work, it was also observed that a fresh precipitate of lanthanum fluoride can be dissolved in excess of lanthanum through formation of LaF^{2+}. An aged precipitate, on the other hand, cannot be dissolved either by heating or by prolonged storing at room temperature.

The time-dependence reported above can be explained by an ageing of the lanthanum fluoride precipitate with a corresponding decrease of the solubility product. Support for this explanation is given by the constancy of β_1 and β_2. The change in fluoride activity with time is also independent of concentration at constant La_{tot}/F_{tot} ratio except for curve 1 in Fig. 4. At very low concentrations the solution becomes supersaturated and it takes a much longer time to reach equilibrium. Therefore curve 1 in Fig. 4 deviates from the runs made at higher concentrations. The titration curves 1 in Figs. 6 and 8 also show irregular behaviour.

Analogous behaviour has been observed for lanthanum hydroxide formation[11,12]; the solubility product of a fresh precipitate was $10^{-18.93}$ and of an aged precipitate $10^{-20.98}$.

Thorium

Titrations of fluoride with thorium show much greater dependence on the titration rate than the corresponding titrations with lanthanum. There are obviously several slow reactions both before and after the end-point as shown in Figs. 1 and 3. The hydrolysis is of importance even in acidic solutions as summarized by HIETANEN AND SILLÉN[13]. A detailed evaluation must take this and the kinetic aspects into account.

The best analytical results were obtained by using fast titrations and this explains why thorium has been popular as a titrant. The slow titrations in Fig. 5 show that the end-points for curves 4 and 5 come much too early. In fact, the end-points occur closer to a composition corresponding to ThF_5^- than to ThF_4. Separate titration in media containing different amounts of sodium chloride indicates the slow formation of $NaThF_5$.

Conclusions

Determinations of fluoride with ion-selective electrodes can be made according to several procedures.

Direct potentiometry. This method is affected by errors from liquid junction potential, changes in the lanthanum fluoride-membrane standard potential, changes in the ionic medium, pH changes, and possible complexation. It is difficult to control these factors to better than a few millivolts. Each millivolt corresponds to an analytical error of 3.8 % and this method thus provides results of only moderate accuracy.

Titration to steepest potential change. Titration can be made with thorium or lanthanum solution. The end-point will differ from the equivalence point as the curves are asymmetrical. The potential change at the end-point will also depend on the rate of titration. This procedure is not suitable for accurate titrations.

Titration to a preselected potential. This method with thorium or lanthanum titrants was evaluated by LINGANE[2]. The value of the preselected potential is affected by all the errors of the direct potentiometric method but their influence on the analytical result is, of course, smaller. This method presupposes that the end-point potential is stable but as shown in this paper this is not the case.

Straight-line regression of a titration. The GRAN plot can be extended to obtain straight-line functions as shown by ANFÄLT *et al.*[4]. If lanthanum is used as a titrant and only points well before the end-point are used the evaluation can be made from stable potential readings. The results will be independent of titration rate and of electrode standardization. If thorium is used as a titrant or if points after the end-point in a lanthanum titration are used, additional errors will arise as shown by the present results. The points on the plot may deviate from a straight line and there may be a systematic error in the end-point from reactions between the potential readings. The magnitude of these errors will depend on the titration rate.

The results obtained in this work can be summarized in a few recommendations for fluoride titrations.

Accurate titration of fluoride should employ lanthanum as a titrant in an unbuffered medium. Fluoride activity and pH should be measured at a number of points well before the end-point and the results computer-evaluated with the constants $\beta_1 = 10^{5.15}$ (β_2 can be neglected), $K_{s0} = 10^{-17.66}$ and $K_1 = 10^{-2.94}$ in a medium of constant ionic strength such as 1 M potassium nitrate or sodium chloride (calcium- and magnesium-free). The fluoride concentration should be 1 mM or higher.

Solutions which are 0.2–1 mM can be titrated with thorium with fair accuracy if the medium is low in sodium ($<$ 100 mM). The titrations should not be excessively slow. The reference electrode should be of the open-bridge type. Evaluation can be made either by titration to a selected potential or by the straight-line regression method.

The authors wish to thank Dr. OLLE GINSTRUP for valuable discussions. Dr. MICHAEL SHARP kindly revised the English of the manuscript.

SUMMARY

Some of the difficulties encountered in the titration of fluoride with fluoride-selective electrodes and lanthanum and thorium titrants have been studied in unbuffered media. The solubility product of lanthanum fluoride decreases with time as the precipitate ages and this accounts for a drift of the potential towards decreasing fluoride activity after the end-point. The solubility product of lanthanum fluoride was determined to be $10^{-17.66}$ at 25.0° in 1 M potassium nitrate or 1 M sodium chloride and the β_1 value of $La^{3+} + F^- \rightarrow LaF^{2+}$ was found to be $10^{5.15}$ under the same conditions. In accurate titrations of fluoride, lanthanum is recommended for fluoride solutions stronger than 1 mM, with computer evaluation. Thorium is recommended as a titrant in the range 0.2–1 mM fluoride.

RÉSUMÉ

Une étude est effectuée pour déterminer les conditions optimales du titrage potentiométrique des fluorures, à l'aide de lanthane et de thorium, en milieu non-tamponné. Le produit de solubilité du fluorure de lanthane diminue avec le temps; il est de $10^{-17.66}$ à 25° en milieu nitrate de potassium 1 M ou chlorure de sodium 1 M; la valeur β_1 de $La^{3+} + F^- \rightarrow LaF^{2+}$ est de $10^{5.15}$, dans les mêmes conditions. Pour des titrages précis de fluorure, on recommande le lanthane pour des concentrations supérieures à 1 mM, avec ordinateur. Le thorium convient pour des concentrations de l'ordre de 0.2 à 1 mM en fluorure.

ZUSAMMENFASSUNG

Einige der Schwierigkeiten, die bei der Titration von Fluorid mit fluoridselektiven Elektroden und Lanthan und Thorium als Titrationsmitteln aufgetreten sind, sind in ungepufferten Medien untersucht worden. Das Löslichkeitsprodukt von Lanthanfluorid nimmt mit der Zeit durch Alterung des Niederschlages ab. Dies erklärt die einer abnehmenden Fluoridaktivität entsprechende Potentialdrift nach dem Endpunkt. Das Löslichkeitsprodukt von Lanthanfluorid bei 25.0° in 1 M Kaliumnitrat oder 1 M Natriumchlorid wurde zu $10^{-17.66}$ bestimmt; für den β_1-Wert von $La^{3+} + F^- \rightarrow LaF^{2+}$ unter denselben Bedingungen wurde $10^{5.15}$ gefunden. Bei genauen Titrationen wird für stärkere als 1 mM Fluoridlösungen Lanthan und Auswertung mit einem elektronischen Rechner empfohlen. Thorium als Titrationsmittel wird empfohlen im Bereich 0.2–1 mM Fluorid.

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IODINE MONOCHLORIDE AS AN OXIDIMETRIC REAGENT FOR THE DETERMINATION OF SOME WATER-INSOLUBLE IODIDES, SULPHIDES, XANTHATES AND DITHIOCARBAMATES AND SOME DIFFICULTLY OXIDIZABLE REDUCTANTS

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Iodine monochloride is probably best known in analytical chemistry as an intermediate in oxidations with potassium iodate in strong hydrochloric acid media in Andrew's type titrations[1]. However, in recent years, it has been proposed as an oxidimetric titrant for various determinations, usually by direct titration procedures, but occasionally, *e.g.* for thiols, by back-titration methods[2]. Back-titration methods can be very useful when the nature of the reductant precludes direct titration, *e.g.*, when the reductant is insoluble. In the present paper, such procedures, with iodine monochloride as the oxidant are described for the determination of the following compounds:

(*a*) water-insoluble iodides (AgI, CuI, PbI_2, Hg_2I_2, HgI_2, TlI and BiI_3); (*b*) water-soluble sulphides (CdS, MnS and ZnS); (*c*) water-soluble potassium ethylxanthate; (*d*) water-insoluble zinc ethylxanthate and copper ethylxanthate; (*e*) water-soluble sodium diethyldithiocarbamate; (*f*) water-insoluble zinc diethyldithiocarbamate and copper diethyldithiocarbamate; (*g*) other reductants such as sodium hypophosphite, sodium dithionate, rongalite and thiocarbanilide.

It should be mentioned that, while several methods are available for the determination of water-soluble reductants, good procedures are not available for water-insoluble ones, although such reductants often are of industrial and commercial importance. Thus dithiocarbamates of zinc are well known vulcanization accelerators and several insoluble xanthates and dithiocarbamates are widely used as fungicides and insecticides. The methods developed for the simple oxidimetric assay of these compounds may therefore be of interest. The combined action of the strongly acidic medium employed (5 *M* hydrochloric acid) and the oxidizing action of iodine monochloride makes the present procedures ideally suited for these cases.

EXPERIMENTAL

Reagents

Stock solutions of iodine monochloride in 5 *M* hydrochloric acid were prepared by standard methods[2-4]. These solutions were stored in contact with a layer of carbon tetrachloride which served to extract away any trace of iodine from the aqueous phase. The solutions were shaken and after separation, the aqueous layer was always standardized before use. (It may be noted that in the 5 *M* hydrochloric acid medium employed, iodine monochloride exists mostly as the complex anion ICl_2^- and hence under these conditions its solubility in carbon tetrachloride is small[5].)

The insoluble iodides and sulphides were prepared from analytical reagent-grade salts of the metals, the purities of which were checked by standard methods. Special precautions were taken in the case of silver iodide to prevent exposure to light. Standard solutions of potassium ethylxanthate (Riedel de Haen), sodium diethyldithiocarbamate (B. D. H., AnalaR), sodium hypophosphite (May & Baker), sodium dithionate (B.D.H.) and rongalite (May & Baker) were prepared and their strengths were checked, respectively, by the following standard procedures against: chloramine-T[6], chloramine-T[7], cerium(IV) sulphate[8], potassium dichromate[9], and iodine[10]. Xanthates and dithiocarbamates of zinc and copper were prepared by double decomposition and their purities were checked by determination of total sulphur[11]. Standard solutions of recrystallised thiocarbanilide were prepared in glacial acetic acid and the strength was checked by total sulphur determination in measured aliquots of the solution[11].

All other reagents employed were of analytical reagent-grade purity.

Procedure 1

In this case the iodine produced during the reaction was quantitatively separated from the unconsumed iodine monochloride by successive extractions and was separately determined; the unconsumed iodine monochloride was also titrated.

A known volume (50 ml) of the standard iodine monochloride solution was pipetted into a tightly stoppered separating funnel. A weighed quantity of the insoluble reductant, or a measured aliquot of the solution of the soluble reductant, was added and the mixture was shaken thoroughly. After the completion of the reaction, the iodine produced was successively extracted with 15-ml portions of carbon tetrachloride. The last extract was colourless, indicating completeness of the extraction. The extracts were combined and back-extracted with aqueous 10% (w/v) potassium iodide solution and the iodine was titrated with standard thiosulphate solution.

The unconsumed iodine monochloride in the aqueous layer was determined by adding potassium iodide (20 ml of 10% solution), shaking and titrating the iodine produced with standard thiosulphate solution.

This procedure was found to be convenient for insoluble iodides, for which Procedure 2 is inapplicable (see DISCUSSION). On the other hand, Procedures 2 and 3 are simpler and are recommended for the other reductants mentioned.

Procedure 2

In this procedure no attempt was made to remove the iodine; instead it was determined along with the unconsumed iodine monochloride.

A known volume of standard iodine monochloride solution (50 ml) was pipetted into a 500-ml stoppered conical flask and either a known weight of the insoluble reductant or a measured aliquot of the soluble reductant solution was introduced. After completion of the reaction, 20 ml of 10% potassium iodide solution was added. The total iodine produced was determined by titrating with standard thiosulphate solution. Blanks were done concurrently.

Since 1 mole of iodine monochloride produces 2 equivalents of iodine during its reaction with iodide, but only one equivalent of iodine during its reaction with any other reductant, the experimental results of Procedure 2 are useful for the determination of reductants other than iodides only. The method was successful in the determination of sulphides, rongalite and thiocarbanilide. In the case of xanthates and dithiocarbamates of zinc, it was found advantageous to effect a prior treatment with 5 *M* potassium hydroxide; similarly, treatment with pyridine to effect prior dissolution of the sample was found necessary for the xanthates and dithiocarbamates of copper.

Procedure 3

In the case of hypophosphite or dithionate, the reaction was slow at ambient temperatures. The possibility of heating the solution was explored. It was found that solutions of iodine monochloride in 5 *M* hydrochloric acid could be refluxed (water condenser) for up to 1 h with practically no loss from volatilization or decomposition.

A known volume (50 ml) of standard iodine monochloride solution was pipetted into a 500-ml conical flask fitted with a standard ground-glass reflux condenser. After measured aliquots of the hypophosphite or dithionate solutions had been introduced, the system was refluxed for different time intervals, at the end of which the solutions were cooled, the iodine was quantitatively extracted with portions of carbon tetrachloride and the unconsumed oxidant in the aqueous layer was determined iodimetrically as usual. This procedure is applicable to all the other reductants mentioned also.

TABLE I

DETERMINATION OF WATER-INSOLUBLE IODIDES WITH IODINE MONOCHLORIDE

No.	*Reductant*	*Reductant taken (mmol)*	*Iodine produced (meq)*	*Equivalents of iodine produced per mole of reductant*
1	AgI	0.6068	1.218	2.006
2	AgI	0.9103	1.831	2.011
3	AgI	1.213	2.436	2.007
4	CuI	0.5077	1.523	3.000
5	CuI	0.7964	2.397	3.011
6	CuI	0.3744	1.130	3.018
7	PbI_2	0.4741	1.893	3.995
8	PbI_2	0.4399	1.752	4.030
9	PbI_2	0.3258	1.344	3.983
10	TlI	0.5077	2.032	4.021
11	TlI	0.4776	1.888	3.954
12	HgI_2	0.6407	2.564	4.002
13	HgI_2	0.6331	2.555	4.004
14	Hg_2I_2	0.3112	1.855	5.960
15	Hg_2I_2	0.1795	1.069	5.955
16	Hg_2I_2	0.2892	1.745	6.033
17	Hg_2I_2	0.3656	2.171	5.955
18	BiI_3	0.3333	1.986	5.957
19	BiI_3	0.1302	0.7861	6.036
20	BiI_3	0.2978	1.778	5.973

RESULTS AND DISCUSSION

Typical results are presented in Tables I–V.

It can be seen from Table I that the number of equivalents of iodine produced per mole of the reductant changes according to the reductant used. The reactions involved in the cases specified in Table I are as follows:

$AgI + ICl \rightarrow AgCl + 2I$

$CuI + 2ICl \rightarrow CuCl_2 + 3I$

$PbI_2 + 2ICl \rightarrow PbCl_2 + 4I$

$Hg_2I_2 + 4ICl \rightarrow 2HgCl_2 + 6I$

$HgI_2 + 2ICl \rightarrow HgCl_2 + 4I$

$TlI + 3ICl \rightarrow TlCl_3 + 4I$

$BiI_3 + 3ICl \rightarrow BiCl_3 + 6I$

It is clear that a titration of either the iodine produced or the iodine monochloride consumed alone is sufficient for the determination of the insoluble iodides; however, titrations of both could act as a check on the values.

It was observed that while the iodides of Cu, Tl, Hg and Bi dissolved easily, silver chloride and lead chloride were precipitated when silver iodide and lead iodide were analysed. It was further found that only freshly precipitated silver iodide reacted quantitatively to produce the stoichiometric requirement of iodine and silver chloride.

The results in Table II show that the sulphides are oxidized only to the elemental sulphur stage under the experimental conditions described. Here, the precipitated elemental sulphur adhered to the carbon tetrachloride–water interface during attempts at extraction. Accordingly, Procedure 2 was preferred to Procedure 1 in these cases. The experimental results agree with the following oxidation schemes.

$ZnS + 2ICl \rightarrow ZnCl_2 + 2I + S$

$CdS + 2ICl \rightarrow CdCl_2 + 2I + S$

$MnS + 2ICl \rightarrow MnCl_2 + 2I + S$

The results in Tables III and IV show that the water-soluble and -insoluble xanthates and dithiocarbamates studied undergo oxidation consuming 14 moles of

TABLE II

DETERMINATION OF SULPHIDES WITH IODINE MONOCHLORIDE

No.	*Reductant*	*Reductant taken (mmol)*	*ICl consumed (mmol)*	*Moles ICl consumed per mole of reductant*
1	ZnS	0.3533	0.7063	1.999
2	ZnS	1.296	2.387	1.996
3	ZnS	0.7943	1.581	1.991
4	ZnS	0.5923	1.184	1.999
5	CdS	0.4508	0.8928	1.981
6	CdS	0.7223	1.455	2.015
7	MnS	0.6476	1.319	2.037
8	MnS	0.5453	1.090	1.995

TABLE III

DETERMINATION OF XANTHATES WITH IODINE MONOCHLORIDE

No.	*Reductant*	*Reductant taken (mmol)*	*ICl consumed (mmol)*	*Moles ICl consumed per mole of reductant*
1	Potassium ethylxanthate[a]	0.03550	0.4891	14.06
2	Potassium ethylxanthate[a]	0.05241	0.7288	13.91
3	Potassium ethylxanthate[a]	0.08736	1.217	13.93
4	Potassium ethylxanthate[a]	0.1048	1.472	14.06
5	Potassium ethylxanthate[a]	0.1398	1.954	13.97
6	Zinc ethylxanthate[a]	0.01813	0.5055	27.87
7	Zinc ethylxanthate[a]	0.02720	0.7605	27.96
8	Zinc ethylxanthate[a]	0 03626	1.016	28.01
9	Zinc ethylxanthate[a]	0.04533	1.266	27.93
10	Zinc ethylxanthate[a]	0.05441	1.522	27.98
11	Copper(I) ethylxanthate[b]	0.02351	0.3259	13.87
12	Copper(I) ethylxanthate[b]	0.04701	0.6518	13.87
13	Copper(I) ethylxanthate[b]	0.07052	0.9826	13.93
14	Copper(I) ethylxanthate[b]	0.09402	1.306	13.92
15	Copper(I) ethylxanthate[b]	0.1175	1.627	13.87
16	Copper(I) ethylxanthate[b]	0.1432	1.980	13.85

[a] Standing time of 60 min.
[b] Standing time of 90 min.

TABLE IV

DETERMINATION OF DITHIOCARBAMATES WITH IODINE MONOCHLORIDE

No.	*Reductant*	*Reductant taken (mmol)*	*ICl consumed (mmol)*	*Moles ICl consumed per mole of reductant*
1	Sodium diethyldithiocarbamate[a]	0.05202	0.7283	14.00
2	Sodium diethyldithiocarbamate[a]	0.06243	0.8720	13.96
3	Sodium diethyldithiocarbamate[a]	0.07283	1.021	14.02
4	Sodium diethyldithiocarbamate[a]	0.08324	1.169	14.05
5	Sodium diethyldithiocarbamate[a]	0.1200	1.692	14.10
6	Sodium diethyldithiocarbamate[a]	0.1200	1.688	14.06
7	Zinc diethyldithiocarbamate[a]	0.03681	1.029	27.95
8	Zinc diethyldithiocarbamate[a]	0.04907	1.375	28.02
9	Zinc diethyldithiocarbamate[a]	0.06134	1.708	27.97
10	Zinc diethyldithiocarbamate[a]	0.06134	1.708	27.97
11	Zinc diethyldithiocarbamate[a]	0.04907	1.375	28.02
12	Zinc diethyldithiocarbamate[a]	0.04907	1.371	27.94
13	Copper(II) diethyldithiocarbamate[b]	0.01467	0.4000	27.28
14	Copper(II) diethyldithiocarbamate[b]	0.02200	0.5975	27.11
15	Copper(II) diethyldithiocarbamate[b]	0.02933	0.7950	27.11
16	Copper(II) diethyldithiocarbamate[b]	0.04399	1.185	26.95
17	Copper(II) diethyldithiocarbamate[b]	0.05866	1.590	27.11

[a] Standing time of 60 min.
[b] Standing time of 90 min.

TABLE V

DETERMINATION OF MISCELLANEOUS REDUCTANTS WITH IODINE MONOCHLORIDE

No.	*Reductant*	*Reductant taken (mmol)*	*ICl consumed (mmol)*	*Moles ICl consumed per mole of reductant*	*Refluxing (or standing) time (min)*
1	Sodium hypophosphite	0.2375	0.9501	4.000	60
2	Sodium hypophosphite	0.1663	0.6640	3.994	60
3	Sodium hypophosphite	0.2137	0.8506	3.979	60
4	Sodium hypophosphite	0.1425	0.5670	3.979	60
5	Sodium dithionate	0.4165	0.8312	1.995	30
6	Sodium dithionate	0.1665	0.3311	1.988	30
7	Sodium dithionate	0.2500	0.5021	2.009	30
8	Sodium dithionate	0.3324	0.6643	1.998	30
9	Sodium dithionate	0.08326	0.1666	2.001	30
10	Sodium dithionate	0.1246	0.2477	1.992	30
11	Sodium dithionate	0.2914	0.5833	2.002	30
12	Formaldehyde sulphoxylate	0.2158	0.8654	4.010	10
13	Formaldehyde sulphoxylate	0.2877	1.152	4.005	10
14	Formaldehyde sulphoxylate	0.3596	1.444	4.016	10
15	Formaldehyde sulphoxylate	0.1843	0.7372	4.000	10
16	Formaldehyde sulphoxylate	0.2457	0.9831	4.000	10
17	Formaldehyde sulphoxylate	0.3071	1.234	4.018	10
18	Thiocarbanilide	0.04753	0.3775	7.945	45
19	Thiocarbanilide	0.1488	1.185	7.960	45
20	Thiocarbanilide	0.08056	0.6403	7.949	45

the oxidant per mole of xanthate or dithiocarbamate grouping according to the following scheme.

$$ROCSS^- + 14ICl + 10H_2O \rightarrow 2SO_4^{2-} + ROH + HCOO^- + 14I + 14Cl^- + 18H^+$$

$$R_2NCSS^- + 14ICl + 10H_2O \rightarrow 2SO_4^{2-} + R_2NH + HCOO^- + 14I + 14Cl^- + 18H^+$$

It may be noted that while the zinc xanthate and zinc dithiocarbamate require 28 moles of iodine monochloride per mole of the reductant, as expected, the stoichiometry with the copper compounds is different .Thus, for copper(II) diethyldithiocarbamate, while 28 moles of iodine monochloride are expected to be consumed per mole of the compound, the experimental value is only 27. This is because, during the final iodimetric titration, copper(II) is converted to copper(I) producing an equivalent of iodine. In the case of copper(I) xanthate, the oxidant oxidises the xanthate to sulphate and the copper(I) to copper(II); however, during the final iodimetric estimation, copper(II) is reconverted to copper(I), and so the experimental value agrees with the expected value (14).

Separate investigations showed that under the experimental conditions described oxidation of formic acid (a reaction product) or pyridine (which is used to dissolve the copper compounds) by iodine monochloride is negligible.

Table V summarises typical results with miscellaneous reductants. The moles of iodine monochloride consumed per mole of the various reductants are in agreement with following reaction schemes.

$$H_2PO_2^- + 4ICl + 2H_2O \rightarrow H_3PO_4 + 4I + 3H^+ + 4Cl^-$$

$$S_2O_6^{2-} + 2ICl + 2H_2O \rightarrow 2SO_4^{2-} + 2I + 2Cl^- + 4H^+$$

$$CH_2(OH)SO_2^- + 4ICl + 2H_2O \rightarrow CH_2O + SO_4^{2-} + 4I + 4Cl^- + 5H^+$$

$$Ph\,NH.CS.NH\,Ph. + 8ICl + 6H_2O \rightarrow 2Ph\,NH_2 + 8I + 8Cl^- + CO_2 + SO_4^{2-} + 10H^+$$

It is interesting to observe that even the difficultly oxidizable reductants such as hypophosphite and dithionate are easily oxidized with solutions of iodine monochloride on heating. The quickest method at present available for the determination of hypophosphite in aqueous medium is the cerimetric method[8]; the present method may be considered as a useful alternative to it. Thiourea has been previously oxidized[3] with iodine monochloride; the present work with thiocarbanilide shows that organic derivatives of thiourea may also be determined. The versatility of back-titration procedures with iodine monochloride is remarkable as may be seen from the diverse nature of the reductants examined in the present study. Further work is in progress.

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SUMMARY

Back-titration procedures with iodine monochloride as the oxidant in 5 *M* hydrochloric acid medium are described for the following reductants: iodides of copper(I), lead, thallium, silver, mercury(I) and mercury(II), and bismuth; sulphides of zinc, cadmium and manganese; ethylxanthates of potassium, zinc and copper; diethyldithiocarbamates of sodium, zinc and copper, sodium hypophosphite and sodium dithionate.

RÉSUMÉ

On décrit des méthodes de titrage en retour à l'aide de monochlorure d'iode comme oxydant, en milieu acide chlorhydrique 5 *M*, pour le dosage des produits réducteurs suivants: iodures de cuivre(I), de plomb, de thallium, d'argent, de mercure(I) et (II), et de bismuth; sulfures de zinc, de cadmium et de manganèse; éthylxanthates de potassium, de zinc, et de cuivre; diéthyldithiocarbamates de sodium, de zinc et de cuivre, hypophosphite et dithionate de sodium.

ZUSAMMENFASSUNG

Es werden Rücktitrationsverfahren mit Jodmonochlorid als Oxydationsmittel in 5 *M* salzsaurem Medium für die Bestimmung von folgender Reduktionsmittel beschrieben: Jodide von Kupfer(I), Blei, Thallium, Silber, Quecksilber(I), Quecksilber(II) und Wismut; Sulfide von Zink, Cadmium und Mangan; Äthylxanthate von Kalium, Zink und Kupfer; Diäthyldithiocarbamate von Natrium, Zink und Kupfer; Natriumhypophosphit und Natriumdithionat.

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THE DETERMINATION OF SULPHATE IN SEA WATER BY MEANS OF PHOTOMETRIC TITRATION WITH HYDROCHLORIC ACID IN DIMETHYL SULPHOXIDE

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A vast number of methods have been suggested for the determination of sulphate but few of these are applicable to sea water, owing to the high salt content. The sulphate concentration in sea water, which is approximately 0.029 *M* at 35‰ salinity[1], is normally determined gravimetrically as the barium salt, and results from sulphate analyses in different sea water samples have been summarized by CULKIN[2]. Apart from being time-consuming, the gravimetric method suffers from errors caused by co-precipitation mainly by calcium and alkali metals. As demonstrated by ROSS AND FRANT[3], the potentiometric titration of sulphate with lead nitrate using an ion-selective lead electrode does not give satisfactory results in media with high chloride concentrations. Attempts to titrate sulphate with barium nitrate by following the decrease in sulphate concentration with a silver sulphide membrane electrode made sensitive to sulphate by immersion in an ethanol–water mixture in which lead sulphate and lead sulphide were then precipitated also failed to give acceptable results[4].

In the titration method described in this paper, sulphate is titrated in dimethyl sulphoxide solution with hydrochloric acid to hydrogen sulphate, using bromocresol green as indicator. The end-point is determined graphically from the photometric titration data.

THEORY

Dimethyl sulphoxide can be characterized as a non-protonic dipolar solvent with a dielectric constant of 48.9 at 20° [5]. The pK_a value of the protonated dimethyl sulphoxide in aqueous solution has been determined by WADA[6] to be -1.04 at zero ionic strength and the acidic properties of the unprotonated solvent are so weak that they do not affect the titration of sulphate with hydrochloric acid[7,8].

The use of dimethyl sulphoxide as a solvent for analytical purposes has been extensively reviewed[9]. SCHLÄFER AND SCHAFFERNICHT[5] have covered the solubility of inorganic salts in dimethyl sulphoxide while the corresponding aspects in organic chemistry have been reviewed by MARTIN *et al.*[10]. Different electroanalytical applications of the solvent have been summarized by BUTLER[11]. Recently, dimethyl sulphoxide has been used, by HILLER[12], as medium in the conductometric titration of a large number of weak acids.

A very high apparent stability constant, which is mainly due to hydrogen bonding with the solvent, for hydrogen sulphate in dimethyl sulphoxide, corresponding to a pK_a value for HSO_4^- of 9.1 has been reported by KOLTHOFF AND REDDY[7]. In a later investigation KOLTHOFF AND CHANTOONI[13] redetermined this value to be 14.5 and the earlier, lower value was explained by incomplete dissociation of $NaSO_4^-$ in the medium. Even though the pK_a value is, of course, dependent on the molar ratio of water and on the ionic composition and strength of the solution, it would appear to be sufficiently high to permit the titration of sulphate in sea water with hydrochloric acid. Moreover, sulphuric acid is a strong acid in dimethyl sulphoxide and the homoconjugation reaction $SO_4^{2-} + HSO_4^- \rightleftharpoons H(SO_4)_2^{3-}$ can be neglected[6,13]. Owing to the lack of relevant stability constants it was not possible to perform a rigorous calculation of the titration curve. The difference in the dielectric constants of water and dimethyl sulphoxide, which implies[7] an increase in the stability constant for a univalent negatively charged acid by a factor of approximately 200, in combination with the apparent stability constants given above, suggested that, *e.g.*, sulphonphthaleins with colour transition intervals in the pH range 3.5–5.5 ought to be suitable as indicators for the photometric detection of the end-point. Both dibromodichlorophenolsulphonphthalein (bromochlorophenol blue) and dimethyltetrabromosulphonphthalein (bromocresol green) were found to be satisfactory, the latter being slightly superior. The absorption spectra for the acid $HA^{\pm-}$ and basic $A^{\pm2-}$ forms of bromocresol green were registered both in water and dimethyl sulphoxide solution and were found to be almost identical. The acid form has an absorption maximum at 420 nm and the basic form at 620 nm in both solvents.

EXPERIMENTAL

Reagents

All reagents were of analytical grade.

Dimethyl sulphoxide (Fisher Scientific Reagent) was used without further purification.

Bromocresol green solution. An 0.1 % solution, by weight in doubly distilled water, was prepared from the acid form of the indicator (Merck AG, Darmstadt) and an equivalent amount of sodium hydroxide.

Standard sulphate solution. An 0.029 *M* solution was prepared by weighing sodium sulphate (Merck AG, Darmstadt) previously dried at 100° for 12 h. In order to simulate the salt content of sea water, the solution was made 0.43 *M* in sodium chloride (maximum sulphate content 0.007 %), 0.01 *M* in calcium chloride and 0.05 *M* in magnesium chloride. Dilute standard sulphate solution was prepared by volumetric dilution of the standard sulphate solution with doubly distilled water.

Standard carbonate solution. An 0.0100 *M* solution was prepared by weighing sodium carbonate (Urtitersubstanz, Merck AG, Darmstadt) previously dried at 270° for 1 h.

Standard hydrochloric acid. An aqueous 0.020 *M* solution was prepared and standardized against the standard sulphate solution according to the titration procedure described below. Lower hydrochloric acid concentrations were obtained by volumetric dilution.

Standard Sea Water (chlorinity 19.3745 ‰) was purchased from I.A.P.S.O., Standard Sea Water Service, Charlottenlund Slot, Denmark. Dilute standard water was obtained by volumetric dilution.

Apparatus

Photometer. The titration curve was registered on an EEL Quantitrator (Evans Electroselenium Ltd, Halstead, England). The current output from the selenium photocell was led through a resistance of approximately 1500 Ω and the voltage drop was followed by means of a digital voltmeter (Dynamco 2006) which could measure to four significant figures in the range 0–100 mV. The load resistance of the photocell was too high to permit a linear response between the illumination energy falling on the photocell and the voltage drop, E mV, over the resistance. Nevertheless, it was found that, in the energy interval relevant to a titration, the absorbance value, A, corresponding to a specific e.m.f. value, E, could be approximated as:

$$A \propto \text{constant} - \log E$$

Since, in the method chosen to evaluate the equivalence point, only differences in absorbance readings were required, these approximate values for the absorbance were sufficiently accurate.

The photometer was equipped with an Ilford narrow band filter No. 606 of peak wavelength 580 nm.

Electrode couple. The potentiometric titrations were performed with a glass electrode (Radiometer G202 B) and a calomel reference (Radiometer K 401).

Semi-automatic titrator. The titrations were either performed manually, or with a semi-automatic titrator[14]. The titrator operates with discrete increments of titrant of pre-chosen magnitude and can be programmed to wait a pre-set duration of time between each new addition of titrant. The syringe buret (Metrohm Dosimat E 415) had a volume of 10 ml.

Pipets. All pipets used for sampling and diluting were calibrated, before use, against the weight of doubly distilled water held at 23°.

Recommended titration procedure

Approximately 5 ml of accurately measured sea water is slowly added from a pipet to 120 ml of dimethyl sulphoxide, the solution being stirred during the addition. If the sample is added too quickly there is a risk of precipitation; this precipitate, calcium sulphate, is often only clearly visible in the beam of light from the photometer. Once formed, however, it does not redissolve on addition of the hydrochloric acid titrant and the sample must therefore be discarded.

Indicator (about 6 drops) is then added to the titration vessel together with *ca.* 90% of the volume of hydrochloric acid needed for equivalence. Titrant increments of 0.05 ml are then added and the corresponding voltage readings registered. In the close vicinity of the equivalence point (before and after) voltage readings can be obtained rapidly. At the very beginning of the titration it is, however, necessary to wait up to 1 min between each new titrant increment in order to obtain stable voltage readings.

Automatic procedure

The sampling technique is the same as for the manual titration. The titrator is programmed to deliver 0.05-ml titrant increments and the time between each new titrant increment is set to 1 min. Since such a long time interval is necessary only at the beginning of the titration, the interval is decreased to 10 sec during the course of the titration.

Evaluation of the equivalence point

The titration curve $A \propto -\log E$ is plotted against v ml titrant added and the tangent to the steepest part of the titration curve is drawn. The intersection between this tangent and the gradient of the linear part of the titration curve for v values greater than the equivalence volume then gives the end-point. This procedure is illustrated in Fig. 1.

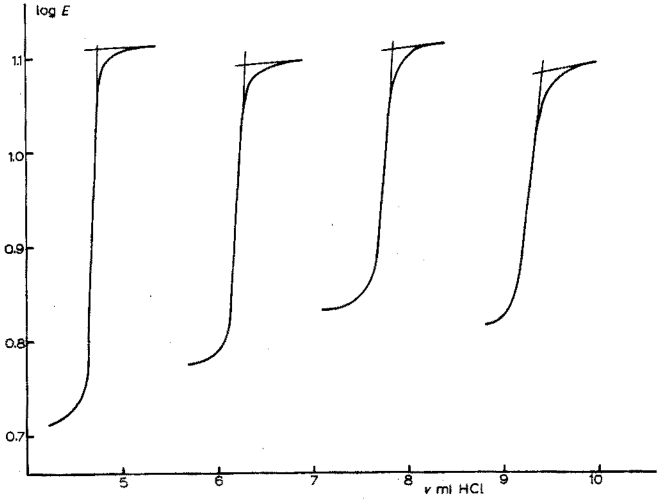

Fig. 1. Titration curves (log E (mV) against ml titrant added) for the titration of *ca.* 3, 4, 5 and 6 ml of Standard Sea Water with v ml of 0.02002 M hydrochloric acid. The curves have been corrected for basic impurities and indicator error.

Standardization of hydrochloric acid

The hydrochloric acid solutions were standardized against standard sulphate solutions by the titration procedure described above. The sulphate concentration of the standard solution should be chosen close to that of the sea water to be titrated. Approximately the same amount of sample should be used in the standardization as in the sea water titrations. The systematic error introduced by the method to evaluate the equivalence point can, in this way, be almost eliminated.

Impurities in dimethyl sulphoxide

The amount of basic impurities in dimethyl sulphoxide and the magnitude of the indicator error were determined by titration. Indicator (18 drops) and *ca.* 15 ml of doubly distilled water were added to 360 ml of dimethyl sulphoxide. The solution was titrated with hydrochloric acid and the equivalence point was extrapolated as described above. The indicator error together with the amount of basic impurities in the dimethyl sulphoxide–water mixture was of the order of 0.013 mM. This value was subtracted from the values of the equivalence volume obtained in the standardizations and sea water titrations.

Other methods of determining the end-point

Potentiometric titration. Attempts were first made to follow the titration curve potentiometrically with glass and reference electrodes. The end-point was evaluated by means of the GRAN[17] method, the function

$$F_1=(v_0+v)\ 10 \exp EF/RT \ln 10$$

being plotted against v ml of titrant for e.m.f. values obtained after the equivalence point. Owing to slow response and non-Nernstian behaviour of the electrode this method was discarded. The standard deviation obtained from sixty different titrations was approximately ± 2 %.

Visual indication. The titration can, of course, be performed visually and the magnitude of the colour transition interval can be estimated from Fig. 1. The colour transition from green to yellow is taken as end-point. Since, however, these colours are difficult for the human eye to distinguish, the precision is considerably lower than that obtained photometrically.

INTERFERENCES

All species which can accept a proton will, in principle, interfere with the titration. The predominant basic species in sea water belong either to the carbonate or to the borate systems. The ability of a sea water sample to consume protons is known as its alkalinity and is defined as

$$\text{Alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [B(OH)_4^-]$$

All carbonate species were shown, by the following procedure, to be completely converted to carbon dioxide during the titration of sulphate. Different volumes of standard carbonate solution *i.e.* 1, 2, 3 and 4 ml portions, respectively, were added to four solutions containing 120 ml of dimethyl sulphoxide and 4 ml of standard sulphate solution. The solutions were then titrated with hydrochloric acid. The resulting increase in the equivalence volumes showed that all carbonate was completely converted to carbon dioxide. Moreover, the form of the titration curves did not change on addition of carbonate which indicated that carbonate was titrated before sulphate.

TABLE I

RESULTS FROM 20 TITRATIONS OF *ca.* 3, 4, 5 AND 6 ml OF STANDARD SEA WATER (CHLORINITY = 19.3745 ‰) IN 120 ml OF DIMETHYL SULPHOXIDE WITH v ml OF 0.02002 M HYDROCHLORIC ACID (*cf.* Fig. 1)

No. of titrations	*ml sample*[a]	*g sample*[b]	*$[SO_4^{2-}]$ (mM)*	*$[SO_4^{2-}]$ (mmol kg^{-1})*	*$[SO_4^{2-}]$ (g kg^{-1}) / chlorinity (‰)*	*Standard deviation (%)*
5	5.988	6.135	28.97	28.27	0.1402	0.08
5	5.002	5.125	28.96	28.26	0.1401	0.10
5	3.989	4.088	28.92	28.23	0.1400	0.09
5	2.992	3.066	28.92	28.23	0.1399	0.18
Mean value	—	—	28.94	28.25	0.1401	0.11

[a] According to weight-calibrated pipet.

[b] Density of sea water 1.0246 g cm^{-3}.

The alkalinity of the sea water sample, which is determined as a routine procedure, should thus be subtracted from the results for sulphate.

The alkalinity of the Standard Sea Water was determined to be 2.652 mmol kg^{-1} by potentiometric titration[15,16]. Since the error in the alkalinity determination is less than 0.1 % and the alkalinity of sea water is normally less than 10 % of the total sulphate content, the contribution of the error from the alkalinity determination to the sulphate determination is negligible.

TABLE II

RESULTS FROM 15 TITRATIONS OF *ca.* 3, 4, 5 AND 6 ml OF DILUTED STANDARD SEA WATER (1:10 BY VOLUME
CHLORINITY = 19.3745 $^{0}/_{00}$) IN 120 ml OF DIMETHYL SULPHOXIDE WITH *v* ml OF 0.00500 *M* HYDROCHLORIC ACI

No. of titrations	*ml sample*	*g sample*[a]	*$[SO_4^{2-}]$*[a] *(mM)*	*$[SO_4^{2-}]$*[a] *(mmol kg^{-1})*	*$[SO_4^{2-}]$*[a] *(g kg^{-1}) / chlorinity ($^{0}/_{00}$)*	*Standard deviation (%)*
3	5.988	0.6135	29.00	28.30	0.1403	0.14
5	5.002	0.5125	29.05	28.36	0.1406	0.11
4	3.989	0.4088	28.83	28.13	0.1395	0.16
3	2.992	0.3066	28.86	28.17	0.1397	0.24
Mean value	—	—	28.94	28.24	0.1400	0.16

[a] Refers to undiluted Standard Sea Water.

RESULTS

High salinity sea water

The results from twenty titrations of 35$^{0}/_{00}$ Standard Sea Water are given in Table I and the corresponding titration curves are shown in Fig. 1. Table I shows that the precision obtained for a specific amount of sea water is high and, furthermore, since the amount of sea water titrated is, obviously, not a very critical parameter, the method yields an acceptable accuracy. In routine analysis it is, of course, recommendable always to use the same amount of sample in order to keep the water molar ratio constant.

Titrations were also carried out on sea water samples drawn from 1–30 m depth at the fjord of Gullmaren, north of Göteborg. Twenty titrations of water samples with chlorinities of 15–19$^{0}/_{00}$ yielded a mean value of 0.1401 (9) for the ratio g SO_4^{2-} per kg/chlorinity ($^{0}/_{00}$), the standard deviation being less than 0.1 %.

Low salinity sea water

The results from fifteen titrations in low salinity sea water (Standard Sea Water diluted 1:10 by volume) are given in Table II. The precision and accuracy are seen to decrease in diluted sea water, but, even so, they are both satisfactory. At even lower salinities the accuracy will decrease steadily and the method cannot therefore be used to determine sulphate in fresh water.

DISCUSSION

The results obtained for the sulphate concentration in sea water are in good agreement with those obtained gravimetrically[1] and the accuracy and precision are compatible with this method. The time needed for a photometric titration is very much less than that required by a gravimetric analysis. A single titration can be performed in 15 min, including the time needed for the evaluation of the equivalence point. If a semi-automatic titrator is used, several titrations can be run simultaneously and determinations can thus be performed more rapidly.

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SUMMARY

The sulphate concentration in sea water has been determined by photometric titration to hydrogen sulphate in dimethyl sulphoxide solution with hydrochloric acid, using bromocresol green as indicator. The end-point is evaluated graphically and a complete titration can be performed in less than 15 min. Since borate, carbonate and hydrogen carbonate interfere, a separate determination of the alkalinity is necessary. The method can be used satisfactorily for sea water samples with a chlorinity of at least 2 $^0/_{00}$.

RÉSUMÉ

On propose une méthode pour le dosage des sulfates dans l'eau de mer, par titrage photométrique à l'aide d'acide chlorhydrique, en solution diméthylsulfoxyde, et en utilisant le vert de bromocrésol comme indicateur. Le point final est déterminé graphiquement; un titrage complet peut être effectué en moins de 15 min. Borates, carbonates et bicarbonates gênent; il faut alors procéder à une détermination préalable de l'alcalinité.

ZUSAMMENFASSUNG

Die Sulfatkonzentration in Meerwasser ist durch photometrische Titration bestimmt worden. In Dimethylsulfoxid-Lösung wird mit Salzsäure Hydrogensulfat gebildet; Bromkresolgrün dient als Indikator; der Endpunkt wird graphisch ermittelt. Eine vollständige Titration kann in weniger als 15 min ausgeführt werden. Da Borat, Carbonat und Hydrogencarbonat stören, ist eine getrennte Bestimmung der Alkalität erforderlich. Die Methode ist bei Meerwasserproben mit einem Chlorgehalt von mindestens 2$^0/_{00}$ zufriedenstellend.

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A RAPID SEMI-AUTOMATIC METHOD FOR THE DETERMINATION OF THE TOTAL HALIDE CONCENTRATION IN SEA WATER BY MEANS OF POTENTIOMETRIC TITRATION

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Methods for determining the chlorinity of sea water by means of potentiometric titration were first devised by WEST AND ROBINSON[1] and have subsequently been improved by several other workers[2-5]. DYRSSEN AND JAGNER[6] suggested that, if the GRAN[7] method were used to evaluate the equivalence volume from several titration points, a higher precision could be obtained. The development of this procedure is discussed in this paper.

Since it is desirable to reduce the time needed for each titration, a semi-automatic titrator[8] is used which, in combination with computer evaluation of the equivalence volume, considerably reduces both the titration time and the errors involved in the determination, the method having previously[9] been devised for ordinary titration apparatus.

EXPERIMENTAL

Reagents

All reagents were of analytical grade.

Standard silver nitrate solution (*ca.* 0.3 *M*) was prepared by dissolving the salt in doubly distilled water. The solution was standardised against *Standard Sea Water* (chlorinity 19.3745 ‰) purchased from I.A.P.S.O., Standard Sea Water Service, Charlottenlund Slot, Denmark, by the titration procedure given below. This sea water has been used as standard in all previous methods.

Standard acidic potassium nitrate solution was prepared by dissolving potassium nitrate in doubly distilled water. Nitric acid was then added until the solution was 0.05 *M* with respect to both nitric acid and potassium nitrate.

Ethanol (95% by volume; AB Vin och Spritcentralen, Sweden). The ethanol and acidic potassium nitrate solutions were carefully checked for chloride impurities by the titration procedure described below and were found to contain no measurable amounts of chloride.

Apparatus

Titration vessel. The titrations were carried out in polyethylene vessels of total volume 250 ml. A lid was fitted on to each vessel in order to prevent evaporation during the weighing-in of the samples. Each vessel was used only once. Vigorous stirring was provided by means of a magnetic stirrer equipped with a heavy rod magnet.

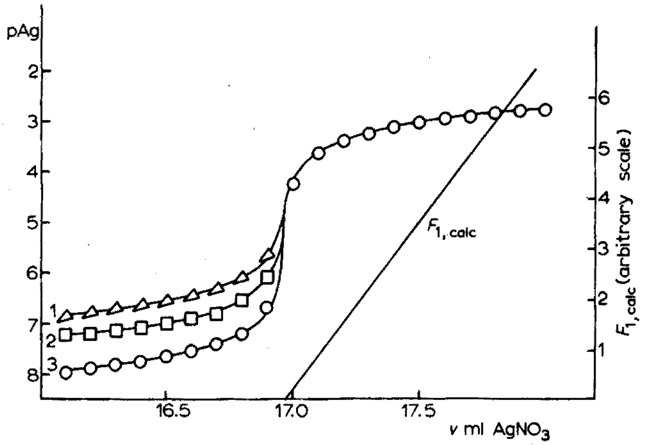

Fig. 1. Experimental points pAg against v ml of titrant added for the titration of three *ca.* 10.201-g samples of Standard Sea Water with v ml of 0.32876 M silver nitrate. The samples were diluted with a ml of ethanol and $(150-a)$ ml of acidic potassium nitrate solution. The solid curves through the experimental points were calculated by the computer using those pK_{s0} values giving the best fit to experimental data. The GRAN plot $F_{1,\mathrm{calc}} = (160 + v)10^{-\mathrm{pAg}}$ was calculated from the computer results. (△) $a = 0$ ml, (□) $a = 50$ ml, (○) $a = 100$ ml. The experimental points coincide for $v > 17.0$ ml.

TABLE I

THE TEXT ON THE TELETYPE WRITER AND DATA TAPE FOR THE TITRATION OF 10.2012 g OF STANDARD SEA WATER WITH v ml OF 0.32876 M SILVER NITRATE

(Explanations added within parentheses are not included on the data tape)

100 ml EtOH/50 ml KNO$_3$;		(title, followed by semicolon)	punched manually
160		(v_0 ml)	
22		(°)	
0.32876		(concentration of silver nitrate)	
10.2012		(weight of sample, g)	
1		(number of titration vessels)	
87 + 8050	89 — 1179		punched automatically
87 + 8100	89 — 1232		
87 + 8150	89 — 1279	(87 = channel number for buret reading followed by 500 x ml titrant (*e.g.* 8050 = 16.10 ml titrant))	
87 + 8200	89 — 1326		
87 + 8250	89 — 1384		
87 + 8300	89 — 1431		
87 + 8350	89 — 1513		
87 + 8400	89 — 1642		
87 + 8450	89 — 1941		
87 + 8500	89 — 3375	(89 = channel number for electrode couple followed by 10 x potential reading in mV (*e.g.* $-1179 = -117.9$ mV))	
87 + 8550	89 — 3727		
87 + 8600	89 — 3873		
87 + 8650	89 — 3961		
87 + 8700	89 — 4031		
87 + 8750	89 — 4078		
87 + 8800	89 — 4131		
87 + 8850	89 — 4160		
87 + 8900	89 — 4195		
87 + 8950	89 — 4225		
87 + 9000	89 — 4248		
/	(end of titration)		

Aluminium foil was wrapped around the titration vessel to protect the contents from direct light during the titration.

Electrode system. The potential was measured with the following electrode couple:

Ag/titration vessel//0.05 M KNO_3+0.05 M HNO_3/saturated calomel.

This couple was calibrated against known concentrations of silver nitrate in water–ethanol solutions (0–60 % ethanol by volume) and showed a Nernstian response for silver ions in the concentration range used in the titrations. The saturated calomel reference electrode (Radiometer K 401) was bridged to the titration vessel with standard acidic potassium nitrate by means of a glass finger with a very fine hole. There was no indication that chloride ions from the saturated calomel electrode migrated through the glass finger into the titration vessel or that silver ions migrated into the glass finger. The silver rod used as indicator electrode was polished after about twenty titrations to remove the adhering silver chloride precipitate.

Other electrode couples were also tested and were found to work satisfactorily. For example, the system: Ag_2S/titration vessel//0.05 M HNO_3+0.05 M KNO_3/saturated calomel, where Ag_2S denotes a silver sulphide membrane electrode (Orion Research Inc.; Model 94-16) proved satisfactory. The use of commercial electrodes would, however, make the method unnecessarily expensive if several titrations are to be carried out simultaneously.

After this investigation had been completed, it was found that if a mixture of silver sulphide and silver bromide was pressed under high pressure to form a pellet of approximate radius 0.5 cm, and this pellet was then used as a membrane, analogously to the Orion electrode discussed by Ross[10], a silver ion electrode which was far more rapid and stable than the silver rod was obtained. Moreover, owing to the shape of the electrode, the silver chloride formed during titrations did not adhere to the electrode surface so that it was no longer necessary to polish the electrode periodically. The electrode couple suggested by HERRMANN[3] (Ag/titration vessel//titrant solution/Ag) which necessitates the dipping of the buret tip into the titration vessel has given good results[9], but is not practical for use in combination with the automatic titrator.

Titrator. The titrations were carried out with the semi-automatic titrator described by JAGNER[8]. This titrator, which does not charge samples automatically, can provide titrant increments of pre-set magnitude to the titration vessels and be programmed to wait a pre-set period of time to ensure complete mixing and precipitation. The results (total volumes of titrant added and electrode potentials) are then printed out on a teletype writer and on punched tape ready for subsequent computing. The titrant is added by means of motor-driven syringe burets of total volume 20 ml, the axles of the syringe burets being coupled to potentiometers which deliver voltage signals proportional to the total volume of titrant added. The tip of each buret, which is drawn out to a fine capillary, is not immersed in the titrant during titration but is covered both inside and outside by a thin layer of grease to minimise the size of the adhering droplet. The magnitude of this droplet was estimated, by weighing, to be 0.002 ml, this value being reproducible to within 10 % after each new addition of titrant.

Since the titrator has ninety channels available for input data, up to forty-five titration vessels can be used at the same time, each titration vessel being identified in the computation by a channel number which is punched automatically on the data tape before each potential and buret reading. The buret and electrode potential readings are transferred *via* a scanner to a digital voltmeter with a resolution of ± 0.1 mV in the voltage range 0–1 V.

Titration procedure

Samples of sea water are introduced into a weighed titration vessel by means of a volumetric pipet, after which the vessel is immediately sealed and reweighed. During the weighing-in procedure, extreme care must be taken to avoid warming the air in the polyethylene beakers with the hands. In order to obtain optimum precision in the volume reading, the amount of sample and the titrant concentration should be chosen so that the equivalence point is 15–18 ml[8]. In practice, an approximate value of the chlorinity of the sample is usually known and the required amount of sample can be estimated from the relation:

$$\text{gram}(\approx \text{ml})\ \text{sample} \cdot \text{titrant concentration} \cdot \text{chlorinity} \approx 60 \qquad (1)$$

i.e., for a chlorinity of 19 ‰, approximately 10-ml samples should be taken if 0.3 M silver nitrate is used as titrant. The samples are first diluted with 50 ml of acidic potassium nitrate solution and then with 50–100 ml of ethanol. The burets are then refilled and automatically set to read zero. The droplets adhering to the buret tips are then removed. The rinsed electrode couples are immersed in the samples which are then stirred vigorously. The titrator is programmed to wait 20 sec between each new addition of titrant and subsequent reading of potential and buret volume. A titrant increment of 0.1 ml was found to be optimal.

In the GRAN method used here to evaluate the halide concentration of the sample, only titration data after the equivalence point are used. In order to reduce the time needed for a titration, it has proved practical to add most of the equivalence volume of the titrant before the titrator is started. It should be stressed that from the precision point of view it is of minor importance how close to the equivalence point one can come during this addition as it will affect only the titration time. It is, moreover, of no importance if the equivalence volume is slightly exceeded when the major part of the titrant is added.

By means of the teletype writer a suitable title is punched for each sample together with the corresponding sample weight. The silver nitrate concentration, the sample temperature and the number of titration vessels run parallel are also punched manually, after which the titrator is started. The titration should be continued until at least ten titration points have been registered after the equivalence point. It is, however, of no consequence if more titration points are included, since, in the subsequent computation, the computer program selects those data within the optimum mV range which is here approximately $E > -425$ mV. Additional titration points registered by the titrator are thus not included in the computation of v_{eq}.

The time needed for each titration depends mainly on the number of titration vessels operated simultaneously. If only one titration vessel is used each titration will take *ca.* 15 min, including the time needed for sampling. When several burets are operated, it is advantageous to rinse electrodes, weigh samples and refill burets for half of the titration vessels while the remaining burets are titrating. The time needed to weigh in the samples accurately will then be the time-limiting factor for one titration. Since the titration data are processed by a computer the time needed for calculation, editing and printing out of the results is negligible.

A representative titration curve (pAg against v ml titrant added) for the titration of 10.2012 g of Standard Sea Water, diluted with 50 ml of standard potassium solution and 100 ml of ethanol, with v ml 0.32876 M silver nitrate is shown (open circles) in Fig. 1, while the corresponding text on the data tape and teletype writer is given in Table I.

THEORY

Chemical equilibria

In sea water of normal ionic composition, the chloride concentration is equal to 0.54587 mol kg^{-1} at a chlorinity of 19.374 ‰ (salinity 35 ‰). The bromide concentration is 0.00084 mol kg^{-1} and the iodide concentration is so low that it does not affect the results of a potentiometric titration with silver nitrate. The stability constants and solubility products for the silver–chloride–bromide system in aqueous solution at 0.1 M ionic strength are summarised in Table II; constants determined by BERNE AND LEDEN[11] were used. The stability constants for the mixed complexes were estimated from the formula

TABLE II

STABILITY AND SOLUBILITY CONSTANTS FOR THE SILVER–CHLORIDE–BROMIDE SYSTEM AT 0.1 M IONIC STRENGTH IN WATER

Reaction	*Stability constant*	
$AgCl(s) + Ag^+ \rightleftharpoons Ag_2Cl^+$	$\log K_{s12} = -4.60$;	$\log \beta_{12} = 4.80$
$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$	$\log K_{s0} = -9.40$	
$AgCl(s) \rightleftharpoons AgCl$	$\log K_{s11} = -6.60$;	$\log \beta_{11} = 2.80$
$AgCl(s) + Cl^- \rightleftharpoons AgCl_2^-$	$\log K_{s21} = -4.70$;	$\log \beta_{21} = 4.70$
$AgCl(s) + 2Cl^- \rightleftharpoons AgCl_3^{2-}$	$\log K_{s31} = -4.40$;	$\log \beta_{31} = 5.00$
$AgCl(s) + 3Cl^- \rightleftharpoons AgCl_4^{3-}$	$\log K_{s41} = -3.50$;	$\log \beta_{41} = 5.90$
$AgBr(s) + Ag^+ \rightleftharpoons Ag_2Br^+$	$\log K_{s12} = -5.04$;	$\log \beta_{12} = 7.06$
$AgBr(s) \rightleftharpoons Ag^+ + Br^-$	$\log K_{s0} = -12.10$	
$AgBr(s) \rightleftharpoons AgBr$	$\log K_{s11} = -7.45$;	$\log \beta_{11} = 4.65$
$AgBr(s) + Cl^- \rightleftharpoons AgClBr^-$	$\log K_{s111} = -5.85$;	$\log \beta_{111} = 6.25$
$AgBr(s) + 2Cl^- \rightleftharpoons AgCl_2Br^{2-}$	$\log K_{s121} = -5.76$;	$\log \beta_{121} = 6.34$
$AgBr(s) + 3Cl^- \rightleftharpoons AgCl_3Br^{3-}$	$\log K_{s131} = -5.0$;	$\log \beta_{131} = 7.10$

$$\beta_{AgCl_nBr_m} = \frac{N!}{m!n!} (\beta^n_{N(Cl)} \cdot \beta^m_{N(Br)})^{1/N} \qquad (N = m + n) \tag{2}$$

which takes into account the fact that the formation of mixed complexes is favoured statistically[12]. A logarithmic diagram based on these constants, which illustrates the dependence of the concentrations of the different species on the free silver ion concentration is shown in Fig. 2. From this figure it is obvious that, in the pAg region in the neighbourhood of the equivalence point, the concentrations of all soluble species can be neglected in comparison with the free silver and chloride ion concentrations. The form of the potentiometric titration curve will therefore mainly be governed by the solubility product for silver chloride. This assumption is, no doubt, also valid for water–ethanol solutions.

Since an approximate solubility product for silver chloride relevant to the medium used in the titration is necessary for the determination of the systematic errors involved in the evaluation of the equivalence volume, this product was determined using a curve-fitting procedure. Several theoretical titration curves were generated for different pK_{s0} values by means of the computer program HALTAFALL[13].

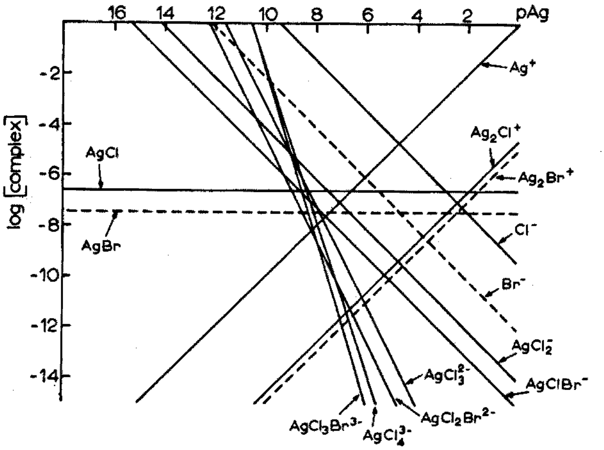

Fig. 2. A logarithmic diagram of the silver–chloride–bromide system at 0.1 M ionic strength in water.

The concentrations of all soluble species other than chloride and silver ion were neglected in the calculations. All calculations were performed as titrations of 10.2012 g of sea water of 19.3745 ‰ chlorinity diluted to a total volume of 160 ml. The decrease in volume obtained when aqueous and ethanol solutions were mixed was neglected. In the calculations, which were performed with an accuracy[13] of 0.001 % for the total amounts of both silver and chloride, the diluted sea water was titrated with v ml of 0.32876 M silver nitrate, yielding a theoretical equivalence volume of 16.9649 ml. The set of computed titration curves (pAg$_{\text{calc}}$ against v ml of titrant added) obtained for different pK_{s0} values was then curve-fitted to experimental data (pAg$_{\text{m}}$ against v ml titrant added) obtained for three different ethanol concentrations.

The pAg$_{\text{m}}$ values were calculated from the relation

$$E_{\text{m}} = E^0 - RTF^{-1} \ln 10 \log[\text{Ag}_{\text{m}}^+] \tag{3}$$

and the relevant E^0 value for each ethanol concentration was calculated from measured e.m.f. data, E_{m}, obtained after the equivalence point.

The calculated curves giving the best fit to the experimental data are shown as the solid curves 1–3 in Fig. 1. Curve No. 1, which has a pK_{s0} value equal to 9.5(4), should be compared with the experimental points shown by triangles (0 % ethanol, 10.195 g of sea water). For *ca.* 30 % ethanol the best pK_{s0} value was 10.0(3) as is seen from the experimental squares in Fig. 1 (10.202 g of sea water) and for *ca.* 60 % ethanol the best pK_{s0} value is 10.6(9), the experimental points being denoted by circles (10.201 g of sea water).

Gran extrapolation method

The electrode couple measures the silver ion concentration according to

$$E = E^0 - RTF^{-1} \ln 10 \log f[\mathrm{Ag}^+] + E_j \qquad (4)$$

where E_j represents the sum of the liquid junction potentials and f is the activity coefficient. Since, however, the ionic strength and concentration of ethanol changes only slightly in the volume region after the equivalence point used to compute the equivalence volume both E_j and f can be considered to be constant, *i.e.*

$$E = E_1^0 - RTF^{-1} \ln 10 \log [\mathrm{Ag}^+] \qquad (5)$$

or

$$[\mathrm{Ag}^+] \propto 10 \exp(-EF/RT \ln 10) \qquad (6)$$

The GRAN method is based on the assumption that shortly after the equivalence point, v_{eq}, all chloride ions have been precipitated so that additional silver ions from the buret form either free silver ions or the complexes Ag_2Cl^+ or Ag_2Br^+, *i.e.*

$$(v_0 + v)\ ([\mathrm{Ag}^+] + [\mathrm{Ag_2Cl}^+] + [\mathrm{Ag_2Br}^+]) = t(v - v_{eq}) \qquad v > v_{eq} \qquad (7)$$

where v_0 denotes the initial volume in the titration vessel and t the concentration of silver nitrate in the buret. Since, however, the ratios $[Ag_2Cl^+]/[Ag^+]$ and $[Ag_2Br^+]/[Ag^+]$ must be constant in a solution containing the two solid phases AgCl and AgBr, eqn. (7) can be written as

$$(v_0 + v)\ [\mathrm{Ag}^+] = k\ (v - v_{eq}) \qquad v > v_{eq} \qquad (8)$$

where k is a constant. Combination of eqns. (6) and (8) yields

$$F_1 = (v_0 + v)\ 10 \exp\ (-EF/RT \ln 10) \propto (v - v_{eq}) \qquad v > v_{eq} \qquad (9)$$

From eqn. (9) it is seen that when F_1 is plotted against v, a straight line is obtained, which, when extrapolated to $F_1 = 0$, intersects the v axis at $v = v_{eq}$.

The validity of the assumptions made in the derivation of the GRAN plot, F_1, can be confirmed by means of the computer calculations. As is seen from Fig. 2 the theoretical GRAN plot

$$F_{1,\mathrm{calc}} = (160 + v)\ [\mathrm{Ag}^+{}_{\mathrm{calc}}] \qquad (10)$$

is linear and, moreover, intersects the v axis at $v = 16.963$ ml which, taking into account the magnitude of the error in the graphical estimation of the equivalence volume (*ca.* ± 0.002 ml), does not differ significantly from the theoretical v_{eq} value, $v_{eq} = 16.9649$ ml.

Computer evaluation of v_{eq}

Since the graphical evaluation of the titration data is time-consuming and has, moreover, limited precision, a computer program was constructed to evaluate the halide concentration of the samples directly from the punched tape data. The program, which is based on straight-line regression according to the GRAN[7] method is similar to that described in detail by DYRSSEN *et al.*[12] and has been written in Algol, in Fortran IV and in Basic*.

A typical set of input data with explanations is shown in Table I. After the data have been read into the computer, those titration points with e.m.f. values less than −425 mV are discarded. The reason for this is that for v values several ml greater than v_{eq}, a slight curvature of the GRAN plot may be observed. For all other v values

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* The complete programs can be obtained from the authors.

the computer then calculates a value of F_1 according to

$$F_1=(v_0+v)\ 10 \exp(300-E)F/RT \ln 10 \qquad (11)$$

Starting with the last five titration points the program calculates the best line through these using the statistical formulae for regression to a straight line. The average deviation from the titration points to this straight line is then calculated, one more titration point is included, and the average deviation is recalculated. This procedure is repeated until all titration points have been included, and as long as the titration points lie on a straight line the average deviation decreases, although slight increases may be obtained if incorrect e.m.f. values have been assigned to one or more titration points. Since the GRAN plot is linear only for titration points corresponding to $v > v_{eq}$ the average deviation reaches an absolute minimum value for a certain number of points through which the best straight line is computed. This line is extrapolated to $F_1=0$ and from the intersection, v_{eq}, on the v axis the chlorinity, Cl, is calculated according to the formula

$$Cl=v_{eq}\cdot t\cdot 107.868\cdot 328.5233/1000\cdot \text{gram sample} \qquad (12)$$

and the salinity, S, according to the KNUDSEN relation

$$S=1.805\cdot Cl+0.03 \qquad (13)$$

The values of the total number of points, the number of points used in the straight line regression, v_{eq}, Cl and S are then printed out on the line-printer preceded by the sample title.

The magnitude of the systematic error introduced into the analysis by the computer evaluation was estimated from the theoretically calculated titration curves 2 and 3 in Fig. 1. The calculated pAg_{calc} values were converted into e.m.f. values according to

$$E_{calc}=E^0+RTF^{-1}\ln 10\cdot pAg_{calc} \qquad (14)$$

an arbitrary value being assigned to E^0. The calculated e.m.f. values, E_{calc}, were then fed into the computer together with their corresponding v values and the equivalence volume was calculated. For both the titration curves 2 and 3 of Fig. 1, the calculated equivalence volume differed from the theoretical value of 16.9649 ml by less than 0.005 % and, since this is appreciably less than the precision of the titration method, the systematic error caused by computation errors may be considered to be negligible. An exact determination of this systematic error is not possible since the HALTAFALL calculations are associated with numerical approximations.

RESULTS

Precision

The results from fifteen standardisations of the silver nitrate titrant against Standard Sea Water are shown in Table III. Approximately 10-g samples (*cf.* eqn. (1)) were weighed in and diluted with 50 ml of acidic potassium nitrate solution and 100 ml of ethanol. The silver nitrate concentration, calculated from the experimental data in Table III and the known value of the chlorinity of Standard Sea Water, 19.3745$^0/_{00}$ was found to be 0.32876 M. This titrant concentration was used to calculate all the chlorinity values given in Tables III and IV. It should be stressed that a precision of the order of magnitude of 0.02 % is only obtained if extreme care is exercised during sampling and titration. Factors influencing the magnitude of the experimental errors are discussed below.

TABLE III

COMPUTER AND GRAPHICALLY EVALUATED RESULTS FROM FIFTEEN STANDARDISATIONS OF SILVER NITRATE WITH STANDARD SEA WATER (CHLORINITY 19.3745 $^0/_{00}$)

(The mean value of the titrant solution was calculated to be 0.32876 *M*)

Sample no.	*Weight of sample (g)*	*Computer evaluation*		*Graphical evaluation*	
		Chlorinity	*Deviation from mean value*	*Chlorinity*	*Deviation from mean value*
1	10.28250	19.3727	0.0018	19.385	0.009
2	10.42295	19.3794	0.0049	19.372	0.004
3	10.15545	19.3752	0.0007	19.381	0.005
4	10.39955	19.3784	0.0039	19.384	0.008
5	10.34000	19.3790	0.0045	19.385	0.009
6	10.20950	19.3720	0.0025	19.377	0.001
7	10.28650	19.3713	0.0032	19.366	0.010
8	10.16320	19.3793	0.0048	19.380	0.004
9	10.27535	19.3732	0.0012	19.377	0.001
10	10.32930	19.3687	0.0058	19.365	0.011
11	9.98560	19.3750	0.0005	19.378	0.002
12	9.98175	19.3797	0.0052	19.377	0.001
13	10.16270	19.3704	0.0041	19.374	0.002
14	10.28560	19.3682	0.0063	19.366	0.010
15	10.19705	19.3747	0.0002	19.376	0.000
Mean value		19.3745	± 0.0033	19.376	± 0.0054
Mean value ± δ		19.3745 ± 0.021 %		19.376 ± 0.034 %	

TABLE IV

COMPUTER AND GRAPHICALLY EVALUATED RESULTS FROM TWELVE TITRATIONS OF PIPETTED 10-ml SAMPLES OF STANDARD SEA WATER (CHLORINITY 19.3745 $^0/_{00}$) WITH 0.32876 *M* SILVER NITRATE

(The mean weight of a 10-ml portion was determined separately to be 10.2008 g, from which value the chlorinities were calculated)

Titration no.	*Computer evaluation*		*Graphical evaluation*	
	Chlorinity	*Deviation from mean value*	*Chlorinity*	*Deviation from mean value*
1	19.3719	0.0025	19.371	0.003
2	19.3807	0.0063	19.386	0.012
3	19.3791	0.0047	19.381	0.008
4	19.3649	0.0095	19.365	0.008
5	19.3642	0.0102	19.361	0.013
6	19.3770	0.0026	19.366	0.007
7	19.3681	0.0063	19.371	0.003
8	19.3638	0.0106	19.361	0.013
9	19.3753	0.0009	19.374	0.001
10	19.3868	0.0124	19.386	0.012
11	19.3859	0.0115	19.382	0.009
12	19.3752	0.0008	19.379	0.005
Mean value	19.3744	± 0.0065	19.374	± 0.0078
Mean value ± δ	19.3744 ± 0.041 %		19.374 ± 0.047 %	

The results obtained from the computer evaluation of the chlorinities are compared in Table III with those obtained graphically. It is obvious that the precision of the method is increased by the increased resolution of v_{eq} obtained with a computer. The difference in the mean value of the chlorinity obtained by the computer and that obtained by the graphical evaluation is probably due to a systematic error in the latter method introduced when the human eye approximates the best straight line through the experimental points.

Factors influencing accuracy and precision

Chemical interference. No chemical interference from other components normally present in sea water was detected. Precipitation of silver carbonate is prevented by the nitric acid and the titration curves showed no indication that the solubility product of silver sulphate was exceeded.

Surface adsorption. It is well-known that in a solution containing precipitated silver chloride and an excess of silver ions the latter tend to be adsorbed on the precipitate and are thus associated with a chemical potential different from that of the free silver ions. The extent to which this occurs in water–ethanol solutions is not easily estimated but adsorption is, no doubt, decreased by the high hydrogen, potassium and sodium ion concentrations present. Moreover, the amount of silver ions adsorbed can be assumed to be proportional to the solid phase area, and, if the sampling is performed in accordance with eqn. (1), similar amounts of solid phase are present in all titrations; accordingly, provided that the same titration procedure is always followed, the amount of silver ions adsorbed on the precipitate ought to be reproducible. Since the silver nitrate titrant is standardised against Standard Sea Water the systematic error introduced by surface adsorption is eliminated.

Photodecomposition of silver chloride. Even if the titrant solution and titration vessels are protected during titration from direct light by aluminium foil, photodecomposition of the precipitate cannot be completely eliminated. The rate of decomposition of silver chloride in direct light has, however, been estimated by CHAMPION AND MARINENKO[14] to be 0.5 μeq h^{-1} for a sample containing a total of 2 millimoles. It can therefore be concluded that photodecomposition ought not to have any appreciable effect on the accuracy of the titration.

Titration time. The rapid attainment of equilibrium during a titration is, of course, imperative. The addition of ethanol has a positive effect on the time needed for precipitation but, even so, a pause of at least 20 sec between successive titrant increments is necessary. This time interval is, however, still not sufficient before and in the close vicinity of the equivalence point, but such titration points are not required by the GRAN extrapolation method. This is therefore one of the main advantages of the GRAN extrapolation procedure compared to evaluation of the equivalence point by means of maximum slope of the titration curve or from a pre-chosen e.m.f. value.

Sample measurement. One of the most serious sources of error lies, without doubt, in the weighing-in of the samples, the main difficulty being the variation in temperature of the air in the titration vessel during the weighing. The precision of the procedure was tested by consecutive reweighing of the same sample. The lid of the titration vessel was removed and replaced before each reweighing in order to simulate the weighing-in process. The maximum difference in two consecutive weighings was found to be 0.006 % of the total sample weight, which was 10 g.

The precision of the determination of the chlorinity of pipetted samples was also investigated. Portions (10 ml) of Standard Sea Water were measured with a volumetric pipet and the samples were titrated with 0.32876 *M* silver nitrate. The results of twelve such titrations are shown in Table IV. The mean value of the sample weight was determined separately to be 10.2008 g from which value the chlorinities given in Table IV were calculated. As seen from this Table the use of pipets leads to a decrease in precision.

Buret and voltmeter precision. The standard deviation of the total volume of titrant added from the buret has previously been determined[8] to be ± 0.005–0.01 %. An increase in the precision of the titration should be achieved if the major part of the titrant were weighed in, the final stages of the titration being performed with more dilute silver nitrate. Since, however, this would considerably increase the time required for each titration, no attempt was made in this direction. Errors in the voltage readings were estimated to give precision in the same order of magnitude as the buret.

The authors are indebted to the head of the department, Professor DAVID DYRSSEN, for valuable discussions and to Dr. OVE LINDGREN for adapting the punched tape code to the IBM computer. Financial support from the Swedish Natural Science Research Council, Carl Tryggers Stiftelse and Chalmers' Technical University, the latter to cover the costs of the computer work, are gratefully acknowledged. The English text of this paper has been revised by Dr. SUSAN JAGNER.

SUMMARY

A semi-automatic potentiometric titration of the total halide concentration in sea water with silver nitrate is described. The titration is followed with a silver electrode and the titration data, which are recorded directly on punched tape and typewriter, are evaluated by means of a computer program based on the GRAN extrapolation method. The determinations have a precision of ±0.02 % and, since many samples can be titrated simultaneously, the time for a single determination including evaluation and editing of titration data can be reduced to less than 5 min.

RÉSUMÉ

On décrit une détermination de la concentration totale en halogénure d'une eau de mer, à l'aide de nitrate d'argent, par titrage potentiométrique semi-automatique. On utilise une électrode d'argent; les résultats sont enregistrés directement sur machine à écrire et interprétés à l'aide d'un programme d'ordinateur. La précision est de ±0.02 % et la durée totale d'un dosage peut être inférieure à 5 min, plusieurs échantillons pouvant être titrés simultanément.

ZUSAMMENFASSUNG

Es wird eine halbautomatische potentiometrische Titration der Gesamt-Halogenkonzentration in Meerwasser mit Silbernitrat beschrieben. Die Titration wird mit einer Silberelektrode verfolgt. Die Messergebnisse werden unmittelbar auf Lochstreifen und Schreibmaschine übertragen und mittels eines Rechenprogramms, das

auf der Extrapolationsmethode von GRAN beruht, ausgewertet. Die Bestimmungen haben eine Genauigkeit von ±0.02%. Da gleichzeitig viele Proben titriert werden können, kann die Zeit für eine einzelne Bestimmung einschliesslich Auswertung und Ausgabe der Titrationsergebnisse auf weniger als 5 min verringert werden.

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FLUORESCENCE AND METALLIC VALENCY STATES

PART IV. AROMATIC CARBOXYLIC ACIDS AS NEW FLUORESCENT DETECTION AGENTS FOR COPPER AND VANADIUM

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Continuing investigation of fluorimetric methods for transition metals[1-3] has shown that aromatic carboxylic acids give characteristic fluorescent reactions with copper and vanadium in the presence of reducing agents.

Fluorimetric determination of copper (6 p.p.m.) with thiamine has recently been reported[4,5]; copper (15–600 p.p.b.) has also been determined[6] with 1,1,3-tricyano-2-amino-1-propene as a reagent. Copper can be detected at the 20 p.p.b. level by the method proposed here and 100-fold amounts of most cations (including cobalt and nickel) do not interfere. Picogram amounts of copper have been detected under controlled conditions with a spectrophotofluorimeter.

No detection method based on fluorescence production has been reported for vanadium; methods are either colorimetric (0.1–2.5 p.p.m.) or precipitation (0.05–0.25 p.p.m.) spot tests[7] subject to many interferences. By the procedure proposed, 0.2 p.p.m. of vanadium can be detected in the presence of most common cations.

EXPERIMENTAL

Apparatus and reagents

A 230-W mercury ultraviolet lamp, Hanovia type 16106 (excitation λ_{max} ~360 nm), was employed for visual observations and an Aminco Bowman spectrophotofluorimeter was used for obtaining excitation and emission spectra.

Stock reagent solutions (0.2 and 1%) were prepared. The aromatic carboxylic acids were dissolved in 2–5 ml of concentrated ammonia liquor, 10 ml of doubly distilled water were added and the solutions were adjusted to pH 5.5 with hydrochloric acid before dilution to 100 ml with distilled water. Both uncrystallized and recrystallized reagents gave the same reaction with copper and vanadium.

The acetate buffer, pH 5.2, contained 100 ml of 1 *M* sodium acetate and 20 ml of 1 *M* hydrochloric acid in a volume of 250 ml.

The 10% (w/v) solution of hydroxylamine hydrochloride was stored in an amber glass bottle.

The zinc amalgam was made by heating 15 g of pure zinc (20 mesh) with 25 ml of mercury and 15 ml of 1+1 hydrochloric acid for 1 h on a water bath in a well ventilated fume hood. The amalgam, after cooling, was washed several times with dilute hydrochloric acid and the liquid amalgam was separated from the solid with a

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separatory funnel. The amalgam was stored in contact with acetate buffer to prevent oxide formation.

A standard copper solution was prepared by dissolving 0.25 g of pure copper wire in a small amount of 1+1 nitric acid. After boiling to remove oxides of nitrogen, the solution was diluted to 250 ml with distilled water. This solution contained 1,000 p.p.m. of copper; 1 and 10 p.p.m. copper solutions were made as required from this stock solution.

The standard vanadium solution contained 1.0 mg of vanadium per ml. Vanadium pentoxide (0.4464 g of analytical reagent) was dissolved in 1–2 ml of concentrated ammonia liquor which was then neutralized with dilute hydrochloric acid to a pH of *ca.* 5.5; the solution was then diluted to 250 ml with distilled water. Other solutions (1, 10 and 100 p.p.m.) were made as required from this stock solution.

Procedure for copper

Add 3 ml of a 1% solution of 1,3-benzenedicarboxylic acid to 3 ml of acetate buffer in a 10-ml test tube. Mix thoroughly and divide into two equal portions. Add 1 drop of unknown solution and 3 drops of 10% hydroxylamine hydrochloride to one portion; add the same amount of hydroxylamine hydrochloride to the second portion which serves as a blank. Mix thoroughly and observe under the ultraviolet lamp after 5 min. If copper (>20 p.p.b.) is present a strong blue fluorescence is observed; the blank solution exhibits only a weak fluorescence.

Copper is selectively detected with all the aromatic carboxylic acids studied; 20 p.p.b. were detected in the presence of 100-fold amounts of alkali and alkaline earth ions, Cd^{2+}, Co^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Pd^{2+}, Zn^{2+}, Al^{3+}, Bi^{3+}, Cr^{3+}, Rh^{3+}, Hf^{4+}, Ir^{4+}, Os^{4+}, Th^{4+}, Zr^{4+}, U^{6+} and W^{6+}; a 10-fold amount of Ce^{4+}, Sn^{4+}, Ti^{4+} and V^{5+} did not interfere. Common anions such as acetate, halides, nitrate, perchlorate, phosphate and sulphate also caused no interference. Cyanide quenched the fluorescence.

Procedure for vanadium

To *ca.* 0.5 ml of the amalgam in a 10-ml test tube add 1 drop of unknown solution (pH 4–7), 3 drops of 0.5% 1,3-benzenedicarboxylic acid solution and 3 drops of

TABLE I

RELATIVE INTENSITY OF THE FLUORESCENCE OF THE REACTION SYSTEM WITH COPPER

Acid	*Excitation λ*	*Emission λ*	*R.I.*[a]
Benzoic	325	455	1.3
4-Cyanobenzoic	320	445	0.02[b]
1,2-Benzenedicarboxylic	325	440	0.3[c]
1,3-Benzenedicarboxylic	335	460	2.0
1,4-Benzenedicarboxylic	315	440	
	355	540	0.5
1,2,3-Benzenetricarboxylic	315	425	0.3
1,2,4-Benzenetricarboxylic	325	450	0.4

[a] The relative intensity (R.I.) is the intensity of the reaction product compared with a 1 p.p.m. quinine sulphate standard.
[b] 0.02% solution.
[c] 1.0% solution.

acetate buffer; mix thoroughly for 1 min and add a further 1 ml of reagent. If vanadium is present a blue fluorescence is observed under the ultraviolet lamp; a reagent blank should be run concurrently.

Vanadium (0.2 p.p.m.) was easily detected; 100-fold amounts of the ions listed above for copper, including copper(II) and cerium(IV), did not interfere. Vanadium was easily detected in the presence of a 10-fold amount of titanium(IV) and a 50-fold amount of iron(III) could be tolerated in the presence of phosphate.

Similar fluorescent reactions were observed with all of the aromatic carboxylic acids investigated (Table I); with 1,4-benzenedicarboxylic acid, however, the fluorescence was yellow in color.

RESULTS AND DISCUSSION

Factors affecting fluorescence

With the exception of the 1,4-acid, the fluorescence spectra (Table I) showed excitation maxima from 315 to 335 nm and emission maxima from 420 to 460 nm. For the 1,4-acid two characteristic excitation (315 and 355 nm) and emission (440 and 540 nm) spectra were observed. The results given in Table I are for 1 p.p.m. of copper in solutions containing equal volumes (2.5 ml) of 0.2% reagent and acetate buffer with 0.5 ml of 5% hydroxylamine hydrochloride added; measurements were made after 30 min against a reagent blank.

The fluorescence intensity increased gradually as the pH was increased from 4.7 to 6.5; rapid fluorescent reactions were observed at pH 6.5 in phosphate-buffered solutions but high reagent blanks were also obtained. Results were good, however, in acetate buffered solutions (pH 5.2); the reaction rate was satisfactory and the blank showed only a weak fluorescence. Below pH 5, most of the reagents precipitated as the water-insoluble acids.

The fluorescence intensity increased markedly as the concentration of the reagent was increased; at high reagent concentrations the reaction was very sensitive for copper but the fluorescence intensity of the blank was also increased. Reagent concentrations of 0.2–1% are therefore recommended for easy detection.

Nature of reaction

The fluorescent reaction products obtained on reacting aromatic carboxylic acids with metallic ions in reduced valency states are not formed unless oxygen is present. Reagent solutions that were degassed with nitrogen before addition of copper(I) chloride showed no fluorescence but, on contact with air, fluorescence was initiated at the surface and slowly spread throughout the body of the solution; similar results were obtained for degassed reagent solutions containing copper(II) and hydroxylamine hydrochloride or vanadium and zinc amalgam. Radiolysis of reagents with a cobalt-60 γ-ray source and electrolytic reduction of aqueous reagent solutions produced similar fluorescence to that obtained with reduced valency states of the metal ions. Dihydrocarboxylic acids are formed, via protonated intermediate alcohols, when aromatic carboxylic acids are electrolytically reduced[8] and it has also been suggested that the dihydro acid is formed on reduction of phthalic (1,2-benzenedicarboxylic) acid[9].

These results suggest that the fluorescence product is formed, in the presence of oxygen, through an electron transfer process from the reduced state of the metallic ion to the aromatic carboxylic acid. Whether the intermediate so formed is directly responsible for the fluorescence or whether a further reaction with oxygen is also involved is not yet clear. Further studies are in progress.

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SUMMARY

Copper (20 p.p.b.) in solution is selectively and simply detected with aromatic carboxylic acids by observing, under the ultraviolet lamp, the fluorescence produced in the presence of reducing agents. Vanadium (0.2 p.p.m.) can also be detected, without interference from copper, if zinc amalgam is used as the reducing agent. Few ions interfere.

RÉSUMÉ

Le cuivre en solution (20 p.p.b.) peut être décelé facilement et sélectivement à l'aide d'acides aromatiques carboxyliques en examinant dans l'ultraviolet la fluorescence produite en présence d'agents réducteurs. Le vanadium (0.2 p.p.m.) peut également être décelé, sans interférence du cuivre, en utilisant un amalgame de zinc comme réducteur. Peu d'ions gênent.

ZUSAMMENFASSUNG

Kupfer (20 p.p.b.) wird in Lösung selektiv und einfach mit aromatischen Carbonsäuren nachgewiesen, indem unter der Ultraviolettlampe die in Gegenwart von Reduktionsmitteln auftretende Fluoreszenz beobachtet wird. Es kann auch Vanadin (0.2 p.p.m.) ohne Störung durch Kupfer nachgewiesen werden, wenn Zinkamalgam als Reduktionsmittel verwendet wird. Wenige Ionen stören.

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GAS CHROMATOGRAPHIC DETERMINATION OF TRIMETHYLSILYLATED MONO- AND DISACCHARIDES IN SUGAR CANE JUICE

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The gas chromatographic investigation of carbohydrates and carbohydrate-containing natural products was significantly advanced with the successful application of the powerful technique of trimethylsilylation by WELLS *et al.*[1,2]. Their work was an extension of earlier work by MAKITA AND WELLS[3] concerning the trimethylsilylation of bile acids, and overcame the difficulty experienced by previous workers in preparing suitable volatile derivatives of polyhydroxy compounds[4].

Application of the method to both artificially prepared[5-7] and naturally occurring[8-10] systems rapidly appeared in the literature. Recently, a comprehensive review and reference volume has been prepared by PIERCE[11].

Despite the appearance of a large number of papers dealing with carbohydrates[11], few papers have dealt with analyses related to the sugar cane industry[12]. This paper describes the application of the method of SWEELEY *et al.*[2] to the analysis of sugar cane juice for mono- and disaccharides with two isothermal gas–liquid chromatographic procedures and myoinositol as internal standard.

EXPERIMENTAL

Reagents and materials

Chemically pure carbohydrates were used as supplied from commercial sources without further purification. Three commercial glucose preparations were compared including β-D-glucose (Sigma Chemical Co.), D-glucose (anhydrous; Eastman Organic Chemicals), and β-glucose (C.P., Mann Research Laboratories). Reagent-grade pyridine was distilled from and stored over solid potassium hydroxide pellets. Trimethylchlorosilane and hexamethyldisilazane (Peninsular ChemResearch, Inc.) were used without further purification. Myoinositol, labelled "*i*-Inositol (Meso)" (Nutritional Biochemicals Corp.) was used.

Preparation of standards

Separate sets of standards were prepared for the monosaccharide and disaccharide analyses in this work. This was a matter of choice and, in practice, especially where temperature programming is available, it would be preferable to prepare solutions containing all sugars of interest. Aqueous solutions (50 ml) containing sugars as follows were prepared as stock solutions: inositol, 0.50694 g; D-glucose, 1.00372 g; fructose, 0.53285 g; sucrose, 5.38950 g. Each weight was obtained by difference on a Sartorius, Model 2600, balance. Since D-glucose yielded approximately equal α- and β-anomer peaks, twice as much of this sugar was weighed out as fructose, which essentially gives one major peak, so that all peak sizes would be similar.

Into each of the drying tubes used was introduced 1 ml of the internal standard solution followed by varying amounts of fructose and glucose solutions from 0.3 to 2.0 ml. This produced a series of monosaccharide standards of known concentrations. Similarly, the sucrose stock solution was used to prepare a set of disaccharide standards by using varying amounts of sucrose solution and 1 ml of internal standard solution (containing 10.0139 mg of inositol per ml). The ratio of the weight of each sugar to the weight of internal standard present was calculated for each container. In practice, the stock solutions were kept refrigerated between uses and were found to be stable for at least several weeks without detectable evidence of bio-degradation.

Preparation of cane juice samples

Cane juice was supplied frozen in one gallon containers (which was larger than the amount needed for analysis). The containers were placed in warm water and kept closed until the contents were completely melted. Sampling was accomplished by placing a 5-ml pipette into the center of the liquid. The containers were then refrozen for future use. Samples (1 ml) were placed into tared drying tubes and accurately weighed by difference. Each sample weighed *ca.* 1 g.

Reaction vessels

The drying assembly described below required the use of test tubes as sample containers; the tubes used were 20 mm (o.d.) x 150 mm. The pertinent sugar solutions were pipetted into test tubes, the samples were dried in the drying assembly, and the residue was reacted with pyridine and the silylation reagents. Although rubber stoppers were used, trimethylsilylchloride and rubber react to produce a vile odor; thus plastic stoppers are strongly recommended.

Drying apparatus

The sample drying system is a highly efficient one which has been used routinely in these laboratories for several years. The heart of the system is a Rotary Evapo-Mix (Buchler Instruments, Inc.). The inner tube of the Buchler manifold was cooled by a VirTis Circulating Cold Bath Model #10-900-A. Attached to the Buchler manifold in series were the following: a 500-ml filter flask liquid condensate trap, three dry ice and acetone vapor traps in series, and finally two Welch "Duo-Seal" high-vacuum pumps pulling in parallel. Also connected in parallel with the first dry ice trap was a mercury manometer for measuring the vacuum at any given time. The Buchler water bath was maintained at 30–35°, but could probably be raised to as high as 60° without undue complication (and quicker drying capability). An infrared lamp was used above the Buchler to prevent moisture condensation between the drying tubes and cold traps.

Drying of the cane juice and standard samples

Use of the sample drying apparatus described above required that the sample be placed in test tubes instead of the 1-dram containers commonly used as reaction vessels. Samples were either pipetted or, in the case of the cane juice, weighed into these test tubes, the internal standard introduced, and the tubes positioned as required for drying. Depending on the number of samples being dried and the amount of liquid in each, drying usually required 30–60 min. This time was shortened to about 20 min when only one or two samples were handled, *e.g.* when cane juice samples were dried alone. By raising the temperature of the water bath, the overall drying time could probably be safely shortened to 15 min or less.

Trimethylsilylation

To the dried samples (standards and cane juice samples) was added in sequence 5 ml of pyridine, 1 ml of hexamethyldisilazane, and 0.5 ml of trimethylsilylchloride. In practice a Vortex Junior mixer was used to assist dissolution, particularly after the addition of pyridine and before the addition of silylation reagents. Only in the case of sucrose, where the amount of sugar involved was about ten times greater than the amount in the monosaccharide samples, was difficulty in dissolution encountered and slight warming necessitated. Even in this case, sucrose which did not immediately dissolve did go into solution as the silylation reaction proceeded.

After the addition of these reagents the samples were either allowed to stand at room temperature until injection into the gas chromatograph, or when more rapid reaction was desired, placed in a 45° water bath for at least 15 min. Despite the claims of rapid reaction at room temperature by some workers, the results of McDONALD[13] and others[14] have strongly indicated that this claim is incorrect, at least for some sugars and at room temperature.

Gas chromatography

Gas chromatography was performed with a MicroTek Model 1600 single-column instrument equipped with a hydrogen flame ionization detector and Westronics LS11A recorder. Although the recorder was equipped with a Disc Chart Integrator, a Hewlett-Packard Model 3370-A electronic digital integrator connected between the chromatograph and recorder was used for peak integration. The gas chromatograph was further modified by substitution of a Trācor Model 8176 solid-state electrometer for the original. Also to improve the temperature regulation of the 1600, which originally used a rheostat, a proportional temperature control from MicroTek Model 2500 was wired into the system. Gases for the flame detector were regulated through a flow control cabinet removed from the Model 2500. Flow rates for helium, hydrogen, and air were optimized at 91, 75, and 335 ml min^{-1} respectively.

A 9′×1/4″ (o.d.) coiled, stainless-steel column was packed with 3% SE-52 on Gas Chrom Q, 100–120 mesh, and conditioned overnight at 255°. For all analyses the inlet and detector temperatures were maintained at 300 and 310°, respectively. Monosaccharides were determined by using a column temperature of 168°. For the determination of sucrose this temperature was raised to 238°.

Sampling

Samples were removed from the reaction test tubes and injected into the gas chromatograph with a 10-μl Hamilton syringe equipped with a plunger guide. Between 1.5 and 2.0 μl were usually injected.

Calculations

Use of an internal standard makes absolute measurement of the amount of sample injected unnecessary. Instead of absolute amounts of standard materials being measured, the ratio of the area of the appropriate sugar peak divided by the area of the internal standard peak is plotted against the weight ratio of sugar to internal standard for each standard solution. Once the standard plot is obtained, calculations involving the cane juice samples are accomplished by the following formula:

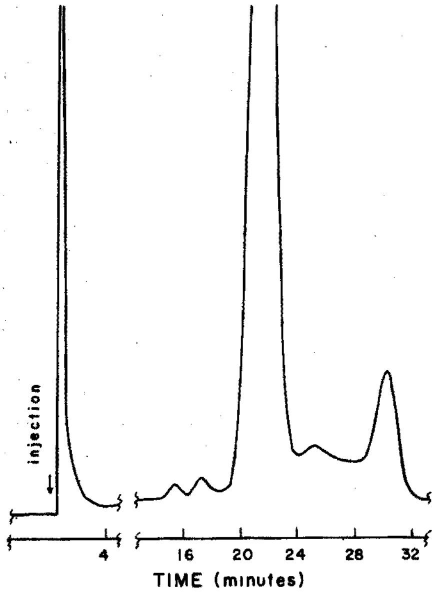
$$\%\ \text{Sugar}_x = \frac{(\text{wt. ratio of sugar}_x)\ (\text{wt. int. std. added to juice sample})\ (100)}{\text{wt. cane juice before drying}} \qquad (1)$$

where all weights are expressed in the same units, usually mg.

The (wt. ratio of sugar$_x$) used in this equation must be calculated from the measured area ratio for that sugar on the cane juice sample, by means of the appropriate standard curve. Since the graph was a straight line in this work, a least-squares analysis of data pertinent to the standard solutions was used to obtain the linear equation relating "area ratio" to "weight ratio". This equation was then used to calculate the "weight ratio" corresponding to each measured "area ratio" on the cane juice samples.

RESULTS

Figure 1 represents the chromatogram obtained for the fructose derivative after sufficient time had elapsed for complete reaction at room temperature. The occurrence of three peaks for this sugar, even after standing for 24 h, is in conflict with



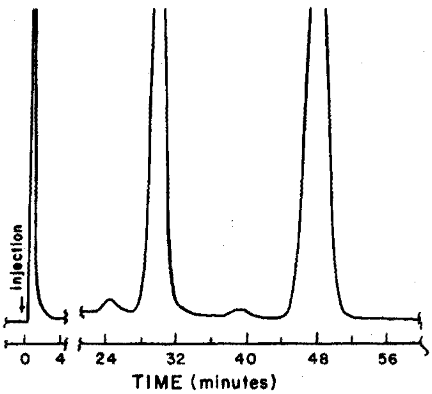


Fig. 1. Chromatogram obtained on a trimethylsilylated fructose sample.

Fig. 2. Trimethylsilylated D-glucose displayed two prominent peaks for the α-, and β-D-glucopyranose anomers and smaller peaks possibly due to other structures in solution.

the results of SWEELEY *et al.*[2] who reported only one peak. However, the presence of more than one peak is in agreement with subsequent work by others[13-15]. Similarly, the chromatogram for a mutarotated D-glucose sample (Fig. 2) displayed two very prominent peaks attributable to the α- and β-anomers. Also present were two very small peaks, one just before α-D-glucose and one between the two major anomers. Their presence has not been mentioned by other workers. Possibly they are due to impurities in manufactured glucose, but, if so, the impurity is consistent in the three commercial sugars which were checked. Assuming equal response to each anomer by the flame ionization detector, the percentage of each anomer in a mutarotated aqueous solution is as follows: first minor component, 0.69%; α-D-glucose, 42.61%; second minor component, 0.34%; β-D-glucose, 56.36%. A small peak appears not well separated from and immediately following the large α-glucose peak. Its area is included with that of α-glucose. Conceivably, these five peaks for D-glucose could be due to the five possible forms of the sugar in solution: α- and β-D-glucopyranoside, α- and β-D-glucofuranoside, and the straight chain form. The percentage composition of each component in the fructose chromatogram is more difficult to assess because of peak overlap, but the total of the two minor components appears to be about 10% of the major one.

It is interesting that the third peak for fructose overlaps with the peak for α-D-glucose. Significant separation was not achieved between these two peaks in a mixture under a variety of experimental conditions. Similarly, the very small first peak for D-glucose overlaps with the small second peak for fructose. Because of the overlapping of two peaks between sugars, it was considered that one was an impurity in the other. Two observations showed that this was not the case. First, in no chromatogram did the fructose sample derivative yield a peak which could be attributed to β-D-glucose which would have to be present in the mutarotated sample. Second, highly concentrated solutions of fructose gave negative results with the enzymatic Glucostat (glucose oxidase, Worthington Biochemical Corp.) quantitative test for the presence of glucose. In a like manner, the presence of fructose in glucose was ruled out by the lack of appearance in the glucose derivative chromatogram of the major

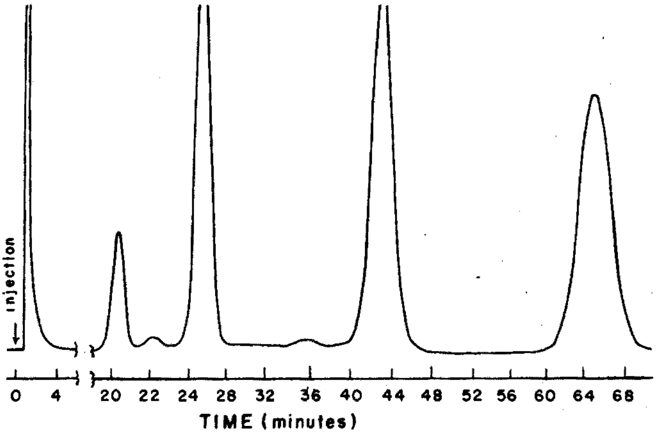


Fig. 3. Chromatogram obtained on a standard solution of fructose, glucose, and myoinositol trimethylsilyl derivatives.

fructose peak. Certainly, if the two minor peaks are observed, the major one would have to be displayed.

Because of the overlap of α-D-glucose with a peak due to fructose, these combined peaks were not usable for quantitative work. For this reason, only the first major fructose peak was measured as the "fructose area". Likewise, only the β-D-glucose peak was measured as the "glucose area" and all correlations were based on these areas. That this procedure is valid is an assumption based on each sample of sugar in aqueous solution mutarotating to the same extent. Thus the area of each particular anomer is always proportional to the original weight of sugar present.

Figure 3 shows the chromatogram obtained with one of the monosaccharide standards. All other such standards differed from this one only in the relative sizes of the various sugar peaks as each sugar concentration was varied. Table I summarizes the average values of data for triplicate runs per sample. Also included in this Table is information relative to the determination of sucrose.

TABLE I

CHROMATOGRAPHIC DATA FOR VARIOUS SUGARS

Sugar	*Wt. ratio to internal standard*	*Area ratio to internal standard*
Glucose	2.0047	1.000
Glucose	1.0023	0.6164
Glucose	0.6014	0.4401
Fructose	1.0660	0.5808
Fructose	0.7462	0.4027
Fructose	0.3198	0.1652
Sucrose	15.84	11.37
Sucrose	12.33	8.802
Sucrose	8.821	6.223

TABLE II

LINEAR EQUATIONS FOR DIFFERENT SUGARS

Sugar	*Equation*
Glucose	$Y = 0.3827\,X + 0.2328$
Fructose	$Y = 0.5570\,X - 0.0129$
Sucrose	$Y = 0.7333\,X - 0.2434$

A least-squares analysis of the data yields linear equations relating Y, the area ratio to internal standard for each sugar, to X, the weight ratio to internal standard, as presented in Table II. This analysis was done with a card-programmed Wang Model 360 calculator.

The determination of sucrose is much simpler than the determination of monosaccharides since there is only one peak for this sugar and since no other disaccharides are known to be present in quantitatively significant concentrations. Operating at such a temperature that the monosaccharides are eluted soon after the solvent, but still allowing an accurate measurement of the internal standard, gives a nicely separated sucrose peak. Figure 4 shows the results obtained on a sample of cane juice.

Once the appropriate runs for monosaccharides and sucrose have been made and data obtained, the appropriate equation in Table II converts measured area ratio into a weight ratio. Substituting this value, the weight of internal standard and the weight of cane juice initially into eqn. (1) gives the percentage of each sugar present on a whole juice basis. Typically such calculations gave the following results for several runs on a particular Louisiana cane juice sample: 16.13% sucrose, 0.740% fructose and 0.399% D-glucose. These results agree with older techniques[16] which give the following average values on a whole juice basis: 10–20% sucrose, and 0.5–2.5% reducing sugars (glucose and fructose).

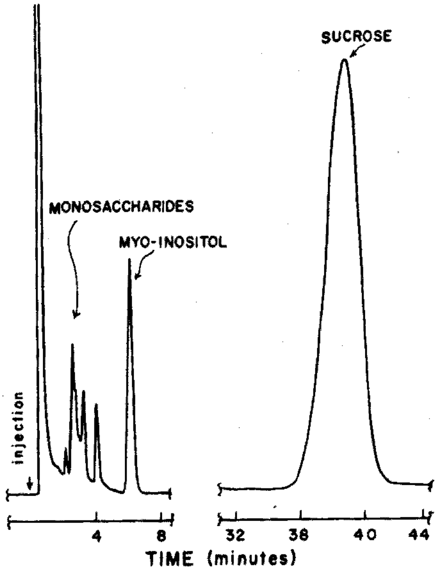


Fig. 4. Isothermal analysis of a sugar cane juice sample for sucrose.

Repetitive runs on a second series of standards and cane juice samples to which had been added known amounts of sucrose and myoinositol were obtained. For this study, freshly prepared solutions of sucrose and internal standard were pipetted into test tubes. An amount of internal standard approximately the same as the amount of sucrose present was used in order to have their respective peaks approximately the same size. A straight-line relationship was obtained as the standard curve relating weight ratio to area ratio for sucrose and internal standard. Similarly, dilution of 5.4284 g of cane juice with water to a total volume of 50 ml produced a standard solution of cane juice; 1-ml samples, each containing 108.568 mg of cane juice, were placed in test tubes with internal standard and varying amounts of sucrose solution. After these samples were dried and treated according to the method of SWEELEY *et al.*, the data shown in Table III were obtained.

In this analysis, the sucrose in cane juice was determined as 16.4%, which agrees well with the value obtained several weeks earlier of 16.1%. All data and values were reproducible to within 5% and generally to within 3%.

TABLE III

ANALYSIS OF STANDARDS AND CANE JUICE WITH ADDED SUCROSE

(3.986 mg of internal standard added in all cases)

Sample number	*Sucrose added (mg)*	*Sucrose, cane juice (mg)*	*Total sucrose added (mg)*	*Wt. ratio*	*Area ratio*	*Total sucrose found (mg)*	*% Error*
STD-1[a]	11.079	—	11.079	2.7805	1.837	—	—
STD-2	16.619	—	16.619	4.1707	2.765	—	—
STD-3	18.835	—	18.835	4.7268	3.182	—	—
STD-4	33.238	—	33.238	5.5609	3.858	—	—
Juice-1	—	—[b]	—[b]	—	2.979	17.832	—
Juice-2	1.108	17.8324	18.940	4.7511	3.190	19.096	0.86
Juice-3	2.216	17.8324	20.048	5.0291	3.308	19.803	1.23
Juice-4	3.324	17.8324	21.156	5.3070	3.418	20.462	3.39
Juice-5	11.079	17.8324	28.912	7.2524	4.858	29.088	0.61

[a] Standard samples are related by the equation: $Y = 0.1669X + 0.00216$, where $Y \equiv$ area ratio and $X \equiv$ weight ratio.

[b] The sucrose content of cane juice is unknown in the first juice sample. In subsequent samples, the amount found in juice sample one is assumed constant through all samples since the same amount of juice had been added to all.

DISCUSSION

Selection of operating conditions

The analysis of cane juice for mono- and disaccharides was accomplished in two separate isothermal analyses since the instrumentation used had a single column and could not be properly temperature-programmed. Based on the comparisons of BROBST AND LOTT[17], as well as other workers concerning isothermal g.c. and temperature-programmed gas chromatography, the method used here should be applicable where adequate instrumentation is available for the latter method.

Operating isothermally at a low (160–200°) temperature, the monosaccharides (fructose and glucose) appear well separated from one another and from the pyridine solvent peak. Tests with several different gas chromatographs and columns showed that the exact monosaccharide operating temperature must be determined for the particular equipment being used. For example, whereas 180° produced good separation of the sugars from one another and from the pyridine peak on one instrument, on another instrument, the temperature had to be lowered to 160° in order to free the sugars from the pyridine tail. For this reason each instrument and column must be adjusted for its own particular optimum performance. Another consideration is the method of integration to be used, electronic integrators being the best able to compensate for solvent tailing. With the instrument used, the optimum operating temperature was 168°. At this low temperature, disaccharides (sucrose) do not elute and the retention of sucrose by the column from one injection to the next does not affect the separations obtained. Periodically, the temperature of the column was raised to elute any retained sucrose.

At a higher isothermal operating temperature (anywhere from 230 to 260°), the monosaccharides are rapidly swept through the column a few minutes after the solvent. Well separated from them with a retention time which depends upon the exact operating temperature, sucrose appears as a single symmetric peak.

Since it was preferable to use only one internal standard, it was desirable that its retention time be somewhere between the last eluted monosaccharide, β-D-glucose, and sucrose. In this position, it would serve as an internal standard during the isothermal monosaccharide analysis (as long as it was eluted at the monosaccharide analysis operating temperature). Similarly, as long as it was eluted sufficiently after β-D-glucose to be separated from it at the higher disaccharide operating temperature, it could be used as internal standard in the determination of sucrose. Thus, the retention time of the internal standard is critical. The longer the standard is retained by the column, the longer will be the monosaccharide analysis. On the other hand, if the separation of internal standard from the monosaccharides is not sufficient, it will elute with them in the sucrose analysis.

Selection of the internal standard

To overcome the difficulties in quantitation of results, the use of internal standards has repeatedly been suggested. Myoinositol[18], sorbitol[5], α-methyl-D-galactopyranoside[19], and α-methyl-D-mannoside[13] have been suggested for use as internal standards in carbohydrate analyses. HALPERN *et al.*[7] objected to the use of internal standards which consume trimethylsilylation reagent; they suggested the use of inert internal standards such as terphenyl or triphenylethylene and showed that the use of these inert standards gave results which were reproducible to ±1% in the determination of glucose. They also suggested the possibilities of other polycyclic, high-boiling, inert substances such as chrysène and pyrene, as internal standards in determinations of D-glucose.

JANSEN AND BAGLAN[20] have recently investigated the recovery of ^{14}C-labelled sugar and alcohol derivatives, including the trimethylsilyl derivatives in gas chromatography. They determined that approximately 25% of the glucose, fructose, and sucrose derivatives were recovered from the column. Since radioactivity was found throughout the length of the column, it was decided that decomposition and/or deposition of the derivatives occurred throughout the column. It is important to note in this work that other types of compounds gave other absolute recoveries of trimethylsilyl derivatives; 80% of the glycerol derivative and only 25% of the stearyl alcohol derivative were recovered. Thus the use of internal standards structurally similar to the compounds being analyzed seems preferable to using compounds which might have a different recovery coefficient than the ones being investigated, especially where differing amounts of internal standard are added to a series of samples being analyzed. Unfortunately, none of the internal standards suggested above was studied for absolute recovery.

For the present work, it seemed advisable to eliminate any possibility of different recovery coefficients between the carbohydrates being studied and internal standard used. The next requirement was that the retention time of the internal standard be such that it appears after the monosaccharides and before sucrose in such a position as to allow the desired two isothermal analyses. Myoinositol proved the best choice. The objection of poor solubility for this compound by HALPERN *et al.*[7] was overcome by increasing the absolute amounts of pyridine and silylation reagents. No difficulty was experienced. DAVISON AND YOUNG[21] have recently applied an analytical procedure similar to the one given here to plant extracts, although with temperature-programmed gas chromatography, and apparently experienced no difficulty from myoinositol as internal standard.

Analysis of cane juice

Table III presents the data pertaining to an analysis of cane juice for sucrose. The numbering of standard solutions prepared to obtain a working plot of "area ratio" *versus* "weight ratio" is prefixed by the abbreviation "STD". In order to test the validity of this method of analysis for sugar cane juices containing differing concentrations of sucrose, known amounts of the sugar were added to a sample of cane juice. This produced the series of samples denoted by Juice-1, Juice-2, etc.

The percent error obtained by analyzing these prepared juice samples indicates the method gives results which are accurate to at least 5% over the sucrose concentration range expected for normal sugar cane juice samples. The method could accurately distinguish between the synthetically prepared juice samples with relatively small differences in sucrose concentration. Moreover, in Juice-5, the concentration of sucrose was increased by more than 50% over the concentration in Juice-1 with less than 1% error in the sucrose determination.

No efforts were made to determine the influence of small changes in concentration on the fructose and glucose analytical results, but it is expected that results on these sugars would be the same as those for sucrose. Testing the method on the monosaccharides is more difficult than for sucrose because of the several peaks obtained.

The two analyses for sucrose for which data are presented herein were run entirely independently on the same cane juice sample. In the several intervening weeks between runs, the sample was kept frozen. That the results obtained were in good agreement from one run to the next (16.1% and 16.4%) indicates the reproducibility of the method. Although the same gas chromatograph was used for each analysis, all standard solutions, cane juice samples, etc. were freshly prepared for the second analysis.

CONCLUSION

Despite the introduction of a multitude of automated or semiautomated instrumental methods, the industrial use of these methods has been delayed significantly. The molasses industry, for example, still uses analytical procedures which are 50–100 years old[22]. Except for the introduction of some of the methods of paper and column chromatography and at least one example of the technique of isotope dilution for the analysis of sucrose[23], new techniques have rarely been suggested and, for the most part, not industrially employed. Old techniques such as polarimetry and the reduction of Fehling's solution for the "reducing sugars" present are still used as indicators of the "true" sucrose and monosaccharide contents of juices and syrups, despite the known presence of many interfering species.

The use of gas–liquid chromatography for analysis of mixtures competes favorably with most other methods because of the overall picture of the mixture's composition. The development of the technique of silylation by SWEELEY *et al.* allowed this powerful method of analysis to be applied to carbohydrates.

The application to sugar cane juice presented in this paper seems a logical extension of previous work. The procedure could be used commercially to determine sucrose content of juices and light syrups without modification. The use of temperature-programming would allow the analysis of mono- and disaccharides in one chromatogram.

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SUMMARY

The gas chromatographic determination of the mono- and disaccharides in sugar cane juice is accomplished by drying the sample under reduced pressure and converting the common free sugars into their trimethylsilyl derivatives. Myoinositol was found to be a suitable internal standard for both the isothermal monosaccharide analysis and the isothermal disaccharide (sucrose) analysis. Accuracy is assessed to be within 5%.

RÉSUMÉ

On propose une méthode pour le dosage de mono- et disaccharides dans le jus de canne à sucre par chromatographie gazeuse, en séchant l'échantillon sous pression réduite et par conversion des sucres libres en leurs dérivés triméthylsilylés. Le myoinositol convient bien comme étalon interne, soit pour l'analyse de monosaccharides, soit pour l'analyse de disaccharides (sucrose). L'exactitude est de 5%.

ZUSAMMENFASSUNG

Die Mono- und Disaccharide in Zuckerrohrsaft können gaschromatographisch bestimmt werden, indem die Probe unter vermindertem Druck getrocknet und die üblichen freien Zucker in ihre Trimethylsilyl-Derivate umgewandelt werden. Myoinosit eignet sich als innerer Standard für die isotherme Monosaccharid-Analyse und die isotherme Disaccharid (Rohrzucker)-Analyse. Die Genauigkeit liegt innerhalb 5%.

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DESIGN AND EVALUATION OF A MICRORADIOMETRIC DETECTOR FOR COLUMN LIQUID CHROMATOGRAPHY

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To avoid the time-consuming work of collecting and analyzing large numbers of radioactive fractions of effluents from liquid chromatography columns, automatic fraction collectors and sample changers, in which the fractions can be measured by the use of scintillation tubes[1] or other scintillation materials[2] have been introduced. Continuous monitoring of a radioactive eluate has also been achieved by means of flow cells, filled with scintillator[3] or continuous flow G. M.counters. None of the radiometric detectors used so far[3] has a cell volume smaller than 0.3 cm^3, and accordingly these detectors cannot be used in rapid, high-precision liquid chromatography.

THEORY OF DETECTION

Static signal

A radiometric detector measures the activity present in the detector cell, and converts this to an output signal voltage. The activity A describes the decay rate of a radioactive substance in terms of number of atoms: $A = \mathrm{d}N^*/\mathrm{d}t$, where N^* = number of radioactive atoms. The voltage U, delivered by the detector is a linear function of the activity A_D, which is present in the detector cell:

$$U - U_0 = S_A A_D = S_A V_D M s\, c_D \qquad (1)$$

where U_0 is the voltage from background activity; S_A is the sensitivity of the detector with respect to the activity; s is the specific activity ($s = A/m$, m = mass of the substance); c_D is the average concentration in the detector cell; V_D is the volume of the detector cell; and M is the molecular weight of the radioactive substance

After substituting the equations for the flow rate ($w = \mathrm{d}V/\mathrm{d}t$) and the concentration ($c = \mathrm{d}m/M\,\mathrm{d}V$), the following equation is obtained:

$$U - U_0 = \frac{S_A V_D s}{w} \cdot \frac{\mathrm{d}m}{\mathrm{d}t} \qquad (2)$$

where t is the time, and $\mathrm{d}m/\mathrm{d}t$ the mass flow through the detector.

Dynamic signal

The elution function of a chromatographic column describes the concentration of the sample in the column effluent as a function of time, and for a single component, has the shape of a peak, which approximates generally a gaussian distribution function. The radiometric detector renders the concentration peak as a voltage peak, whose time integral is proportional to the mass of the sample if:

1. the half-life of the radioactive isotope is much longer than the retention time in the detector;
2. the volume of the detector cell is much smaller than the volume in which the elution peak is present.

The expression for the voltage peak area may be obtained by integration of eqn. (2):

$$\text{Area} = \int_{t_b}^{t_e} (U-U_0)\,\mathrm{d}t = \frac{S_A V_D\, s}{w} m = \frac{S_A V_D}{w} A \tag{3}$$

where t_b is the time of beginning of the peak, t_e the time of end of the peak, and $A = sm$ = total activity of the sample component.

The activity is normally induced by irradiation of the sample. In this case the specific activity (immediately after irradiation) is determined by the following equation:

$$s = \Phi \sigma a N_A\ M^{-1}\,[1-\exp(-\ln 2\ t_{irr}/t_{\frac{1}{2}})] \tag{4}$$

where Φ is the flux of the activating particles, σ is the cross-section of the isotope, a is the abundance of the isotope, t_{irr} is the irradiation time, $t_{\frac{1}{2}}$ is the half-life of the isotope, and N_A is Avogadro's number.

The irradiation of the sample under well defined conditions followed by column liquid chromatography with radiometric detection is probably the most advanced method in activation analysis.

The detector is expected to deliver a signal–time function which is a true representation of the elution function. As a precondition for that, mixing processes on the way from the column to the detector cell and within the detector cell itself, must be avoided. A detector consists of the detector cell and the feed line. It is assumed that the feed line is connected directly to the end of the column. A concentration peak leaving the column will disperse further in the feed line and the detector cell. The dispersion can be described in terms of variances:

$$\sigma_v^2 = \sigma_{v0}^2 + \Delta\sigma_v^2 \tag{5}$$

where σ_{v0}^2 is the variance (in volume units) at the beginning of the system, $\Delta\sigma_v^2$ is the increase of the variance in the system, and σ_v^2 is the variance at the end of the system.

The total mixing in a flowing fluid is the result of diffusion as well as convective mixing. For a long and narrow cylindrical tube and laminar flow an equation for the increase of the variance can be derived[4,5]. In the notation of this paper and after substitution of the volume variance instead of the length variance, the flow rate instead of the average fluid velocity, and the length instead of the time, the following equation is obtained, in which the first term describes the effect of diffusion and the second the effect of convective mixing.

$$\Delta\sigma_v^2 = 2\pi^3 r^6 L\ D/w + \pi r^4 L\ w/24D \tag{6}$$

where $\Delta\sigma_v^2$ is the increase of the peak variance in the tube in volume units, r is the radius of the tube, L is the length of the tube, and D is the diffusion coefficient.

Even if the shape of the feed line and the detector cell is not cylindrical or has not a uniform cross-section, eqn. (6) gives an indication of how interfering mixing can be avoided.

Noise

The noise of a detector can be described by the standard deviation of the output signal, which is obtained with a given input signal. The ratio between standard deviation and average value of the signal, the noise-to-signal ratio, is the relative statistical error, which characterises the precision of the measurement. In principle, the noise can be caused by fluctuations of the input signal itself as well as by the measuring process. Particularly in the case of a radiometric detector, the momentary value of the activity will not be constant since radioactive decay is a statistical process.

For the noise a general expression can be given as

$$\sigma_A = [(\bar{A} + 2\bar{A}_0)/t_c]^{\frac{1}{2}} \tag{7}$$

where σ_A is the standard deviation of the activity of the sample, $\bar{A}$ is the average activity of the sample, $\bar{A}_0$ is the average background activity, and $t_c = V_D/w$ is the counting time, which is the retention time in the detector cell. This relationship determines the precision of the measurement. The noise of the background limits the measurement of low activities.

APPARATUS

The apparatus shown in Fig. 1 was used for the study of the peak-broadening effects in the radiometric detector. The eluant reservoir (1) is placed 1 m above the rest of the apparatus, in order to obtain a constant flow through the system. Various flow rates are established by the use of different capillary restrictors (7). The flow rate is measured by collecting the eluant during a given time in a micro-burette (8). The sample is dissolved in the eluant and injected by a 10-μl precision syringe (Hamilton 701 N) through a self-sealing membrane. The injection port (2) is constructed

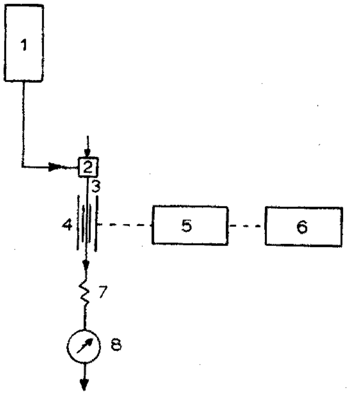

Fig. 1. Scheme of the apparatus. (1) Eluant reservoir, (2) injector, (3) tube, (4) G.M. counter, (5) ratemeter, (6) recorder, (7) restrictor, (8) flowmeter.

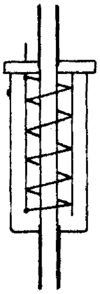

Fig. 2. Continuous flow G.M. counter (schematic).

from titanium and allows the injection of the sample directly on to the top of the column[6]. A Teflon tube (3) connected to the injector (2) and conducted through a Geiger–Müller counter (4) (Fig. 2) forms the feed line as well as the detector cell. The length of the detector cell in which the activity is measured by the counter is 36 mm. The length of the feed line, which is the initial part of the tube from the injector to the detector cell is 30 mm. Tubes with different inner diameters were tested.

The continuous flow G.M. counter (4) (Philips 18510) counts the disintegrations in the detector cell. The efficiency of the counter depends on the energy and type of the radiation and on the material and the thickness of the walls of the tube forming the detector cell. The counter is placed in a lead pot to shield it from external radiation, and is powered by a high-voltage power-supply (Philips PW 4220).

The ratemeter (5) (Philips PW 4242) converts the pulse rate of the G.M. counter to a voltage, which is amplified and fed to a potentiometric recorder with ball and disc integrator (6) (Servogor, RE 512).

Experiments for the determination of the calibration function and the precision were carried out in a slightly modified apparatus including a column. Constant flow is obtained by controlling the inlet pressure by means of compressed nitrogen gas. A specially constructed pressure vessel is used in order to overcome solution of the gas in the eluant. The outlet pressure is atmospheric. The device will be described in more detail in a following paper.

DETECTOR TESTS

Measurements of the peak-broadening in the sampling device and detector were carried out with the apparatus described above; the eluant was water.

For the determination of the calibration function and the precision, a column with an internal diameter of 5 mm and a length of 50 cm filled with cation exchanger Aminex Q-150-S, diameter 20–35 μm (Biorad Laboratories) was used. The eluant was 2 M hydrochloric acid. The samples for all the experiments were sterile, isotonic solutions (pH 6–8) of the radioisotope compounds ^{86}RbCl (half-life 18.5 days, Philips-Duphar) and ^{137}CsCl (half-life 30.0 years, Philips-Duphar).

Peak broadening

As was pointed out on p. 520 a concentration peak disperses in the feed line and the detector cell, because of diffusive and convective mixing effects. A further peak broadening may occur in the conversion of the concentration peak to a voltage peak by the detector, if the speed of response is too low or the cell volume is too large.

First the contribution of the ratemeter to the peak broadening was investigated. The speed of the ratemeter is characterized by its time constant. With a large time constant, peak broadening occurs, whereas with a small time constant, noise is heavily superimposed on the useful signal peak. In order to determine the optimal time constant, the standard deviation of ^{86}Rb peaks was measured at different time constants and flow rates. The internal diameter of the tube forming the feed line and detector cell was 0.56 mm. In the flow rate range 0.5–5 mm^3 sec^{-1} about the same standard deviation was found for time constants of 0.1 and 1 sec whereas a significant peak-broadening was observed for time constants of 4 and 10 sec. Only the peaks obtained with a time constant of 0.1 sec were unsatisfactory because of excessive noise.

All further measurements were therefore carried out with a time constant of 1 sec.

In order to obtain the best separation, the contributions of sampling device and detector to the variance of the recorded peak must be negligible compared to the contribution of the column. The overall variance should be approximately equal to the variance produced in the column

$$\Delta\sigma_{v\,\mathrm{sampling}}^2 + \Delta\sigma_{v\,\mathrm{detector}}^2 \ll \Delta\sigma_{v\,\mathrm{column}}^2 \approx \sigma_v^2 \qquad (8)$$

The increase of the variance in the feed line and detector cell must be evaluated in order to establish the limitations of the detector. The peak width was determined as a function of flow rate of three tubes with different diameters. The tubes acted as feed line and detector cell. The peaks were found to be asymmetrical so that the usual statistical method was used to determine their variances. The results are presented in Table I and in Fig. 3. The experimental data can be correlated by linear equations, the constants in which were calculated by the least squares method.

Although strictly speaking, eqn. (6) may not be applied because of the small

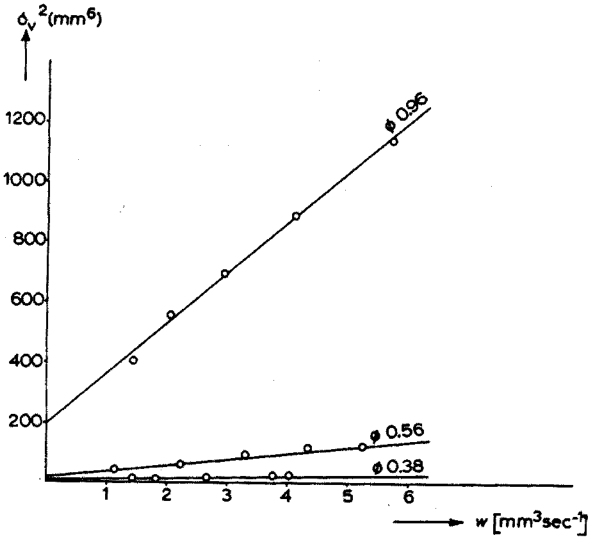

Fig. 3. Relation between flow rate and variances for different tube diameters.

TABLE I

TUBE DIMENSIONS AND CORRELATION EQUATIONS

Tube dimension				*Correlation equation* $\sigma_v^2 = a + bw$		*Calculated diffusion coefficient (cm² sec⁻¹)*
Nominal internal diameter (mm)	*Length (mm)* *Feed line*	*Detector cell*	*Nominal cell volume (mm³)*	*a (mm⁶)*	*b (mm³ sec⁻¹)*	
0.38	30	36	4.2	7.8	4.9	$1.59\cdot10^{-5}$
0.56	30	36	9.1	17.1	21.8	$1.76\cdot10^{-5}$
0.96	30	36	27.2	196	167	$2.00\cdot10^{-5}$

number of theoretical plates involved, it can be used together with eqn. (5) to explain the correlation equation quoted in Table I. Assuming that the variance attributable to the sampling process is independent of flow rate, the a term in the correlation equation describes the effect of the injection ($a = \Delta\sigma_v^2{}_{\text{injection}}$) and the bw term describes the mixing effects in the feed line and the detector cell ($bw = \Delta\sigma_v^2{}_{\text{tube}}$). The comparison of the volume standard deviation with the cell volume shows, however, that at low flow rates, the peak-broadening effect caused by the cell volume can not be neglected. On the other hand, it may be expected that according to eqn. (6), the linear equation for the flow dependence of the volume variance will not hold at very low flow rates, because of the diffusion effects.

The use of eqn. (6) can be justified by calculating the diffusion coefficient from the b factor of the correlation equation according to eqn. (6), the first term of which can be neglected if the flow rate is not extremely low. An effective length of 48 mm was chosen for L, *i.e.* the length of the feed line and half the length of the detector cell. The results, which are included in Table I, show a significant scatter, which can probably be attributed to deviations from the specification of the tube diameter.

In order to confirm the results, experiments were carried out with a longer tube, for which eqn. (6) is more valid. The diffusion coefficient, D, was calculated from the following equation[7] which is equivalent to eqn. (6).

$$L\sigma_t^2/t_R^2 = 2Dt_R/L + r^2L/24Dt_R \tag{9}$$

where t_R is the retention time in the tube, r is the radius of the feed line tube, and L its length. The first term of eqn. (9) is determined by diffusion, and the second by convective mixing. As the diffusion coefficient of liquids is very small, the first term becomes negligible at higher linear velocities (L/t_R). Table II shows the results, which are obtained with a tube 85 cm long and 0.56 mm in diameter.

The high precision of the measurements and the agreement with the value for the same tube diameter in Table I is remarkable. The systematic error may be significant, however, because of inaccuracies in the tube diameter.

TABLE II

DIFFUSION COEFFICIENTS MEASURED IN A LONG TUBE (L = 85 cm, d = 0.56 mm)

σ_t (sec)	t_R (sec)	D (cm^2 sec^{-1})
13.8	105.0	$1.82 \cdot 10^{-5}$
14.0	105.0	$1.75 \cdot 10^{-5}$
15.1	124.5	$1.79 \cdot 10^{-5}$
15.2	128.8	$1.84 \cdot 10^{-5}$

Calibration function

The calibration function of the detector describes the relationship between the output and input signals, *i.e.* the peak area and activity, respectively. Figure 4 shows the linearity of the detector response; the peak areas were measured with a planimeter. As can be seen, the slope of the calibration function is constant, according to eqn. (3), when the flow rate is kept constant. If the specific activity of the sample is known, m can be calculated from the measured activity. In activation analysis, a standard sample is usually irradiated together with the unknown sample, in order to determine the specific activity. The sensitivity of the detector, S_A, depends on the energy and type of radiation, and is illustrated in Fig. 4 and Table III.

In order to study the flow dependence of the detector, the peak area of a given activity was measured by a recorder equipped with a ball and disc integrator at different flow rates. For an activity of 0.5 μCi ^{86}Rb, the product of peak area and flow rate was measured respective five times at five flow rates in the range between 5 and 40 mm^3 sec^{-1}. According to eqn. (3), it was found to be constant with a precision of 3.5 %.

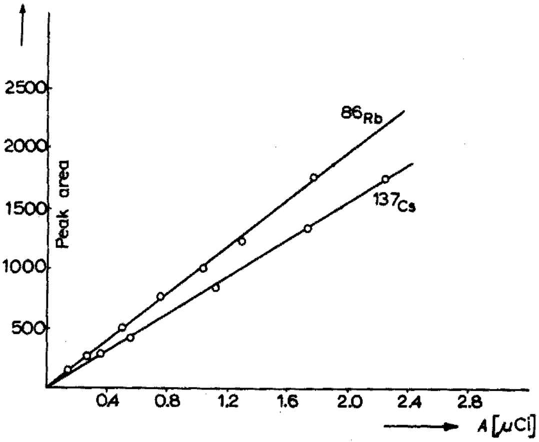

Fig. 4. Linearity and sensitivity of the detector for the isotopes ^{86}Rb and ^{137}Cs. The points are the mean value of 5 measurements.

TABLE III

SENSITIVITY OF THE DETECTOR FOR THE ISOTOPES ^{86}Rb AND ^{137}Cs

Radioisotope	*Radiation*		*Area/μCi*[a]
	β⁻ (MeV)	*γ (MeV)*	
^{86}Rb	1.8	1.1	987
^{137}Cs	1.2	0.7	773

[a] Area is given in arbitrary integration units.

Precision and detection limit

The precision of the measurement is determined by the ratio between the standard deviation and the average value of the output signal. The results presented in Table IV are typical for the precision of the determination of activities by column liquid chromatography with radiometric detection. The standard deviation of the peak area was found to be about 0.015, as far as peak areas larger than 20000 arbitrary integration units are concerned. As the peak area becomes smaller, the relative error increases. In Fig. 5 the results are represented graphically. The perfect linearity of the detector is demonstrated by the 45° slope of the correlation line. It can be seen how the precision decreases with decreasing activity. An arbitrary detection limit may be defined as the activity which can be measured with a given precision (often σ_{area}/average area $= 1/3$ is chosen).

Since the detector responds to other influences as well as eluant activity, there will be a background signal, the noise of which limits the precision of measurement of very low activities. In order to evaluate the background noise, the background signal was integrated for the time, during which the peak elutes (7 min). The standard deviation of the background was found to be 16 arbitrary integration units. From Fig. 5 it can be derived that the standard deviation of the background noise corresponds to an activity of 1.15 nCi for rubidium-86.

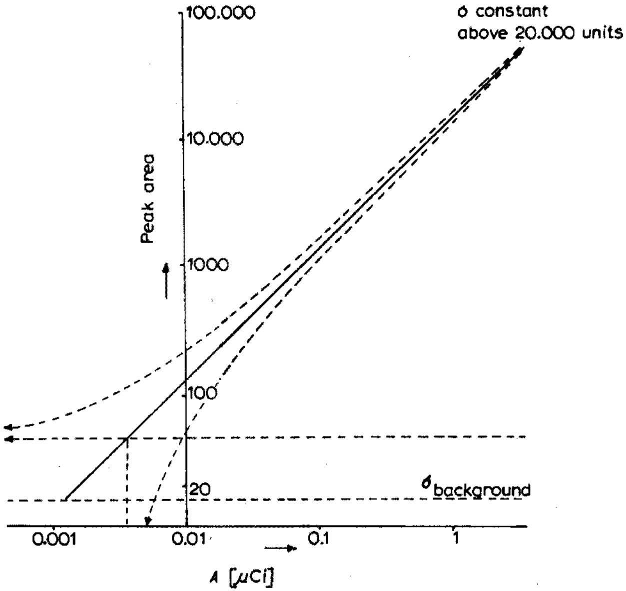

Fig. 5. Logarithmic representation of the relation between peak area and activity. The dashed lines represent the confidence limits at ± 3σ. The thick line indicates the measured range.

TABLE IV

DATA CHARACTERIZING THE PERFORMANCE OF THE DETECTOR

Injection volume (μl)	*A (μCi)*	*Peak area*[a]	σ_{area}[a]	σ_{area}/*average area*
1	0.023	296	41	0.138
4	0.059	720	64	0.100
3	0.069	976	64	0.066
1	0.234	3080	128	0.042
2	0.63	8480	257	0.033
4	1.52	19280	347	0.018
6	2.28	31600	321	0.011
9	3.18	41700	642	0.015

[a] In arbitrary integration units

The authors are indebted to Dr. H. L. POLAK for his useful advice and critical discussions of the radio-activity measurements. The technical assistance of Mr. G. FEENSTRA is gratefully acknowledged.

SUMMARY

The theory of radiometric detection is discussed. An expression for the sensitivity is derived; peak-broadening owing to mixing phenomena in the feed line and the detector cell is described. The significance of the noise is discussed. The detector has been tested with respect to peak-broadening effects, sensitivity, linearity, precision and detection limit. The results demonstrate its excellent performance. It proves to be very suitable for high-speed column liquid chromatography.

RÉSUMÉ

Une étude théorique de la détection radiométrique est effectuée. Le détecteur est décrit et examiné en fonction de l'expansion des pics, de la sensibilité, de la linéarité, de la précision et des limites de détection. Les résultats obtenus permettent de le considérer comme convenant très bien à la chromatographie liquide rapide sur colonne.

ZUSAMMENFASSUNG

Es wird die Theorie radiometrischer Detektoren erörtert. Für die Empfindlichkeit wird eine Formel abgeleitet; es wird die durch Mischungserscheinungen hervorgerufene Bandenverbreiterung beschrieben. Die Bedeutung des Rauschens wird diskutiert. Der Detektor ist auf Bandenverbreiterungseffekte, Empfindlichkeit, Linearität, Genauigkeit und Nachweisgrenze geprüft worden. Die Ergebnisse zeigen seine ausgezeichnete Leistung. Er eignet sich sehr gut für die schnelle Säulen–Flüssig-Chromatographie.

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SEPARATION AND DETERMINATION OF TRACES OF METALLIC IMPURITIES IN SILVER HALIDES

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Silver halides which have been obtained as high-purity materials by zone refining[1], are commonly investigated by emission spectrography. By this technique as little as 1 p.p.m. of several elements can be determined. It seemed of interest to examine the possibility of applying solvent extraction techniques[2,3] to this analytical problem.

Solvent extraction is normally very useful for detecting the impurity content in a matrix even at very low concentrations, and the method allows an enrichment or preconcentration which generally cannot be achieved by the spectrographic method.

With regard to the analysis of silver halides, extraction methods involve two preliminary problems: sample dissolution, and masking of silver. However, since the dissolution of silver halides can be performed only in strongly complexing medium, the dissolution process necessarily involves a strong masking of silver(I) ions. However, this masking process must avoid an excessive complexing of the elements to be detected, so that their extraction by chelating agents remains possible.

In the proposed method, a concentrated solution of potassium iodide is used as the solvent for the silver halides. Under such conditions, the silver(I) ion is strongly complexed so that, in successive extractions with dithizone and oxine, it remains completely masked. When the solution is shaken with dithizone in carbon tetrachloride, zinc, cadmium, lead, copper, cobalt and nickel are extracted. From the residual solution, iron, aluminium and manganese can be extracted with oxine in chloroform. If relatively large amounts of sample are taken and the volumes of the solvents are suitably reduced, a considerable enrichment of trace impurities can be achieved.

EXPERIMENTAL

Apparatus

The extractions were performed in pear-shaped separatory funnels with Teflon stopcocks and a capacity of 50 ml.

Spectrophotometric measurements were performed with a Bausch & Lomb recording spectrophotometer model Spectronic 505, with glass microcells having a capacity of 0.5 ml and a light path of 10 mm.

Reagents

Potassium iodide solution (4.5 *M*) was purified by several extractions with dithizone and oxine.

Concentrated hydrochloric acid (G. R. Merck; maximum declared impurities: Pb 0.05 p.p.m.; Cu 0.05 p.p.m.; Zn 0.1 p.p.m.; Cd 0.01 p.p.m.; Fe 0.5 p.p.m.) and sodium hydroxide pellets (extra-pure G. R. Merck; maximum declared impurities: heavy metals (as Pb) 5 p.p.m.; Fe 5 p.p.m.; Al 10 p.p.m.) were used.

Ammonia solution was obtained by dissolving gaseous ammonia, evolved from the reaction of ammonium chloride with sodium hydroxide, in water previously extracted with dithizone and oxine.

The dithizone solution was $5 \cdot 10^{-5}$ *M* in carbon tetrachloride, and the oxine solution was $1 \cdot 10^{-2}$ *M* in chloroform.

Buffer solutions were prepared from potassium hydrogen phthalate (0.05 *M*; pH 4), ammonium chloride–ammonia (0.5 *M*; pH 8), and 0.1 *M* sodium acetate–hydrochloric acid (pH 4.6). These solutions were stored over dithizone or oxine solution in polyethylene vessels.

Solutions of metallic ions were obtained by dissolving the appropriate salt (chlorides or nitrates) in water containing enough acid to prevent hydrolysis.

Purification of the reagents and solvents

The purest available reagents were purified, when possible, by several extractions with dithizone and oxine till any modification of the spectrum of the extracting agent disappeared.

Distilled water, further treated with dithizone and oxine, was stored in neutral glass vessels over dithizone solution.

Vessels were cleaned with a 1 + 1 mixture of concentrated nitric acid and sulfuric acid.

General procedure

The proposed method is shown schematically in Figs. 1–3.

The spectrophotometric determinations were based on molar absorptivities (ε)

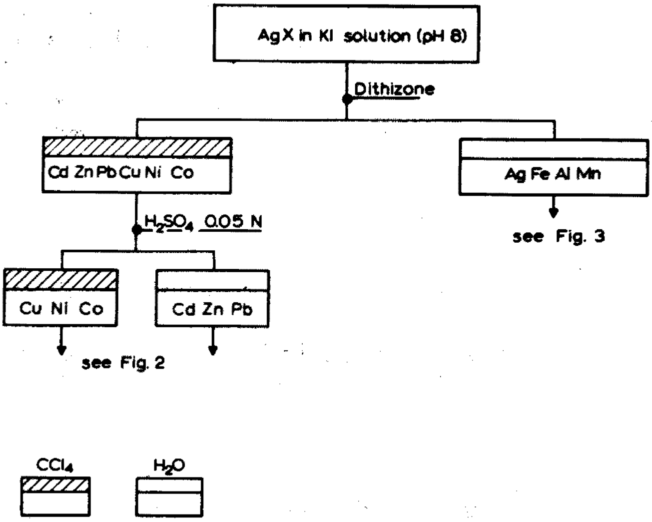

Fig. 1. Schematic procedure for dithizone extractions.

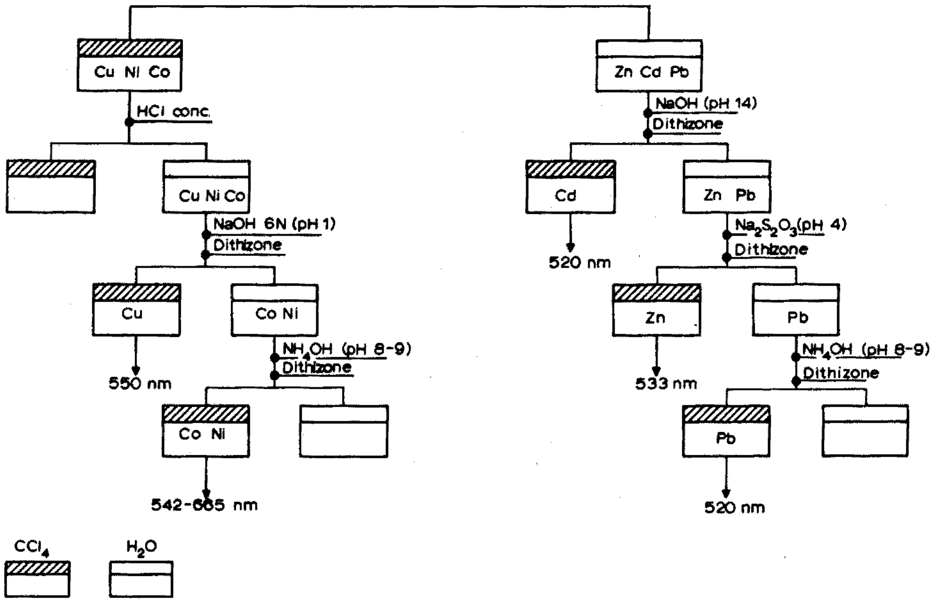

Fig. 2. Schematic procedure for the determination of Cd, Zn, Pb, Cu, Co, Ni.

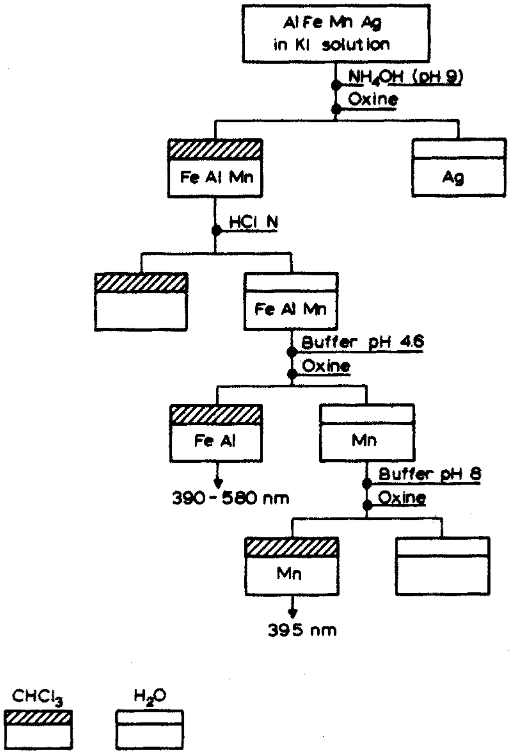

Fig. 3. Schematic procedure for the determination of Fe, Al, Mn.

TABLE I

RESULTS OF SPECTROPHOTOMETRIC DETERMINATION OF Cd, Zn, Pb, Cu, Ni AND Co

Cd			*Zn*			*Pb*			*Cu*			*Ni*			*Co*		
Added (*μg*)	*Found* (*μg*)	*Error* (*%*)	*Added* (*μg*)	*Found* (*μg*)	*Error* (*%*)	*Added* (*μg*)	*Found* (*μg*)	*Error* (*%*)	*Added* (*μg*)	*Found* (*μg*)	*Error* (*%*)	*Added* (*μg*)	*Found* (*μg*)	*Error* (*%*)	*Added* (*μg*)	*Found* (*μg*)	*Error* (*%*)
3.00	2.94	−2	3.00	3.06	+2	3.00	3.02	+0.6	—	—	—	—	—	—	5.00	5.15	+3
1.00	0.98	−2	1.00	0.98	−2	—	—	—	1.00	1.10	+10	—	—	—	1.00	1.14	+14
3.33	3.33	0	—	—	—	1.00	1.00	0	3.85	3.85	0	3.85	3.90	+1.5	3.85	4.20	+10
3.33	3.33	0	3.33	3.00	−10	—	—	—	10.00	10.40	+4	10.00	8.80	−12	10.00	8.70	−13
1.00	1.05	+5	—	—	—	1.00	0.98	−2	1.00	0.95	−5	5.00	5.20	+4	1.00	0.92	−8
2.00	2.02	+1	2.00	2.14	+7	2.00	1.88	−6	7.64	8.30	+9	7.64	7.20	−7	7.64	7.55	−1.2
1.00	0.96	−4	1.00	1.03	+3	1.00	1.06	+6	5.00	4.85	−3	5.00	5.10	+2	5.00	4.70	+6
1.00	0.99	−1	1.00	0.92	−8	1.00	0.96	−4	1.00	0.98	−2	1.00	0.93	−7	1.00	1.06	+6
	Av. err. ± 1.9			Av. err. ± 5.3			Av. err. ± 3.1			Av. err. ± 4.7			Av. err. ± 5.5			Av. err. ± 7.5	

obtained from extractions with the appropriate reagents of standard aqueous solutions of single elements.

The following molar absorptivities were used:

$Cd(HDz)_2$ ε(520 nm) = 87600; $Zn(HDz)_2$ ε(533 nm) = 97000
$Pb(HDz)_2$ ε(520 nm) = 70000; $Cu(HDz)_2$ ε(550 nm) = 46500
$Co(HDz)_2$ ε(542 nm) = 59200; $Ni(HDz)_2$ ε(665 nm) = 19200
$AlOx_3$ ε(390 nm) = 8200 ; $FeOx_3$ ε(580 nm) = 4200
$MnOx_2$ ε(395 nm) = 12900

Sample dissolution

Samples of silver chloride, of the order of 1 g, were dissolved in 10 ml of 4.5 *M* potassium iodide solution.

Separation and determination of Zn, Cd, Pb, Cu, Co and Ni (Fig. 2) with dithizone

Extract the potassium iodide solution of silver chloride, buffered at pH 8 with 1 ml of ammonium chloride–ammonia solution, three times with 5 ml of $5 \cdot 10^{-5}$ *M* dithizone, shaking every time for 30 min. Combine the organic phases and wash twice with 5 ml of 4.5 *M* potassium iodide at pH 8 in order to remove undesirable traces of extracted silver, as well as any residue of the initial aqueous phase, which otherwise would introduce large amounts of silver to interfere with the subsequent procedure. After washing with ammonia–ammonium chloride buffer at pH 8, Zn, Cd, Pb, Cu, Co and Ni are recovered in the organic phase.

Back-extract zinc, cadmium and lead by shaking the organic phase with 2 ml of 0.05 *M* sulfuric acid for 2–3 min.

For the determination of cadmium, add 0.5 ml of 6 *M* sodium hydroxide to the acidic solution, and extract with two 1-ml portions of $5 \cdot 10^{-5}$ *M* dithizone solution, each extraction taking 2 min. The cadmium complex has its maximum absorbance at 520 nm.

For the determination of zinc, neutralize the basic solution derived from the determination of cadmium, by adding about 0.4 ml of concentrated hydrochloric acid. After addition of 3 ml of 10% (w/v) sodium thiosulfate solution as masking agent for lead, and 2 ml of phthalate buffer pH 4, extract zinc by shaking with 1 ml of $5 \cdot 10^{-5}$ *M* dithizone for 5 min. Then shake the extract with dilute ammonia solution (0.01 *M*) to remove the excess of dithizone. Determine zinc spectrophotometrically at 533 nm.

After the separation of zinc, treat the aqueous solution with 0.5 *M* ammonia solution to give pH 9, and extract lead with 1 ml of $5 \cdot 10^{-5}$ *M* dithizone solution for about 5 min. Wash the organic phase with 0.01 *M* ammonia solution and measure the absorbance of the lead dithizonate at 520 nm.

After the separation of zinc, cadmium and lead, shake the organic phase for about 60 min with 3 ml of concentrated hydrochloric acid. Copper, cobalt and nickel are thus back-extracted into the aqueous phase.

For the determination of copper, add enough 1 *M* sodium hydroxide to the strongly acidic aqueous solution to adjust the pH to 1. Then extract copper by shaking with 1 ml of $5 \cdot 10^{-5}$ *M* dithizone solution for 30 sec. After washing with 0.01 *M* ammonia solution, determine copper dithizonate spectrophotometrically at 550 nm.

For the determination of nickel and cobalt, adjust the aqueous solution to about pH 9 by adding 0.5 *M* ammonia solution and extract with 1 ml of $5 \cdot 10^{-5}$ *M* dithizone solution by shaking for 30 min. Determine the two metals simultaneously by measuring the absorbances at 542 and 665 nm, after elimination of excess of dithizone with 0.01 *M* ammonia solution.

Separation and determination of iron, aluminium and manganese with oxine (Fig. 3)

After the removal of Zn, Cd, Pb, Cu, Co and Ni with dithizone, adjust the pH of the aqueous phase to 5 with 2 *M* hydrochloric acid, and wash with carbon tetrachloride to remove the dissolved dithizone. Adjust the solution to pH 9 by adding 0.5 *M* ammonia solution, and extract with two 5-ml portions of 0.01 *M* oxine, shaking for 15 sec each time. Wash the organic phase twice with water and then treat with 3 ml of 1 *M* hydrochloric acid for 30 min so that iron, aluminium and manganese are back-extracted.

For the determination of iron and aluminium, adjust the aqueous phase to pH 4.6 by adding 0.5 *M* ammonia solution and 1 ml of acetate buffer, and extract with 1 ml of 0.01 *M* oxine solution for 30 min. Determine iron and aluminium in the same solution by measuring the absorbances of the organic phase at 580 and 390 nm, respectively.

After separation of iron and aluminium, shake the aqueous phase at pH 8 with 1 ml of oxine solution for 10 min. Measure the absorbance of the organic phase at 395 nm for the determination of manganese.

RESULTS

The method described was checked by adding known amounts of elements to be determined to solutions of silver chloride in potassium iodide, which had been previously extracted with dithizone and oxine. In the procedure given only the elements which are commonly present in detectable amounts in high-purity silver halides have been considered. The results are summarized in Tables I and II. The analyses were carried out on 1-g samples of silver chloride. From a blank carried through all the steps of the separation procedure, the contribution to the absorbances of impurities in the reagents were evaluated and suitable corrections made.

CONCLUSIONS

In the technique described, the relative lower limits of detection are of the

TABLE II

RESULTS OF SPECTROPHOTOMETRIC DETERMINATION OF Fe, Al AND Mn

Fe			*Al*			*Mn*		
Added (μg)	*Found (μg)*	*Error (%)*	*Added (μg)*	*Found (μg)*	*Error (%)*	*Added (μg)*	*Found (μg)*	*Error (%)*
10.00	10.20	+2	10.00	9.80	−2	10.00	10.30	+3
10.00	10.10	+1	10.00	10.90	+9	10.00	8.70	−13
5.00	5.50	+10	5.00	5.20	+4	5.00	6.00	+20
1.00	1.00	0	1.00	1.05	+5	2.00	1.80	−10
1.00	1.01	+1	1.00	0.98	−2	1.00	0.92	−8
Av. err. ± 2.8			Av. err. ± 4.4			Av. err. ± 10.8		

order of 1 p.p.m. with an accuracy better than 10%. Naturally the relative limits of detection can be further increased by taking larger amounts of sample.

The proposed procedure of dissolving the samples in potassium iodide followed by successive extraction with dithizone and oxine, can also be used for the establishment of fast and very sensitive analytical methods utilizing atomic absorption spectrometry.

We wish to thank Professor G. SEMERANO, Director of the "G. Ciamician" Institute, for his active interest in this work and for useful discussions.

SUMMARY

A method for the enrichment and determination of elements present in trace amounts in high-purity silver halides is described. Concentrated solutions of potassium iodide are used as solvents for the samples. The elements determined are concentrated by solvent extraction: zinc, cadmium, lead, copper, cobalt and nickel as dithizonates, and iron, aluminium and manganese as oxinates. The complexes formed are then determined spectrophotometrically. The relative lower limits of detection are of the order of 1 p.p.m. with an accuracy better than 10%.

RÉSUMÉ

On décrit une méthode d'enrichissement et de dosage d'éléments à l'état de traces, dans des halogénures d'argent de haute pureté. Les échantillons sont solubilisés dans des solutions concentrées d'iodure de potassium. Les éléments à doser sont concentrés par extraction dans un solvant: zinc, cadmium, plomb, cuivre, cobalt et nickel sous forme de dithizonates; fer, aluminium et manganèse comme oxinates. Les complexes formés sont dosés par spectrophotométrie. Les limites de détection inférieures sont de l'ordre de 1 p.p.m., avec une exactitude supérieure à 10%.

ZUSAMMENFASSUNG

Ein Verfahren zur Anreicherung und Bestimmung von Spurenelementen in Silberhalogeniden hohen Reinheitsgrades wird beschrieben. Die Proben werden in konzentrierte Kaliumjodid-Lösungen gelöst und die zu bestimmenden Elemente durch Extraktion angereichert: Zink, Cadmium, Blei, Kupfer, Kobalt, Nickel als Dithizonate; Eisen, Aluminium, Mangan als Oxinate. Sie werden dann spektrophotometrisch bestimmt. Die Bestimmungsgrenzen liegen bei 1 p.p.m. mit einer Genauigkeit besser als 10%.

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BIPOTENTIOMETRY IN ORGANIC REDOX SYSTEMS

PART I. OXIDATION OF AROMATIC COMPOUNDS IN TRIFLUOROACETIC ACID

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Intense colors have been observed in spot-test reactions of polynuclear aromatic hydrocarbons oxidized with lead(IV) acetate in trifluoroacetic acid (TFA)[1]. By analogy to electrochemical oxidations, it was postulated that these colors involved radical cation species[2,3]. If these species are sufficiently stable, then they might form electrochemically reversible redox couples that can be detected by means of bipotentiometry. This technique, which has been applied almost exclusively to inorganic systems[4], makes use of a pair of platinum electrodes polarized with several microamperes of direct current. If an electrochemically irreversible substrate is reacted with a reversible titrant, then the potential between the two electrodes (one polarized, the other depolarized) remains high during the titration but drops sharply in the vicinity of the end-point when both electrodes are depolarized. An electrochemically reversible redox couple is one that can depolarize electrodes, because the relatively rapid rate of electron transfer maintains equilibrium at the electrodes.

Organic bipotentiometry, especially that for aromatic compounds, can differ from the above in that during the titration of irreversible substrate with irreversible oxidant, intermediate reversible redox species of short but appreciable half-lives are formed. This is especially true in a solvent medium of low basicity such as TFA.

EXPERIMENTAL

Reagents

Lead(IV) acetate was prepared from red lead(IV) oxide[5], while cobalt(III) acetate was readily obtained from cobalt(II) acetate and lead(IV) acetate[6] in TFA. The solution of the lead(IV) salt, 0.1 *N* in TFA, lost about 1% titer per day, and the solid material slowly decomposed on standing, so that frequent standardization was required.

The oxidants were standardized with bromohydroquinone (K & K Labs), recrystallized from water and standardized with dichromate in aqueous solution using diphenylaminesulfonate indicator. The standardization of oxidant, 0.1 *N* in TFA was done potentiometrically in a 1:1 (v/v) mixture of TFA (Eastman) and dichloromethane containing 0.01 *M* silver trifluoroacetate.

Aromatic compounds investigated were commercially available samples in the purest grades available. Stock solutions $5.0 \cdot 10^{-3}$ *M* in dichloromethane were prepared fresh every other day.

Equipment

Potential measurements were made with a Beckman expanded-scale pH meter connected to a Sargent model MR recorder. Electrodes were made with 1-mm diameter silver or platinum wire. Direct current was provided from a step-down transformer with a selenium rectifier (2.1 V) and a series resistance (0.3 MΩ).

Procedure

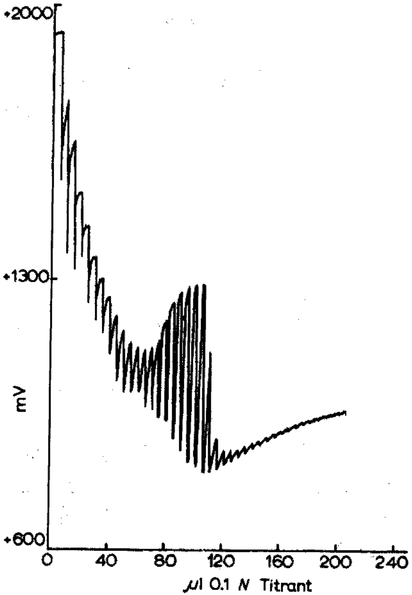
The bipotentiometric titration was performed in a 5-ml beaker with a microbar stirrer and a two-hole aluminum foil cap to minimize evaporation of the solvent mixture which was 1 ml of TFA, 0.50 ml of stock solution, and 0.5 ml of dichloromethane. The substrate concentration was $1.25 \cdot 10^{-3} M$. Air was not excluded from the system, which was run at ambient temperature. The electrodes were 5-cm lengths of platinum wire mounted in a polyethylene cap, spaced 1 mm apart and polarized with 7 μA of applied direct current. Oxidant, 0.10 N in TFA, was introduced with a 2-ml Gilmont microburet in increments of 5 μl, at 15-sec intervals. The chart speed was 0.5 in min^{-1}.

For reasons of economy, the TFA was recovered from the expended solvent mixture by a simple fractionation.

RESULTS AND DISCUSSION

Preliminary experiments

Initial additions of oxidant to an aromatic substrate resulted in an almost instantaneous change in potential (ΔV) between the polarized electrodes, followed



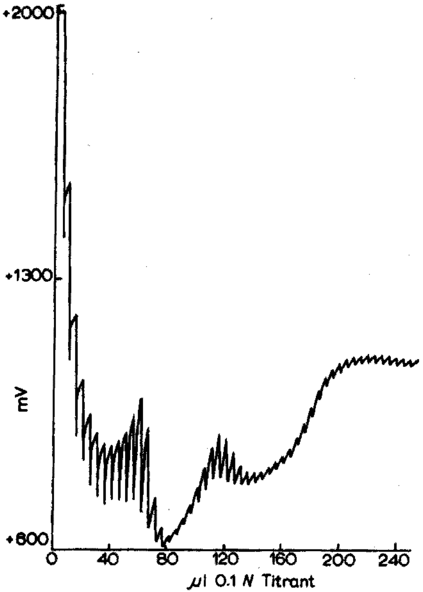


Fig. 1. Bipotentiometric titration of 1-phenylnaphthalene with lead(IV) acetate, a type I BM curve.

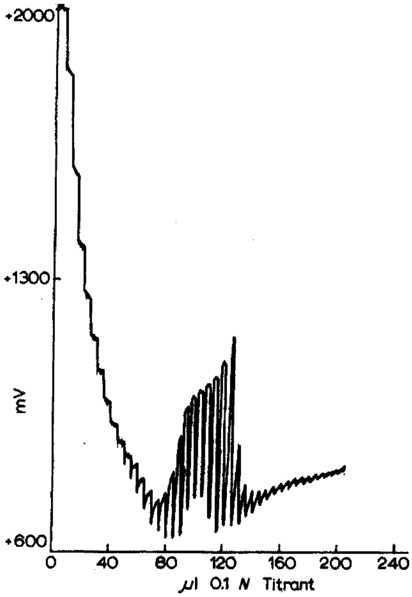
Fig. 2. Bipotentiometric titration of phenanthrene with cobalt(III) acetate, a type III S curve.

by "decay" of potential to a new value. This increment was usually of the "saw-tooth" type. These increments went to make up titration curves that had one or more potential minima regions before the end-point (see Figs. 1–4).

The shape and magnitude of the increments as well as the shape of the titration curve for a given substrate were quite sensitive to a variety of parameters, some of which are considered in detail in this paper. The four major parameters were: co-solvent, oxidant, applied current (more specifically current density) and delay time between additions. Because of the low solubility of many aromatics in TFA, a relatively inert co solvent was required. Dichloromethane was found to be satisfactory and had the added advantage that TFA could be readily recovered by fractionation from mixtures with it. Other polyhalogen alkanes could be substituted with noticeable change in increment shape. Benzene was too reactive to be a suitable solvent.

It was noted that lead(IV) and cobalt(III) oxidants gave only small potential drops in blank titrations, indicating a low degree of electrochemical reversibility and allowing successful titrations to be made. With the various substrates, these two reagents were found to differ in two important ways. With almost all of the compounds tested, cobalt(III), a 1-equivalent oxidant, gave larger ΔV values than lead(IV), a 2-equivalent oxidant. This effect was magnified in very dilute solution (substrate $1.25 \cdot 10^{-4}\,M$). Also, markedly different type curves were often given by both oxidants with a given substrate. Manganese(III) behaved similarly to cobalt(III), while thallium(III) acetate reacted only with the most reactive substrates.

The current applied was 7 μA (2.1 V/0.3 MΩ), but because of high solution resistance, the actual value as measured with a microammeter was only about half.



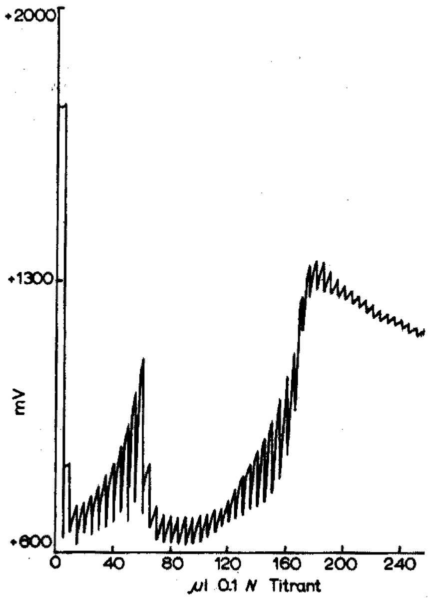


Fig. 3. Bipotentiometric titration of phenanthrene with lead(IV) acetate, a type I AS curve.

Fig. 4. Bipotentiometric titration of 1,2,3,4-dibenzanthracene with cobalt(III) acetate, a type II AS curve.

TABLE I

CLASSIFICATION OF BIPOTENTIOMETRIC CURVES FOR VARIOUS AROMATIC COMPOUNDS

Class		*Compound*	*Classification*	
			Lead(IV) acetate	*Cobalt(III) acetate*
I.	Polynuclear aromatic hydrocarbons 1. Linear	Naphthalene	I AM	II BS
		Anthracene	II BS	I BS[a]
		Naphthacene	I BM	III M
	2. Angular anthracene	1,2-Benzanthracene	II AS	II AS
		1,2,3,4-Dibenzanthracene	I BS	II AS
		1,2,5,6-Dibenzanthracene	I BS	II AS
	3. Angular phenanthrene	Phenanthrene	I AS	III S
		Chrysene	I BM	IV S
		3, 4-Benzophenanthrene	II AS	II AS
	4. Condensed ring	Triphenylene	I BS	I BS
		Pyrene	I BS	I BS
		1,2-Benzopyrene	I BS	I BS
		3,4-Benzopyrene	III M	III M
		Perylene	I BM	I BM
	5. Polyaryl	Biphenyl	I AS	I BS[a]
		p-Terphenyl	I BS[a]	I BS[a]
		1,1-Binaphthyl	I BS	II AS[a]
		2,2-Binaphthyl	II BS	II AS
		1-Phenylnaphthalene	I BM[a]	III M
		2-Phenylnaphthalene	I AM	I BS
		9,10-Diphenylanthracene	II BM	II BM
	6. Non-alternant	Fluorene	I BS	I BM[a]
		Fluoranthene	I BM[a]	I BM[a]
		Acenaphthene	I BS	I BM[a]
		Acenaphthylene	I AS	I BM
		Azulene	I AS	I BM
	7. Polyene	*cis*-Stilbene	I AM	II AS[a]
		trans-Stilbene	I AS	II AM[a]
	8. Miscellaneous	Biphenylene	I BM[a]	I BM[a]
II.	Substituted benzenes 1. Ethers	Anisole	I BS	I BS
		2-Chloroanisole	II AS	I BS
		3-Chloroanisole	Ill-defined	I BS
		4-Chloroanisole	II AS[a]	I BS[a]
	2. Phenols	Phenol	I AM	I BS
		2-Chlorophenol	I AM	I AM
		3-Chlorophenol	I AM	I AS
		4-Chlorophenol	I AM	II BM
	3. Amines	Aniline	Ill-defined	Ill-defined
		2-Chloroaniline	I AS	I BM
		3-Chloroaniline	Ill-defined	Ill-defined
		4-Chloroaniline	Ill-defined	Ill-defined
		Diphenylamine	I BM	I BM
III.	π-Excessive heteroaromatics	Thiophene	I BM	Ill-defined
		Carbazole	I BM	I BM
		Phenothiazine	II AM	II AM
		Phenothioxin	I BM	II BM
		Phenoxazine	II AM	II AM

[a] Relatively large ΔV increments.

This value was just sufficient, under experimental conditions with the majority of compounds (anisoles and phenols required 3.5 μA), to bring the pH meter needle on scale with the asymmetry control. Consequently, the scale included a 1400 mV span between about +600 and +2000 mV. Smaller applied currents changed the ΔV values somewhat but not the shape of the titration curves. With the same current (7 μA and a larger ballast[4] load, 49 V/7 MΩ) less well-defined curves were obtained than with the above. A 15-sec interval between titration additions and a chart speed of 0.5 in min^{-1} were found to be optimal for the qualitative comparison of the compounds studied; but for quantitative studies, other values of current density, ballast load and interval between additions might be more suitable.

Other parameters that were found to affect the shape of increments included: (*a*) presence of added bases[7], such as water (1%) in the solvent mixture, that combined with reactive intermediates; and (*b*) rapidity of reagent addition and stirring, which influenced ΔV values.

Finally, it should be mentioned that inclusion of a third (reference) electrode[4], consisting of a silver wire dipping into the titration mixture containing 0.01 *M* silver trifluoroacetate, gave different curves when reference and anode or reference and cathode potential difference was measured.

Classification of titration curves

Well-defined titration curves were considered to be those with an end-point break and, preferably, one or more potential minima. Certain compounds (*e.g.* aniline, and the π-deficient heteroaromatics—acridine, phenazine, and phenanthridine) gave "saw-tooth" increments but poorly defined curves which lacked both potential minima and end-points.

Classification was based upon titration of fresh stock solutions of assumed relatively pure compounds. Solutions used over more than 1–2 days often gave significantly different results.

The curves for representative compounds of different classes of aromatic compounds with lead(IV) and cobalt(III) are classified in Table I. The curves, representative examples of which are given in Figs. 1–4, are classified on the following basis.

1. Whether the curve had I, II, III, etc. potential minima before the end-point. Potential minima were "troughs" in the titration curves formed by drawing a line connecting increments at their upper tips. With lead(IV) titrant almost all substrates gave a curve having a slight rise after the end-point, which for the purpose of classification was not considered a true potential minimum.

2. Whether the minimum potential was above (A) or below (B), that for the end-point for type I curves; or whether the first minimum was above (A) or below (B), that for the second for type II curves. Type III and IV curves were sufficiently rare that no further subdivision of this type was made.

3. Whether the curve was made up exclusively of "saw-tooth" increments (S) or included a significant number of mixed type increments (M). "Saw-tooth" increments were those where the internal angle of the "saw-tooth" was less than 90°. Other increments were often encountered with angles between 90° and *ca.* 135°. Occasionally inverse increments resulted.

This classification (Table I) leads to the observation that for condensed polynuclear aromatic hydrocarbons and four out of five π-excessive heteroaromatics studied, both oxidants gave curves of the same class type.

Quantitative relationships

Quantitative relationships among the various curves were not studied in any detail in this investigation but would include magnitude of potential drop (ΔV), decay rates of reversible redox couples, and stoichiometry at potential minima and end-points. For these parameters, it would be necessary to control fairly closely such factors as temperature and speed of addition. However, it is noteworthy that under the experimental conditions used, a number of biaryls and *p*-substituted anisoles gave relatively large ΔV values. Decay rates varied considerably (*ca.* 0.1–1 min half-lives), not only from compound to compound but even in various positions of a given titration curve. In many instances, increments in the ascending portion of a curve decayed more rapidly than those in the descending portion. Potential minima often did not correspond to integral oxidation equivalents, possibly indicating concurrent rather than sequential oxidation. For many of the curves, end-points were relatively gradual and non-stoichiometric, which is probably partly due to the non-equilibrium conditions employed. Further, reaction of substrate with oxygen in the air was observed with reactive hydrocarbons such as perylene or rubrene.

Almost all of the compounds examined gave vivid color transitions during the titrations. In a number of instances these changes corresponded to sharp changes in the bipotentiometric curves.

Oxidation mechanisms

For bipotentiometry and biamperometry, electrochemically reversible redox couples are essential. In organic bipotentiometry in a relatively inert solvent, electrochemical reversibility and, consequently, the shape and size of the titration increments will depend essentially upon two equations:

$$\mathrm{Ar} \rightleftharpoons \mathrm{Ar}.^{+} + e^{-} \tag{1}$$

$$2\mathrm{Ar}.^{+} \rightarrow \mathrm{Ar{-}Ar} + 2\mathrm{H}^{+} \tag{2}$$

Oxidations involving loss of an electron (eqn. (1)) are capable of being electrochemically reversible, while loss by substrate of a hydrogen atom (except OH or NH), or a hydride ion generally renders them irreversible. Further, if the rate of dimerization of the radical cation is rapid (relatively unstable radical cation) compared to the rate of initial electron transfer, then reaction (1) will be rendered irreversible.

Electrochemical and/or chemical evidence indicates that for polynuclear aromatic hydrocarbons[8], heteroaromatics[8], and aromatic ethers[9], initial oxidation gives the radical cations $\mathrm{Ar}.^{+}$ and $\mathrm{Ar{-}}\overset{\dot{+}}{\mathrm{O}}\mathrm{{-}R}$, respectively, while phenols[8,10] give $\mathrm{Ar{-}}\overset{+}{\mathrm{O}}$. Amines oxidized electrochemically give $\mathrm{Ar{-}}\dot{\mathrm{N}}\overset{+}{\mathrm{H}}_2$[8], and chemical oxidation produces $\mathrm{Ar{-}}\dot{\mathrm{N}}\mathrm{H}$[11]. These radical cations differ widely in instability with respect to dimerization. Relative stabilities can be estimated by Highest Filled Molecular Orbital calculations[8]. Radical cations from π-deficient heteroaromatics and anilines are particularly unstable[8]. In the current investigation, it was found that all of the examined polynuclear aromatic hydrocarbons, phenols (with cobalt(III) only), and aromatic ethers gave well-defined titration curves, indicating that even the most unstable of these radical cations or cations were sufficiently stable to cause depolarization, while several anilines tested gave poorly defined curves (the *o*-chloro compound being an exception).

One may speculate on the relative size of the potential drops[12]. Since the titration solutions were stirred, mass transfer rates were relatively rapid and, as was observed, radical cation half-lives were of comparable duration to measurement times. Consequently, the electron transfer rate apparently controls the magnitude of ΔV. Since very little information is available on organic electron transfer coefficients, meaningful discussion is not yet possible.

While the first step in the above oxidations is relatively straightforward, subsequent loss of electrons is more complicated. Stoichiometry for organic bipotentiometry indicated that two or more equivalents of oxidant were often involved. Possible reactions for polynucleai aromatic hydrocarbons include oxidation of dimer to radical cation $Ar\text{–}Ar.^{+}$ or to $Ar\text{–}Ar^{2+}$ or oxidation of radical cation to cation Ar^{2+}[13], reactions which may be concurrent or sequential. Further information could be obtained by coupling bipotentiometry with such techniques as spectrophotometry, electron spin resonance, or cyclic sweep voltammetry.

SUMMARY

Bipotentiometric titrations of various polynuclear aromatic hydrocarbons, benzenes substituted with electron-donating groups, and π-excessive heteroaromatics in trifluoroacetic acid–dichloromethane with lead(IV) or cobalt(III) acetate solution resulted in novel titration curves. Optimum qualitative results were obtained with a 15-sec delay between additions of titrant. Each reagent increment usually resulted in the formation of a potential "saw-tooth", indicating formation and decay of reversible redox couples; the final titration curves had one or more potential minima regions before the end-point. Because of considerable differences in number, reversibility and stability of oxidation intermediates, no two aromatics of those tested gave identical curves. However, sufficient similarities existed to permit a system of curve classification and some degree of correlation. The technique is at present essentially a qualitative one. In almost all instances the titration curve for a given aromatic compound is characteristic, somewhat in the manner of a spectrophotometric curve.

RÉSUMÉ

Une étude est effectuée sur les titrages bipotentiométriques de divers hydrocarbures aromatiques polynucléaires, de benzènes substitués et de composés hétéroaromatiques, dans le milieu acide trifluoroacétique–dichlorométhane, à l'aide de solutions d'acétate de plomb(IV) et de cobalt(III). Cette technique est actuellement essentiellement qualitative. Dans presque chaque cas, la courbe de titrage est caractéristique pour un composé aromatique donné, une peu à la manière d'une courbe spectrophotométrique.

ZUSAMMENFASSUNG

Verschiedene mehrkernige aromatische Kohlenwasserstoffe, mit Elektronen-

donor-Gruppen substituierte Benzole und π-elektronenreiche Heteroaromaten wurden in Trifluoressigsäure–Dichlormethan mit Blei(IV)- oder Kobalt(III)-acetat-Lösung bipotentiometrisch titriert. Es ergaben sich neuartige Titrationskurven. Optimale qualitative Ergebnisse wurden erhalten, wenn das Titrationsmittel in Abständen von 15 sec zugegeben wurde. Jede Reagenzzugabe führte normalerweise zu einer sägezahnförmigen Potentialveränderung, die Bildung und Zerfall reversibler Redoxpaare anzeigte. Die schliesslich erhaltenen Titrationskurven hatten vor dem Endpunkt einen oder mehrere Bereiche mit Potentialminima. Wegen der erheblichen Unterschiede in der Anzahl, Reversibilität und Stabilität der Oxidationszwischenstufen waren unter den untersuchten Aromaten keine mit identischen Titrationskurven. Dagegen waren genügend Ähnlichkeiten vorhanden, die ein System der Kurvenklassifizierung erlaubten und in gewissem Grade Beziehungen erkennen liessen. Das Verfahren ist gegenwärtig im wesentlichen für qualitative Zwecke anwendbar. Bei fast allen Beispielen ist die Titrationskurve für eine gegebene aromatische Verbindung charakteristisch, etwa in der Art einer spektrophotometrischen Kurve.

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Short Communications

A computer method for the determination of the formation constants of complex ions from spectrophotometric data

RAMETTE[1] has recently described a computer method for the calculation of formation constants for complexes of the ML or 1:1 type. CHRISTIAN[2] has discussed a rapid graphical method for determination of the formation constants for the addition of a single ligand species to a central metal ion. The present communication discusses still another method for determining the constant for a 1:1 complex. In addition, equations are developed for calculating the overall constants for complexes of the 1:2 and 1:3 types.

Consider the simple case of the reaction of one metal ion with one ligand, $M+L=ML$. In general, a wavelength can be chosen where ML absorbs light and M and L are transparent. Then at one point the absorbance can be written as $A_1=\varepsilon b\,[ML]$ and at a second point as $A_2=\varepsilon b\,[ML]'$. If R is defined as the ratio of A_2 to A_1, then the relation between the concentrations is $[ML]'=R[ML]$, at one specified wavelength, since the molar absorptivity, ε, is then a constant, and the light path length, b, is the same for all measurements.

The equation for the formation constant can be written as either

$$K=\frac{[ML]}{(M-[ML])\,(L-[ML])} \quad \text{or} \quad K=\frac{[ML]'}{(M'-[ML]')\,(L'-[ML]')}$$

where M and L are the total analytical concentrations of the metal ion and ligand, respectively, at one point, and M′ and L′ refer to the total analytical concentrations at a second point.

Substituting $R[ML]=[ML]'$ into the second equation gives

$$K=\frac{R[ML]}{(M'-R[ML])\,(L'-R[ML])}$$

Equating these equations for the formation constant gives the resultant quadratic equation

$$(1-R)\,[ML]^2+(M'+L'-M-L)\,[ML]+M\,(L)-(M')(L')/R=0$$

which can readily be solved for [ML], and subsequently for the formation constant and the molar absorptivity. This process can be done with a computer with a great number of points and at several wavelengths to give statistical validity to the results.

For the 1:2 complex, the overall reaction is $M+2L=ML_2$. If a wavelength is chosen where only ML_2 absorbs light, then $A_1=\varepsilon b\,[ML_2]$ and $A_2=\varepsilon b\,[ML_2]'$. At a fixed wavelength and with matched cells, $[ML_2]'=R[ML_2]$. If the concentration of the intermediate 1:1 complex is negligible, the formation constant equation can be written as either

$$K=\frac{[ML_2]}{(M-[ML_2])\,(L-2[ML_2])^2} \quad \text{or} \quad K=\frac{[ML_2]'}{(M'-[ML_2]')\,(L'-2[ML_2]')^2}$$

Substitution of the ratio equation gives

$$K = \frac{R[\mathrm{ML_2}]}{(\mathrm{M'}-R[\mathrm{ML_2}])\,(\mathrm{L'}-2R[\mathrm{ML_2}])^2}$$

The following cubic equation results when these are equated.

$$(4-4R^2)\,[\mathrm{ML_2}]^3+(4R(\mathrm{M'})+4R(\mathrm{L'})-4\mathrm{M}-4\mathrm{L})\,[\mathrm{ML_2}]^2+(4\mathrm{M}(\mathrm{L})-4(\mathrm{M'})\,(\mathrm{L'})$$
$$-(\mathrm{L'})^2+\mathrm{L}^2)\,[\mathrm{ML_2}]+(\mathrm{M'})\,(\mathrm{L'})^2/R-\mathrm{M}(\mathrm{L})^2=0.$$

Solutions are volumetrically mixed so that the total analytical concentrations are accurately known. Absorbances are determined and ratio values are substituted into the cubic equation. The cubic equation is readily solved at a great number of points with a computer program, using the NEWTON–RAPHSON iteration method[3]. Previously written sub-routines from the computer library for solving cubic, quartic, and higher order equations may be used. The $[\mathrm{ML_2}]$ can be determined for a variety of mixtures of total analytical concentrations of metal and ligand, and can be substituted into the formation constant equation to permit calculation of K.

For the 1:3 complex, the overall reaction is $\mathrm{M}+3\mathrm{L}=\mathrm{ML_3}$. At a wavelength where only $\mathrm{ML_3}$ absorbs light, the absorbance at one point is $A_1=\varepsilon b\,[\mathrm{ML_3}]$ and at a second point is $A_2=\varepsilon b\,[\mathrm{ML_3}]$. If R is the ratio of A_2 to A_1 and a specified wavelength is chosen and matched cells are used, then $[\mathrm{ML_3}]'=R[\mathrm{ML_3}]$. If the concentrations of the 1:1 and 1:2 complex are negligible, the formation constant equation may be written as

$$K = \frac{[\mathrm{ML_3}]}{(\mathrm{M}-[\mathrm{ML_3}])\,(\mathrm{L}-3[\mathrm{ML_3}])^3} \quad \text{or} \quad K = \frac{R[\mathrm{ML_3}]}{(\mathrm{M'}-R[\mathrm{ML_3}])\,(\mathrm{L'}-3R[\mathrm{ML_3}])^3}$$

When these are equated, the following quartic equation results.

$$(27-27R^3)\,[\mathrm{ML_3}]^4+(27R^2(\mathrm{M'})+27R^2(\mathrm{L'})-27\mathrm{M}-27\mathrm{L})\,[\mathrm{ML_3}]^3$$
$$+(27(\mathrm{M})\,(\mathrm{L})-27R\,(\mathrm{M'})\,(\mathrm{L'})-9R\,(\mathrm{L'})^2+9\mathrm{L}^2)\,[\mathrm{ML_3}]^2$$
$$+(9(\mathrm{M'})\,(\mathrm{L'})^2+(\mathrm{L'})^3-9\mathrm{M}\,(\mathrm{L})^2-\mathrm{L}^3)[\mathrm{ML_3}]+(\mathrm{M})\,(\mathrm{L})^3-(\mathrm{M'})\,(\mathrm{L'})^3/R=0$$

This equation is readily solved for $[\mathrm{ML_3}]$ by means of a library computer program. Upon solving the equation for a great variety of mixtures of total analytical concentrations of metal and ligand, an average value for K can be determined.

By similar considerations, equations for higher complexes, ML_n, may be derived.

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A critical analysis of the method of successive dilutions in photometry

The effect of matrix interference on analytical procedures has been discussed recently[1-3]. The various available possibilities of overcoming such an interference have been discussed briefly[1] and a new method has been suggested, the method of Changing Parameter. The possibility of the use of dilution as the changing parameter has been appraised[1,2], and the possibility of the use of other parameters, *e.g.* wavelength, has been discussed[3]. The need for a new and complicated analytical method is not evident, unless the available methods are found to be inapplicable. It has been shown[1] that the method of Standard Addition assumes implicitly the absence of matrix interference, and thus is not suitable in the presence of such an interference. However, the alternative method of Successive Dilutions[4] (or simply "Dilution Method"[5]) is supposed to circumvent the matrix interference. It has been stated[1] that the method of Successive Dilutions appeared to be unsuitable for the determination of substances in the presence of strong interference. In the following analysis, an attempt is made to show rigorously that the very existence of matrix interference invalidates the use of the method of Successive Dilutions.

The main assumptions of the method of Successive Dilutions, as employed for example by GILBERT[6], are that (*a*) the intercept of the plot of the calculated concentration against the relative concentration at infinite dilution (*e.g.* when the relative concentration is 0) yields the true concentration; (*b*) the intercept can be obtained by linear extrapolation of the above plot.

The validity of these two assumptions will now be examined.

The evaluation of the true concentration

It has been shown (eqn. (12) in ref. 1) that the calculated concentration (C_{calc}) equals the true concentration (C_{true}) only when the following relation obtains:

$$R_M(V_s)/k^\infty = [R_M(V_s) - R_I(V_s)]/k(V_s) \tag{1}$$

where R_M is the reading of the photometer after the addition of V_s cm^3 of pure solvent to the original sample of V_x cm^3 of the unknown solution; R_I is the contribution of the interference to the reading R_M (under the same conditions); and k is defined as follows:

$$k(V_s) = (V_x + V_s)\left(\frac{\partial R_M}{\partial m}\right)_{V_x,V_s} \tag{2}$$

where m is the true quantity of the substance measured (in mols), and k^∞ is the limiting value of k when V_s tends to infinity, *i.e.* in pure solvent.

Equation (1), though rigorous, does not allow one to calculate directly the relevant R_M, R_I and k at which the equality holds. To do this it is necessary to assume explicit functions for the above three variables. If hyperbolic functions are assumed, eqn. (1) can be expressed as

$$\frac{(1-k^0/k^\infty)A_k}{A_k+V_s} = \frac{R_I^0 A_I(A_M+V_s)}{(A_I+V_s)R_M^0 A_M} \tag{3}$$

where A_M, A_I and A_k are constants, while R_M^0, R_I^0 and k^0 are the values of R_M, R_I and k, respectively, when $V_s = 0$ (*i.e.* in the undiluted sample).

For experiments conducted on an 8-cm^3 sample of calcium solution ($8.00 \cdot 10^{-5}$ *M*), in the presence of strong interference^1, the best fit for 86 experimental values of R_M was $R_M{}^0 = 52.2$ divisions and $A_M = 11.1$ cm^3 (r.m.s. deviation: 1.0 divisions). For 76 experimental values of R_I the best parameters obtained were $R_I{}^0 = 13.4$ divisions and $A_I = 12.3$ cm^3 (r.m.s. deviation: 1.2 divisions). For 39 experimental values of k the best parameters obtained were $k^0 = 4.94 \cdot 10^5$ divisions mole^{-1}, $k^\infty = 6.52 \cdot 10^5$ divisions mole^{-1} and $A_k = 9.19$ cm^3 (r.m.s. deviation: $0.13 \cdot 10^5$ divisions mole^{-1}). On introducing these values into eqn. (3), V_s can be obtained. As eqn. (3) is quadratic in V_s,two solutions are possible: either -0.45 cm^3 or -12 cm^3. As V_x in our experiment was only 8 cm^3, the second solution is physically impossible, and the relative concentration satisfying eqn. (1) is seen to be 1.07. Such a value corresponds well with the experimental results presented in Fig. 1.

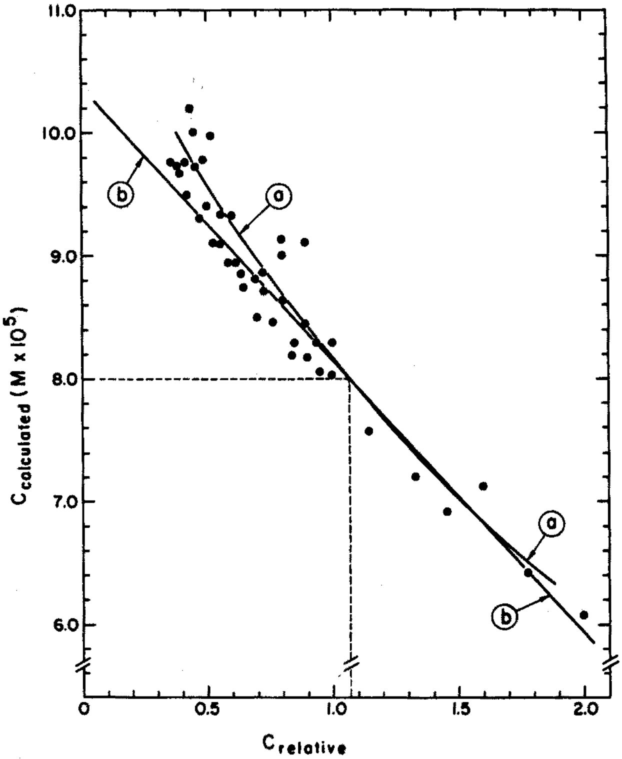

Fig. 1. C_{calc} as function of C_{rel}: (●) experimental results, (a) calculated by integration of eqn. (5), (b) calculated by integration of eqn. (6).

The experimental points appearing in Fig. 1 require some comment. The precision of each measurement was within ±1%. However, the error in C_{calc} is the error of measurement divided by the relative concentration; thus at $C_{rel} < 0.5$ the uncertainty amounts already to more than ±2%. Furthermore, the individual points appearing in Fig. 1 were not obtained in a single series of measurements, but in many separate experiments extending over a number of months, while for each experiment a new set of standards and a new set of samples were prepared. Thus despite the precision of each individual experiment there is a scattering of results within ±4%.

The use of hyperbolic functions for R_M, R_I and k can be disputed at least on two grounds: first, it has been shown[2] that when k is not constant, the R values cannot possibly satisfy a hyperbolic equation; next, it has been shown[1] that if both R_M and R_I are expressed as hyperbolic functions, k cannot possibly be hyperbolic. It should be stressed, therefore, that the hyperbolic forms are used merely as convenient approximations. As it happens, the approximations are so good that they fit the results within the experimental error, as can be seen from the r.m.s. deviations quoted above. One alternative approximation is the use of exponential functions for R_M, R_I and k [of the form $R=R^0\exp(-BV_s)$]. Use of such functions in eqn. (1) yields, instead of eqn. (3), the following result:

$$1-(k^0/k^\infty)=(R_I^0/R_M^0)\exp\left[(B_k+B_M-B_I)V_s\right] \tag{4}$$

The search for the best exponential parameters to fit the experimental values of $R_M(V_s)$, $R_I(V_s)$ and $k(V_s)$ yields the following: $R_M^0=51.7$ div, $B_M=0.054$ cm^{-3}; $R_I^0=14.8$ div, $B_I=0.072$ cm^{-3}; $k^\infty=6.14\cdot10^8$ div cm^3 mole^{-1}, $k^0=4.86\cdot10^8$ div cm^3 mole^{-1}, $B_k=0.14$ cm^{-3}. The r.m.s. deviations for the exponential functions are about twice those obtained for the hyperbolic functions. When the exponential parameters are introduced into eqn. (4), the value of $V_s=-2.22$ is obtained, corresponding to $C_{rel}=1.4$. As can be seen in Fig. 1, the experimental points at $C_{rel}=1.4$ correspond to $C_{calc}\simeq 7\cdot10^{-5}$ *M*, *i.e.* some 12% lower than the true concentration.

It has been shown[2] that the exponential functions are poorer approximations to the true R_M, R_I and k, as can be seen also from the r.m.s. deviations cited above, so that the less accurate value of C_{true} obtained on their use can be understood. It is still of interest that even a poor approximation can give a quantitative insight into the relation between C_{calc} and C_{true}. The conclusion of the above discussion is that the intercept of the curve C_{calc} *vs.* C_{rel} at $C_{rel}=0$ will not yield the true concentration, unless $R_I=0$.

The slope of C_{calc} against C_{rel}

A rigorous expression for dC_{calc}/dC_{rel} has been developed [eqn. (13) in ref. 1]:

$$dC_{calc}/dC_{rel}=-a^{-1}(b+c+d) \tag{5}$$

where $a\equiv V_x^2k^\infty$, $b\equiv(V_x+V_s)^2R_I$, $c\equiv(V_x+V_s)^2C_{true}V_x(dk/dV_s)$, and $d\equiv(V_x+V_s)^3(dR_I/dV_s)$.

The assumption in the method of Successive Dilutions is that this slope is constant. The slope calculated with eqn. (5) is plotted against C_{rel} in Fig. 2.

As eqn. (5) is very sensitive to the values of R_I and dR_I/dV_s, and as these values are small for large V_s, they were calculated from the hyperbolic approximation of R_I, using R_I^0 and A_I as given above. The values of dk/dV_s were introduced from graphical differentiation of the experimental k's against V_s.

It can be seen that dC_{calc}/dC_{rel} is not constant.

Integration of eqn. (5) should allow one to obtain C_{calc} for any C_{rel}, when a reference point is chosen. Assuming that at $C_{rel}=1.07$, the $C_{calc}=C_{true}=8.00\cdot10^{-5}$ *M* (as shown above), a plot of C_{calc} against C_{rel} was obtained through graphical integration of Fig. 2. This plot is presented as curve a in Fig. 1. It can be seen that the curve fits well the experimental results.

The spurious linearity of the C_{calc} *vs.* C_{rel} curve was explained[1] through the use of the hyperbolic approximations. It was suggested that such an apparently constant slope represents:

$$\frac{dC_{\text{calc}}}{dC_{\text{rel}}} \simeq -\frac{C_{\text{true}}A_{\text{K}}(k^{\infty}-k^{0})}{k^{\infty}V_{x}} \tag{6}$$

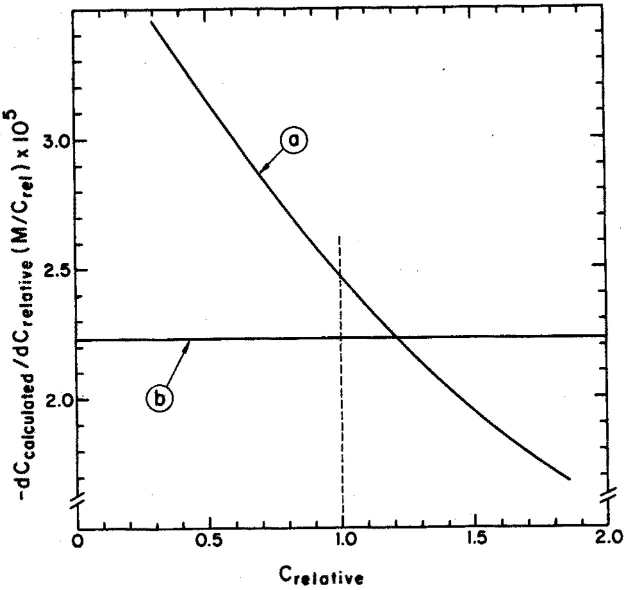

Fig. 2. The slope $dC_{\text{calc}}/dC_{\text{rel}}$ as function of C_{rel}: (a) calculated using eqn. (5), (b) calculated using eqn. (6).

Introducing for the constants of eqn. (6) the values cited above, one obtains $dC_{\text{calc}}/dC_{\text{rel}} = -2.22 \cdot 10^{-5}\ M/C_{\text{rel}}$. This constant value is shown as line b in Fig. 2, and the integral is shown as line b in Fig. 1. It can be seen that such a constant slope approximates the experimental results, and supports the interpretation of the slope in terms of eqn. (6). When only a few experimental points are available, the assumption of a constant slope can be understood.

In conclusion, it appears that the method of Successive Dilutions is inapplicable for analysis in the presence of matrix interference. In this respect, it is similar to the method of Standard Addition, which is also unsatisfactory under such conditions.

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Specific cation-exchange separation of nickel*

Common extractants, as used in the liquid–liquid extraction of metal ions, have recently been investigated with respect to their applicability to ion-exchange separations[1–5]. These studies showed that on the strongly acidic cation-exchange resin Dowex 50, several unusual separations of metal ions are possible in organic solvent media containing extractants such as 2-thenoyltrifluoroacetone (TTA)[1], trioctylphosphine oxide (TOPO)[2–4] and diphenyldithiocarbazone (dithizone)[5]. For instance, the alkali metals can be selectively separated from practically all other elements on this resin with TTA dissolved in pyridine as eluant[1]. With TOPO dissolved in tetrahydrofuran or methanol in the presence of hydrochloric acid or nitric acid, very effective cation-exchange separations of scandium from the rare earths[2], and of hafnium plus zirconium[3] and thorium[4] from accompanying metal ions can be performed. In a tetrahydrofuran–nitric acid system containing dithizone, silver, copper and bismuth can be separated from numerous elements[5].

In the present paper the applicability of organic solvent–dimethylglyoxime–hydrochloric acid systems for the separation of nickel on Dowex 50 was investigated. As a result a very effective and specific method for the separation of nickel from more than 30 elements has been developed.

Reagents and solutions

Ion-exchange resin. Dowex AG 50W-X8 (100–200 mesh; hydrogen form) was used for the column separations and for the batch experiments. Before use the resin was purified by washing it in succession with 6 *M* nitric acid, distilled water and methanol whereafter it was dried in air and stored in an amber bottle. For 1 kg of resin 2 l of 6 *M* nitric acid, 5 l of distilled water and 2 l of methanol were used.

Organic solvents. The following reagent-grade solvents were employed: acetone, tetrahydrofuran, dioxane and methyl glycol (ethylene glycol monomethyl ether).

Eluant solutions. I: 90% acetone–10% 6 *M* hydrochloric acid (v/v). II: 0.25 *M* dimethylglyoxime in 90% acetone–10% 6 *M* hydrochloric acid (v/v).

Tracers. Hydrochloric acid solutions of many radioactive tracers including nickel-63 were used.

The radioactive measurements were performed by standard counting techniques.

Determination of distribution coefficients

The batch distribution coefficients (K_d values) of nickel were determined as described earlier[6].

Working procedure

Pretreatment of resin bed. Soak the resin (1 g) for about 5 min in a few ml of eluant I and transfer the slurry to the ion-exchange column (250 mm long, 5 mm bore), supporting the bed by a pad of glass or quartz wool. Wash with 5–10 ml of eluant I.

Sorption and elution. Mix 1 ml of 6 *M* hydrochloric acid containing up to 10

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

mg of nickel (plus nickel tracer) and other elements with 9 ml of acetone. After 5 min pass this solution through the pretreated resin bed at a flow rate corresponding to the back-pressure of the resin column (about 0.35 ml min^{-1}). Under these conditions Ni, Th, Zr, Hf, Al, Mg, the rare earths, alkaline earths and alkali metals are strongly retained on the resin while Fe(III), Co, Mn(II), Cu(II), Zn, Cd, Hg(II), Pb, Bi, In, Ga, V(V), Mo(VI) and U(VI) pass into the effluent. The complete elution of these non-adsorbable elements is effected by subsequent passage (at the same flow rate as above) of 30–40 ml of eluant I.

Elution of nickel. Selectively elute nickel with 30 ml of eluant II. This separates nickel from all the metal ions which are co-adsorbed with nickel from eluant I. In the eluate, nickel can be determined radiometrically or spectrophotometrically.

Results and discussion

Previous investigations of mixed aqueous–organic solvent systems containing hydrochloric acid have shown that from such media nickel is strongly retained on Dowex 50[7]. Thus, in a medium consisting of 90% acetone and 10% 6 M hydrochloric acid (v/v) (same composition as eluant I), the distribution coefficient of nickel has a value of 227. Under the same conditions the distribution coefficients of thorium, zirconium, hafnium, rare earths, alkaline earth metals and heavy alkali metals exceed 10^3. The coefficients of magnesium and the light alkali metals are of the same order of magnitude as that of nickel. All those elements which readily form anionic chloride complexes have distribution coefficients below 1; these elements include Fe(III), Co(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ga(III), In(III), Bi(III), U(VI), V(V) and Mo(VI). Manganese(II) has a K_d value of 4.

No changes in the extent of adsorption are observed in the presence of dimethylglyoxime except that the distribution coefficient of nickel is reduced from the value of 227 (see above) to a K_d value below 10 if 0.25 M dimethylglyoxime in 90% acetone–10% 6 M hydrochloric acid (eluant II) is used. This behavior of the elements does not change appreciably if tetrahydrofuran is used in place of acetone.

Consequently, the successive use of eluants I and II makes it possible to separate nickel from all the elements mentioned above. Numerous experiments employing

TABLE I

ELUTION VOLUMES OF 10 mg NICKEL (+ TRACER) ON A 1-g COLUMN OF DOWEX 50 WITH VARIOUS ELUANTS

Composition of eluant solution	*Elution volume of nickel (ml)*
0.25 M Dimethylglyoxime in 90% acetone–10% 6 M HCl (eluant II)	30
0.5 M Dimethylglyoxime in 95% tetrahydrofuran–5% 6 M HCl	40
0.25 M Dimethylglyoxime in 95% methyl glycol–5% 12 M HCl	>100
0.25 M Dimethylglyoxime in dioxane saturated with 6 M HCl	30

this method have shown that in all cases complete separations of tracer and macro amounts of nickel from other elements can be achieved.

Removal of nickel from Dowex 50 can also be achieved using the eluants listed in Table I in which for the purpose of comparison eluant II has been included.

If the concentration of hydrochloric acid in the eluants is reduced or increased, the effectiveness of these mixtures to elute nickel is decreased. The same effect is observed if 6 *M* nitric acid replaces 6 *M* hydrochloric acid. In the nitric acid–tetrahydrofuran–dimethylglyoxime system the distribution coefficient of nickel is greater than 10^3.

Less suitable organic solvents than those mentioned in Table I are methanol and glacial acetic acid in which dimethylglyoxime is only sparingly soluble.

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Chromatographic separation of silicate and phosphate

If one wishes to separate chromatographically small amounts of silicate and phosphate, as for example, in a biological extract, then the chromatographic procedure of BAUMANN[1] is not suitable, because the phosphate and silicate react similarly with the color reagents. The ability to differentiate between inorganic silicate and phosphate is not important, because they are separated chromatographically, but in a biological extract, there may be organic phosphate compounds which will run near the silicate spot, and will also produce a color with the spray reagents. Other phosphate spray reagents[2–4] also react with silicate. In the work described here, various combinations of reagent strength and acidity were examined, and spray reagents which are specific for either phosphate or silicate were developed. The chromatographic separation of these compounds was also studied.

Reagents

Phosphate specific spray. 1% ammonium molybdate in 0.6 *M* hydrochloric acid, followed by 1% tin(II) chloride in 10% hydrochloric acid.

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Silicate specific spray. 1% ammonium molybdate in 0.125 *M* sulfuric acid, followed by saturated oxalic acid[5] and 1% tin(II) chloride in 10% hydrochloric acid.

Solvent. Isopropanol:water:acetic acid (20:5:2)[1].

Support. Ecteola Cellulose (Schleicher & Schuell Co., Keene, New Hampshire), 0.6 mm on glass plates.

Procedure

To ensure a clean background, wash the plates, after they have been made and dried, with the solvent, allowing it to run all the way to the top, and dry the plates again. Apply 1 or 2 µl of the sample solution, and dry the spots. Allow the solvent to run to 100 mm (about 1 h), dry the plates and spray with each spray reagent in turn. Allow the plates to dry between each spray reagent (10 min) and in the case of the silicate spray reagents, allow at least 30 min after the oxalic acid spray, before the final spray.

Results

With the method given above, phosphate stays at or near the origin, and silicate runs as a fairly discrete spot with an R_F value of about 0.25. Phosphate may be visualized with the phosphate spray reagents, and silicate does not react. Silicate may be seen with the silicate spray reagents, and phosphate does not react.

Other support powders were tried. Selectacel plain cellulose, Selectacel DEAE cellulose (both from Schleicher and Schuell), and Camag cellulose powder D-5 (A. H. Thomas Co.) containing 5% calcium sulfate as a binder were not as good as the Ecteola cellulose. The cellulose with calcium sulfate binder was especially unsatisfactory and only smears could be seen, with most material remaining at the origin. No doubt this was due to the effect of the binder. On the plain cellulose the silicate ran well, but the phosphate produced a long smear from the origin. If no phosphate is present, this would be a satisfactory support material.

An unsuccessful attempt was made to visualize polymers of silicic acid, such as were reported by BAUMANN[1]. Solutions of silicate as concentrated as 0.02 *M* were adjusted to pH 1, 2, or 3, in order to form polymers, and the solutions applied were run either before or after drying the spots. In some experiments the plates, after development, were sprayed with a solution of sodium carbonate, to aid in depolymerizing any polymers. In no case were any spots visible, other than those due to the silicic acid monomer.

The method is about 20 times more sensitive than the procedure of BAUMANN[1]. The lowest concentration of silicate which can easily be seen is 10^{-4} *M*, when 1 µl is applied. This is about 0.006 µg of silica, or about 0.012 µg cm^{-2} under these conditions.

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Separation of rhenium from molybdenum, vanadium, tungsten and some other elements by tribenzylamine–chloroform extraction from phosphoric acid

Quaternary amines are good extractants for rhenium from alkaline as well as acidic solutions[1], but also extract molybdenum, tungsten, vanadium, copper, selenium, uranium and other elements which interfere in the determination of rhenium by the widely used thiocyanate–tin(II) chloride method, so that additional separations are necessary. Moreover, recovery of rhenium from the solvent is not possible by a simple change of pH.

Of the tertiary amines, tri-isooctylamine extracts rhenium well from nitric acid solution[2]. No other information seems to be available on the use of tertiary amines for the extraction of rhenium from different media in the presence of elements interfering in rhenium determinations. Tertiary amines are cheaper and more easily available than quaternary amines, and they have been found to be equally good extractants for rhenium, providing greater discrimination from other elements. The extracted elements can be recovered by simple stripping with alkaline solution. Because of these advantages, some tertiary amines have been investigated for the separation of rhenium from other elements in various media.

Experimental

Reagents and materials. Perrhenate stock solutions were prepared from "Specpure" potassium perrhenate (Johnson-Matthey and Co., Ltd., London). Solutions of other elements were made from laboratory-reagent-grade salts (L.R., B.D.H.) in water or acid, and were standardised by conventional methods[3].

Tribenzylamine (Fluka, "extra pure", >99%), tri-*n*-butylamine (Fluka, "pract.", 96/98%), tri-*n*-hexylamine and tri-isooctylamine (Koch-Light) were used without further purification. Solvents and other chemicals were of "chemically pure" grade.

Separation procedure. A solution of rhenium (not more than 20 mg/20 ml) and other metal ions was adjusted to 2 *M* in phosphoric acid and extracted twice by shaking for 3 min each time with an equal volume of chloroform containing 1% (w/v) tribenzylamine. The combined solvent layers were shaken thrice with an equal volume of water containing a little more than enough ammonia to neutralise the extracted acid, each time for 2 min. All the rhenium and some accompanying ions were found in the aqueous back-extract.

After the back-extract had been evaporated to a suitable volume, the small amount of molybdenum accompanying rhenium was removed by the thiocyanate–amyl acetate method[4] and the rhenium in the aqueous layer was determined.

The percentage extraction of individual elements with different amines was obtained after a single contact for 3 min of a 20-ml solution containing 100 μg Re or 100 mg of other elements adjusted to the desired concentration of alkali or acid in a 100-ml separating funnel, with an equal volume of chloroform containing an amine (1% w/v). The element in the solvent was back-extracted into water as above and determined. This procedure was used to obtain the data shown in Tables I–IV.

Samples. (*a*) A reverberatory flue dust from copper manufacture containing no rhenium was dried in a nickel crucible with a solution of known rhenium content, and then fused with about 8 times its weight of sodium peroxide; the melt was taken up in water, neutralised carefully under cooling with strong sulphuric acid and then adjusted to slight alkalinity with ammonia. After boiling, the hydroxide precipitate was filtered off. The filtrate and washings were adjusted to 2 *M* in phosphoric acid.

(*b*) Molybdenites were opened up with concentrated nitric acid[5], and nitrate was destroyed by sulphurous acid. The solution was just made alkaline with ammonia, a few drops of hydrogen peroxide were added and the excess was boiled off. Any precipitate was filtered off and the filtrate and washings were adjusted to 2 *M* in phosphoric acid.

TABLE I

EXTRACTION OF RHENIUM(VII) BY SOME TERTIARY AMINES IN CHLOROFORM FROM DIFFERENT MEDIA

Amine[a]	% *Re extraction from 2 N*				
	NaOH	*HNO_3*	*HCl*	*H_2SO_4*	*H_3PO_4*
Tribenzylamine	0	28	60	99.5	82
Tri-*n*-butylamine	0	25	63	95	97
Tri-*n*-hexylamine	0	17	25	56	98
Tri-isooctylamine	0	33	65	97	100

[a] 1% (w/v) except for tri-isooctylamine (0.67% w/v).

TABLE II

DEPENDENCE OF EXTRACTION OF RHENIUM(VII) BY TRIBENZYLAMINE ON THE NATURE AND CONCENTRATION OF ACID

N acid	% *Re extraction*											
	0.0	*0.1*	*0.3*	*0.5*	*1.0*	*1.5*	*2.0*	*2.5*	*4.0*	*6.0*	*8.0*	*10.0*
HCl	7	67	77	72	62	–	60	–	33	26	–	–
H_2SO_4	7	–	–	–	93	98	100	100	100	–	–	–
H_3PO_4[a]	7	–	–	–	60	–	70	–	75	81	82	83

[a] Extraction with 0.5% (w/v) TBA in chloroform.

Determination of the elements. Microgram amounts of rhenium were determined colorimetrically by the thiocyanate–tin(II) chloride method[5] with amyl alcohol extraction of the colored complex. Absorbances were measured with a Spekker Absorptiometer in 1-cm cells with Kodak filter No. 1 (λ_{max} at 430 nm). Milligram amounts were determined gravimetrically by the tetraphenylarsonium chloride method[6].

Small amounts of other extracted elements were determined or their absence ascertained colorimetrically[3,5].

Results and discussion

The extraction of rhenium by tertiary amines from alkali and some mineral acid solutions, is shown in Table I. The highest extraction was found from sulphuric and phosphoric acids, whereas the quaternary amines[1] extract highly from alkali as well as mineral acid solutions. Tri-*n*-hexylamine was a poor extractant except in phosphoric acid media. Tribenzylamine was cheaper than the other tertiary amines with equally high extraction and hence was examined further.

Results of extraction with tribenzylamine from acids of different strengths, are shown in Table II. It can be seen that the optimal extraction of rhenium was obtained from >2 *N* sulphuric acid, 0.3 *N* hydrochloric acid, or 6 *N* phosphoric acid. The extraction of other elements at these acid concentrations is shown in Table III. Though a simple extraction completely removed rhenium into the solvent from 0.3 *N* hydrochloric acid or 2.5 *N* sulphuric acid, turbidities resulted from precipitation of the acids and amine adducts of molybdenum(VI) and tungsten(VI), and these

TABLE III

EXTRACTION OF ELEMENTS BY TRIBENZYLAMINE IN CHLOROFORM FROM MINERAL ACIDS

Element with initial oxidation state	*% Extraction from*		
	0.3 N HCl	*2.5 N H_2SO_4*	*6 N H_3PO_4*[a]
V(V)	0	0.2	0
Cr(VI)	–	–	29.4
Fe(II)	–	–	0.01
Fe(III)	–	–	0.17
Mo(VI)	0.14	1.7	0.13
W(VI)	0	0.45	0
Ru(III)	0.21	0.22	0
Pd(II)	7.2	56.3	59.3
Os(VIII)	6.0	8.6	10.0
Pt(IV)	29.0	9.3	3.4
Si(IV)	–	–	1.3
Se(IV)	–	–	0.02
U(VI)	–	–	0.02

[a] No extraction of Cr(III), Co(II), Ni(II), Cu(II), Te(IV) was found for 6 *N* H_3PO_4 media.

TABLE IV

DEPENDENCE OF RHENIUM(VII) AND MOLYBDENUM(VI) EXTRACTION FROM 2 *M* PHOSPHORIC ACID ON TRIBENZYLAMINE CONCENTRATION

Amine concn. (% w/v)	0.25	0.5	1.0	1.5	2.0	2.5	2.75
% Re extn.	77	81	92	97.0	97.5	98	98.3
% Mo extn.	0.035	0.10	0.12	–	–	0.20	–

increased on shaking with the solvent; separation of layers was possible only after centrifugation. Moreover, the extraction of molybdenum, tungsten and vanadium was higher than from 6 *N* phosphoric acid under conditions of complete extraction of rhenium(VII). Accordingly, the sulphuric and hydrochloric acid media were not further investigated.

With 2 *M* phosphoric acid, two equilibrations with the 1% tribenzylamine in chloroform gave quantitative extraction of rhenium. When tungsten was present, turbidity resulted and phase separation was effected quickly only by centrifugation. However, with up to 200 mg of molybdenum, no turbidity was produced, and with up to 400 mg, no turbidity formed when *ca.* 100 mg of anhydrous sodium sulphate was added to the aqueous solution before extraction. Extraction of both rhenium and molybdenum increased with the amine concentration for 3-min equilibration (Table IV); a 1% (w/v) concentration was chosen as a reasonable compromise.

Vanadium and tungsten are not extracted at all and molybdenum less than 0.3%, under the conditions for complete extraction of rhenium; many other elements were also extracted only in traces or not at all (Table III). As before[7], the thiocyanate–amyl acetate method[4] was preferred for the removal of residual molybdenum. Silicon and traces of selenium carried through the extraction did not interfere with the colorimetric determination of rhenium. Except for ruthenium, platinum metals were slightly extracted and required further separations; osmium and palladium gave rise to a black scum at the interface and platinum to a yellow scum.

The influence of anions added as their sodium salts to give almost saturated solutions was examined. Sulphate and oxalate had no effect on the extraction of rhenium, but the extraction was decreased by fluoride (to 89%) and phosphate (to 84%); chloride, nitrate and acetate interfered considerably. The presence of peroxide increased the extraction of molybdenum.

The wide applicability of the method is shown by the satisfactory analyses of a variety of samples (Table V). There is an estimated loss of 0.6% Re to the raffinate

TABLE V

ANALYSIS OF SAMPLES BY THE PROPOSED METHOD

Composition of sample				*Re found (µg)*
Mo (mg)	*V (mg)*	*W (mg)*	*Re (µg)*	
400	–	–	35	34
200	–	–	15	15
160	50	50	22	21.5
80	25	25	12	12
Mo(40)[a], V(8), W(8), U(8), Fe(III)(6), Cr(III)(4), Co(6), Ni(6), Cu(5), Si(4), Se(4), Te(4)			16	15.5
Mo(60), V(10), W(10), U(10), Fe(III)(9), Co(9), Ni(9), Cu(10), Cr(III)(6), Si(6), Se(6), Te(6)			24	23.5
Flue dust (600)			32	31.5
Flue dust (300)			19	19
Molybdenite (Canada)			0.00204%[b]	0.0020%
Molybdenite (Norway)			0.0036%[b]	0.0039%

[a] Numbers in brackets show mg amount of the element.

[b] Reported values.

after the two tribenzylamine–chloroform extractions and a loss of 0.4% Re to the solvent for each extraction with amyl acetate to remove the residual molybdenum.

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A rapid method for the detection and determination of Captan

Captan (N-trichloromethylthiotetrahydrophthalimide) has various industrial and agricultural applications, being used both as a fungicide at the 100–1000 p.p.m. level and in grain protection at levels above 1000 p.p.m.[1]. The practice of including insecticides such as Aldrin, Lindane, DDT or Dieldrin, with Captan as seed treatments for dual protection against soil insects and soil-borne pathogens has gained widespread acceptance[2].

Many methods have been suggested for detection and determination of Captan. KITTLESON[2] has described a method in which resorcinol and Captan are heated at 135–140° to form an intense red coloured compound; after treatment with acetic acid, the yellow colour is measured at 425 nm. ENGST AND SCHNASK[3] have used a silver nitrate spray followed by ultraviolet irradiation in a thin-layer chromatographic method. IRWIN *et al.*[4] have studied the response of Captan and its structurally related fungicides (Folpet, Difolatan) to several reagents such as resorcinol, permanganate, dimethyl-*p*-phenylenediamine and chromic acid, also for thin-layer chromatography. A colorimetric determination of Captan has been based[5] on its reaction with pyridine and tetraethylammonium hydroxide. Thin-layer chromatographic methods have been used at the nanogram level, and these have been used semiquantitatively[6,7]. In a previous report[8], a rapid semiquantitative method for Captan based on its reaction with monoethanolamine was applied in the presence of Aldrin, DDT, BHC, Malathion, etc. The extension of this method to fully quantitative work is reported here.

Procedure

Prepare a standard solution of Captan (1 mg ml^{-1}) in acetone. To aliquots containing 15–100 μg of Captan, add 1 ml of monoethanolamine, and place the mixture in a boiling water bath for exactly 1 min. Immediately add 1 ml of distilled water and replace in the bath for 9 min. Cool to room temperature, dilute to 50 ml with distilled water, and measure the absorbance at 390 nm against a reagent blank.

Results and discussion

Monoethanolamine hydrolysis has been widely used for chlorinated pesticides analysis[9]. However, fungicides like Captan which contains both sulphur and chlorine behave differently from pesticides like DDT, etc. Captan when hydrolysed with monoethanolamine for 1 min in a boiling water bath, turns immediately blue, which gradually becomes yellow on further heating; concentrations of Captan above 100 μg under identical conditions first turn pale-yellow and then orange red on prolonged heating. The chlorinated insecticides like BHC, DDT, Lindane, Aldrin, Dieldrin and Endrin did not produce the blue colour, hence the reaction can also be used to distinguish Captan from the other chlorinated insecticides. The yellow colour formed on further heating and dilution was stable for 30–40 min. The absorbance spectra showed a maximum at 390 nm and Beer's law was obeyed over the range 15–100 μg ml^{-1} of Captan.

Captan was determined in different formulations consisting of starch and Captan, by means of a calibration curve, and it was established that the precision of the method was $\pm$ 2.5%. For formulations which contain Captan along with chalk powder, extraction with acetone before application of the above procedure is sufficient. A preliminary clean-up procedure based on hexane and acetonitrile extraction is essential for application to wheat, rice, jowar, etc. Fruits and vegetables which contain high percentages of carotenoid pigments interfere with the hydrolysis and subsequent colour formation and normal chromatographic separations are then essential.

Captan in amounts above 100 μg produced different colours depending on the quantity, when hydrolysed with monoethanolamine for 10 min; a yellow colour was observed with 0.1–2.0 mg, an orange colour with 2–4 mg, a red colour with 4–5 mg and a blood-red colour with 5.0 mg. Accordingly, an approximate estimate of Captan concentration can be made in this range.

The authors express their thanks to Dr. H. A. B. PARPIA, Director of the Institute, for his keen interest.

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Errata

Leo Harju, The Stability Constants of Some Metal Chelates of Triethylenetetraminehexaacetic Acid (TTHA), *Anal. Chim. Acta*, 50 (1970) 475–489.

Page 478, in equation (17) the minus sign should be a multiplication sign. Equation (17) should read:

$$\beta_{(M_2L)'} = \beta_{M_2L} \cdot \alpha_{M_2L(H)} = \frac{\alpha_{L(H)}}{[M]^2}$$

Page 484, in Table VI the columns for β_{M_2L} and $K_{M_2L}{}^{M}$ are interchanged from Mg downward. The values of $K_{M_2L}{}^{M}$ for Mg, Mn, La, Nd, Er, Ni, Pb and Zn are thus given in the β_{M_2L} column. On the other hand, the β_{M_2L} values of Ni, Pb and Zn are correspondingly given as $K_{M_2L}{}^{M}$ constants. However, the correct values are given in Tables VIII, IX and X as well as in an earlier paper in *Anal. Chim. Acta*, 49 (1970) p. 226.

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Book Reviews

ROLF NEEB, *Inverse Polarographie und Voltammetrie. Neue Verfahren zur Spurenanalyse*, Verlag Chemie GmbH, Weinheim/Bergstr., 1969, xii + 256 pp., price DM 48,—.

Inverse polarography and techniques related to it have so far been treated only in review papers and in shorter or longer chapters in textbooks; the present monograph is therefore very welcome as it fills a certain gap in the electroanalytical literature. The text is arranged into nine chapters; the first six describing the technique in general, while the last 3 reviewing the determinations of elements and the industrial applications of the method. A short introductory chapter gives a historical and theoretical introduction. Separate chapters describe the electrodeposition process, the stripping process and methods of determination, which involves ordinary and amalgam polarography, A–C and oscillopolarography, chronopotentiometry, and coulometry. Instrumentation is covered separately (Chapter 4), with detailed description of the great variety of electrodes, followed by a chapter on preparation of samples and supporting electrolytes. A description of interferences and their elimination concludes the first part of the book. In the application section, first the determinations of elements are described, in the order of the periodic system, and then industrial, agricultural and biological applications are reviewed. Each chapter is supplemented with a detailed bibliography. A subject index concludes the book. There are numerous, well presented diagrams.

Clearness of presentation, and the good balance between theoretical and practical parts as well as the importance of the topic recommend this book to the analytical chemist, especially if he has electrochemical interests. Anybody having access to a polarograph might find some new practical applications in the book. An English edition would certainly be well received.

G. SVEHLA, Belfast

Anal. Chim. Acta, 52 (1970) 562

J. TRANCHANT (Ed.), *Practical Manual of Gas Chromatography*, Elsevier Publishing Company, Amsterdam, 1969, xix + 387 pp., Price DFl. 85,—.

In the preface to this manual, Professor CHOVIN expresses the hope that it will compete successfully with the considerable number of treatises on gas chromatography now available, particularly as it is designed very much for the practising chromatographer, whether technician, engineer, control chemist or research worker. Necessarily there is some degree of compromise concerning the requirements of this varied readership and it can be said to be only partly successful.

As the format is that of a series of review chapters by different contributors, the style, quality and usefulness are variable. The editor contributes clear and comprehensive chapters on basic principles, isothermal and programmed chromatography and qualitative analysis, though there is some degree of over-elaboration for a laboratory text. The remainder of the book includes an excellent article on columns and good reviews of specific applications and quantitative analyses, but the discussions on detectors and ancillary apparatus are disappointing.

The general acceptance of this volume as a laboratory manual will unfortunately be limited by the high price.

P. C. Uden, Birmingham

Anal. Chim. Acta, 52 (1970) 562–563

Absorption Spectra in the Ultraviolet and Visible Region, Vols. XI, XII and XIII, Edited by Dr. L. Lang, Akadémiai Kiadó, Publishing House of the Hungarian Academy of Sciences, Budapest, each volume 400 pp., price per volume £6.75.

Entre les années 1959 et 1968, ont paru les dix premiers volumes d'un atlas de spectres d'absorptions visibles et ultraviolets de composés organiques en solution.

Cet atlas fournit, pour environ trois mille substances pures, les informations suivantes:

1. un graphique du spectre d'absorption en log ε en fonction de la longueur d'onde en mμ avec l'indication de la formule chimique du composé,
2. un tableau donnant la formule moléculaire, le point de fusion, le poids moléculaire, les absorbances aux différentes longueurs d'onde avec l'indication de la concentration, de la nature du solvant, de l'épaisseur de la cellule et du spectrophotomètre utilisé.

Chaque volume est accompagné d'un index alphabétique reprenant le numéro du spectre et de la page. La présentation de la collection est très soignée.

Les volumes XI, XII et XIII de la même collection viennent de sortir de presse.

Ainsi que j'ai eu l'occasion de l'écrire précédemment, il s'agit d'un travail de grande qualité offrant un intérêt particulier pour les chimistes organiciens, les industries pharmaceutiques et les analystes.

G. Duyckaerts (Liège)

Anal. Chim. Acta, 52 (1970) 563

P. HEDVIG AND G. ZENTAI, *Microwave Study of Chemical Structures and Reactions*, English translation edited by E. D. MORGAN, Iliffe Books Ltd., London, 445 pp., price £5.25.

The title of this book is misleading. From it the reader might expect a treatment of the rotation spectra of gases, of electron spin resonance spectroscopy and possibly of dielectric properties at microwave frequencies. These topics are indeed dealt with, albeit at widely varying length, but in addition there are sections on the radio-frequency techniques of nuclear magnetic and nuclear quadrupole resonance and even on electrical conduction in organic solids. The overall imbalance may be gauged from the fact that approximately half of the book is devoted to e.s.r. and a quarter to nuclear, mainly proton high resolution, magnetic resonance. These phenomena are described at a fairly simple level but with wide coverage of applications to chemical problems backed by adequate references to the original literature. In contrast, pure rotation spectroscopy, referred to as "rotation-inversion spectroscopy" which gives undue prominence to the latter rather limited aspect, receives scant attention with a description of apparatus but no indication of how the technique is applied to the determination of molecular structural parameters. The only reference to data obtained by this method is to a compilation published twenty years ago. The other topics are also treated somewhat sketchily.

Apart from the occasional factual errors and the regrettable use throughout of the superseded c/s as the unit of frequency, the problem in assessing this book is in deciding the category of reader for whom it is intended. As background reading over the range of topics covered it is too uneven, whilst anyone undertaking a study in depth would be better served by a more specialized work in the appropriate subject.

L. F. THOMAS (Birmingham)

Anal. Chim. Acta, 52 (1970) 564

T. S. WEST, *Complexometry with EDTA and Related Reagents*, BDH Ltd., Poole, 1969, 235 pp., price £2.50.

This is the 3rd edition of a well-established book, which for this edition has been extensively revised and rewritten. As before, the author has surveyed the analytical applications of EDTA and many other complexans, some of which are not as well known or as widely used as EDTA. Many of these lesser used reagents and indicators are brought into a more realistic light by the succinct manner in which the author has arranged the divisions and layout in the chapters dealing respectively with EDTA and its complexes, indicators for EDTA titrations and complexometric titrants other than EDTA. The chapter on indicators is particularly useful; the division of the many and varied indicators into "functional type" sections is to be commended. It is, however, in this section that there are one or two points in which readers may be at variance with the author, with respect to his representation of the structural configuration of some of these substances. For example, with xylenol orange, the *p*-quinonoid form is preferable to the ionic form indicated, and for lucigenins the formulation is somewhat surprising.

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However, in this edition the rearrangement of the material and the introduction of new work has resulted in the book being more readable and suitable as a reference book than are the previous editions.

The list of tables dealing with a wide range of data, in conjunction with the background theory and the many titration procedures, enables one to choose readily the optimum parameters for the determination of a metal in a complicated mixture. This book has some faults but overall it is a very useful book, and should be on the bookshelf of all analysts who have to deal with the determination of titratable amounts of metals.

L. S. BARK (Salford)

Anal. Chim. Acta, 52 (1970) 564–565

Progress in Separation and Purification. Vol. 2. Modern Separation Methods of Macromolecules and Particles, Edited by T. GERRITSEN, Wiley–Interscience, New York, 1969, 250 pp., price £7.00.

This volume contains twelve papers covering a wide range of modern separation methods for use in biochemical laboratories. Each paper is written by an expert and the techniques described range from electrophoresis on polyacrylamide gel, zonal ultracentrifuges and countercurrent methods using leaky dialysis membranes, to a complete description of the interesting new technique using two-phase polymer systems. These methods are well described and each paper contains a wealth of practical details which makes the book an excellent experimental manual. The presence of only one theoretical paper is a little disappointing but probably reflects the correct ratio between fundamental knowledge of the mode of operation of the methods compared with the necessary empiricism required for optimum use.

S. P. SPRAGG (Birmingham)

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