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ANALYTICA CHIMICA ACTA

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Provisional Publication Schedule for 1969

In the interests of rapid publication it has been found necessary to schedule 5 volumes for appearance in 1969. Since monthly publication will be maintained, this implies that 2 of the volumes will each consist of three issues, while 3 of the volumes will each consist of only 2 issues. The following provisional schedule applies:

Vol. **44**, No. **1**	January 1969	
Vol. **44**, No. **2**	February 1969	**(completing Vol. 44)**
Vol. **45**, No. **1**	March 1969	
Vol. **45**, No. **2**	April 1969	
Vol. **45**, No. **3**	May 1969	**(completing Vol. 45)**
Vol. **46**, No. **1**	June 1969	
Vol. **46**, No. **2**	July 1969	**(completing Vol. 46)**
Vol. **47**, No. **1**	August 1969	
Vol. **47**, No. **2**	September 1969	
Vol. **47**, No. **3**	October 1969	**(completing Vol. 47)**
Vol. **48**, No. **1**	November 1969	
Vol. **48**, No. **2**	December 1969	**(completing Vol. 48)**

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GENERAL INFORMATION

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Papers will be published in English, French or German.

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Coates Chemical Laboratories,
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Louisiana State University,
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P.O. Box 363
Birmingham 15 (Great Britain)

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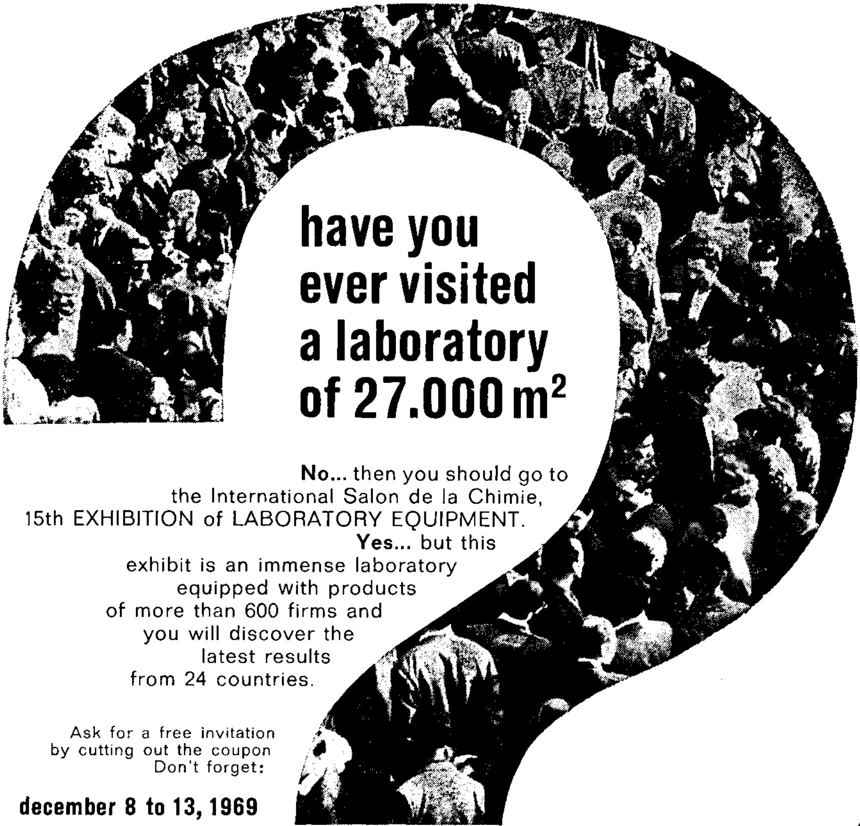

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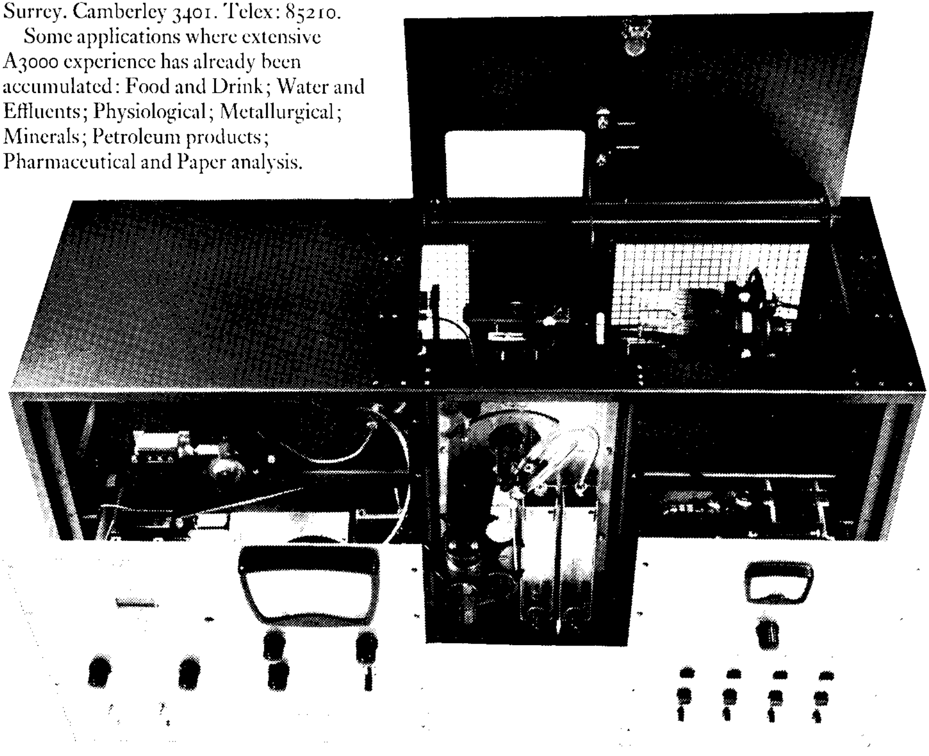

SOUTHERN ANALYTICAL

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 47, No. 1, August 1969

DETERMINATION OF ANTIMONY, IRON, AND MOLYBDENUM IN NICKEL OR URANIUM BY ATOMIC ABSORPTION SPECTROSCOPY

The application of atomic absorption to the microdetermination of antimony, iron, and molybdenum in nickel and uranium is described. These elements are separated and concentrated by a single solvent extraction from 8 *N* hydrochloric acid into *n*-amyl acetate. The extract is then analyzed directly by atomic absorption techniques. For the 95% confidence interval, the limits of error per analysis at the 1-p.p.m. level are ± 4, ± 10, and ± 6% for antimony, iron, and molybdenum, respectively. In general, the described procedure is more rapid and yields more accurate results than colorimetric procedures for these elements. Since the amyl acetate–hydrochloric acid solvent extraction system can separate antimony, iron, and molybdenum from gross quantities of nickel or uranium (*i.e.* up to 25 g), the method is capable of detecting the elements at about 0.05 μg/g.

C. R. Walker, O.A. Vita and R. W. Sparks,
Anal. Chim. Acta, 47 (1969) 1–7

RAPID DETERMINATION OF COBALT AND COPPER IN AN ACETONE–HYDROCHLORIC ACID SYSTEM

Rapid methods have been developed for the direct measurement of cobalt and copper in various alloys. These spectrophotometric methods are based on measurement of the intensely colored complexes formed by cobalt and copper ions in an acetone–hydrochloric acid medium, at 628 and 400 nm, respectively. The cobalt method is highly selective; cobalt can be determined without interference from large quantities of iron, chromium, nickel, vanadium, molybdenum, and copper. In the determination of copper, only large quantities of iron, molybdenum, or vanadium interfere, but their interferences can be easily eliminated by a rapid solvent extraction procedure. The methods are sufficiently sensitive to determine 0.015% cobalt and 0.005% copper in aluminum alloys. Both elements can be determined with a limit of error of 1.2–1.3% at the 95% confidence interval.

C. R. Walker and O. A. Vita,
Anal. Chim. Acta, 47 (1969) 9–18

THE SOLVENT EXTRACTION OF THULIUM WITH ALIPHATIC MONOCARBOXYLIC ACIDS

The extraction of 10^{-4} and 10^{-3} *M* thulium(III) into 4-methyl-2-pentanone and chloroform containing aliphatic monocarboxylic acids has been studied with formic through decanoic acids. Extraction tends to increase with acid molecular weight, acid concentration, and pH up to about 6. Detailed studies with hexanoic acid indicate that the species extracting into 4-methyl-2-pentanone is $TmR_3(HR)$ and the species extracting into chloroform is $TmR_3(HR)_5$. In both cases the predominant aqueous species are Tm^{3+} and $TmOH^{2+}$. From the data first hydrolysis constants of Tm^{3+} have been calculated to be $10^{10.2}$ and $10^{9.7}$, these values being larger than those expected from previous rare-earth hydrolysis data.

G. K. Schweitzer and S. M. Sanghvi,
Anal. Chim. Acta, 47 (1969) 19–25

Photoluminescence of Solutions

With Applications to Photochemistry and Analytical Chemistry

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

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

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

Comprehensive Analytical Chemistry

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

VOLUME IIB: Physical Separation Methods

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

Volume Two, Part B is devoted to physical separation methods. After an account of the theory and practise of liquid chromatography in columns, the volume continues with a lengthy treatment of gas chromatography.
The next chapter, on ion exchangers, is notable for the account it gives of analytical applications, while distillation (theory and technique) is the last topic to be treated in the present volume.

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

Atomic-Absorption Spectroscopy

and Analysis by Atomic-Absorption Flame Photometry

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

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

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

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VOLTAMMETRY OF THE NEPTUNYL GLUTARATE COMPLEX AT THE ROTATING GLASSY CARBON ELECTRODE

The voltammetry of the neptunyl glutarate complex was investigated over widely varying conditions of ligand concentration and pH. A reversible, one-electron wave was obtained in nearly all glutarate concentration ranges investigated over the pH range 0.0–6.6. The half-wave potential was independent of the pH in the ranges 0.0–1.0 and 4.0–6.6, but was a function of the pH in the range 1.0–4.0. The maximum metal–ligand ratio was found to be 1:3 by conductometric and amperometric titrations. The diffusion coefficient was $0.21 \cdot 10^{-5}$ cm^2/sec at pH 3.1 and $0.15 \cdot 10^{-5}$ cm^2/sec at pH 5.3. The stability constant of the neptunyl glutarate complex was determined as $1.6 \cdot 10^{-5}$.

C. E. Plock,
Anal. Chim. Acta, 47 (1969) 27–33

FLUORESCENCE AND METALLIC VALENCY STATES

PART II. DETERMINATION OF MANGANESE

Manganese is selectively and simply determined through the oxidative reaction of permanganate, formed by catalytic oxidation of manganese(II), upon oxine-5-sulphonic acid to produce a highly fluorescent product; the method is 100 times more sensitive than the conventional permanganate method. The fluorescence intensity attains a maximum after 10 min, is constant for 1 h, and is linear for 2.5 p.p.b. to 2.5 p.p.m. of manganese. Few ions interfere and manganese can be accurately determined in steels and other alloys.

B.K. Pal and D.E. Ryan,
Anal. Chim. Acta, 47 (1969) 35–39

DETERMINATION OF SUBMICROGRAM AMOUNTS OF SILVER(I) BY QUENCHING OF FLUORESCENCE

The reaction of the bis-phenanthroline–silver(I) cationic complex with the counter-ion, 2,4,5,7-tetrabromofluorescein (eosin), to form the ternary complex, $\{[Ag(Phen)_2{}^+]_2, TBF^{2-}\}$, has been studied for the determination of submicrogram amounts of silver(I) ions in aqueous media. The eosin itself is fluorescent and in the presence of 1,10-phenanthroline, its sharpest excitation and emission peaks are at 300 and 545 nm, respectively. The addition of silver(I) ions to the eosin–phenanthroline solution causes a quenching of this fluorescence. With this method, silver(I) ions can be determined down to 4 p.p.b., with a reproducibility of 2.7%, in the pH range 3–8. Reaction is instantaneous and the fluorescence remains stable for two weeks. Twenty cations, including the other coinage and most of the other noble metals, and ten anions have been tested for their interferences in the presence of EDTA. Only palladium(II) and cyanides interfere seriously.

M. T. El-Ghamry, R. W. Frei and G. W. Higgs,
Anal. Chim. Acta, 47 (1969) 41–48

TREATISE ON ELECTROCHEMISTRY

Second, completely revised edition

by G. Kortüm
Professor of Physical Chemistry, University of Tübingen, Germany

7 × 10″, xxii + 637 pages, 71 tables, 151 illust., 882 lit.refs., 1965, Dfl. 85.00, £ 10

Contents: 1. Definitions and fundamental laws. 2. Fundamental principles of thermodynamics. 3. The solvation of ions. 4. Weak and strong electrolytes. 5. Theory of ionic interaction. 6. Association and incomplete dissociation of strong electrolytes. 7. The results and applications of conductance measurements. 8. Electromotive forces. 9. Practical applications of potentiometric measurements. 10. Acids and bases. 11. Potential differences at phase boundaries. 12. Electrical polarization and the kinetics of electrode processes. 13. Applications of electrochemical processes. Appendix. Subject index.

OXIDATION AND COMBUSTION REVIEWS

edited by C. F. H. Tipper,

Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, Great Britain

Volume 1

6 × 9″, viii + 344 pages, 29 tables, 45 illus., 815 lit.refs., 1965, Dfl. 40.00, 110s.

Contents: 1. Application of the theory of branched chain reactions in low temperature combustion. 2. Oxidation reactions induced by ionising radiation. 3. Gas phase photo-oxidation. 4 Oxidation reactions involving nitrogen dioxide. 5. Oxidative degradation high polymers. 6. The heterogeneous selective oxidation of hydrocarbons. Author and subject indexes.

Volume 2

6 × 9″, viii + 301 pages, 19 tables, 64 illus., 311 lit.refs., 1967, Dfl. 60.00, 150s.

Contents: 1. Thermal explosion theory. 2. Some fundamentals of combustion instability 3. The use of adiabatic compression and mass spectrometry in the study of combustion. 4. Trapped radicals and combustion. Author and subject indexes.

Volume 3 and subsequent volumes are published as a review journal under the same title

ATMOSPHERIC OXIDATION AND ANTIOXIDANTS

by G. Scott,
Head of Works Research and Development Department, Dyestuffs Division, Imperial Chemical Industries Ltd., Grangemouth, Stirlingshire, Great Britain

7 × 10″, x + 528 pages, 172 tables, 174 illus., 1206 lit.refs., 1965, Dfl. 72.50, £ 8.10.0

Contents: 1. The historical development of antioxidants. 2. Peroxides. 3. Autoxidation. 4. Antioxidants: radical chain-breaking mechanisms. 5. Antioxidants: Preventive mechanisms. 6. Measurement of oxidative deterioration. 7. Oxidative deterioration of saturated oils and polymers. 8. Oxidation of olefinic oils, fats and polymers. 9. Degradation of vulcanised rubber. 10. Mechano-oxidation of polymers. Index.

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APPLICATIONS OF THE FLUORIDE-SENSITIVE ELECTRODE TO THE STUDY OF METAL–FLUORIDE ION ASSOCIATION CONSTANTS

An "Orion" fluoride-sensitive membrane electrode has been examined critically for the measurement of metal–fluoride ion association in aqueous solutions of constant ionic strength, with a calomel reference electrode and sodium chloride salt bridge. Measurements were made with magnesium, calcium, scandium, iron(III), europium(III) and gadolinium ions at 25°; yttrium and "protonation" of $[F^-]$ were studied at 15, 25 and 35° and enthalpy and entropy changes calculated. The electrode is limited to solutions 10^{-6} M or greater in free $[F^-]_{aq}$, with a consequent limitation on the magnitude of the first association constant to $\leqq 10^6$. Further limitations are imposed by the insolubility of most metal fluoride salts. The electrode is less sensitive than the iron(III)–iron(II) electrode system, but is much more convenient. Good agreement with previous results was obtained from measurements at various temperatures.

A. Aziz and S. J. Lyle,
Anal. Chim. Acta, 47 (1969) 49–56

INTERPRETATION OF TITRATION CURVES BY MEANS OF THE COMPUTER PROGRAM HALTAFALL

By the rigorous calculation of two titration curves, the use of the computer program Haltafall in the interpretation of titration procedures is exemplified. General expressions of the type often found in the literature are, moreover, shown to be redundant.

T. Anfält and D. Jagner,
Anal. Chim. Acta, 47 (1969) 52–69

THE BEHAVIOUR OF WATER AND SODIUM HYDROXIDE IN MOLTEN ALKALI CHLORIDES

(in French)

The behaviour of water and sodium hydroxide in molten NaCl–KCl eutectic at 800° has been examined by means of IR spectrometry and titrimetry. The solubility of water is very small. The main reaction that takes place is $H_2O + 2Cl^- \rightarrow 2HCl\uparrow + O^{2-}$. The introduction of sodium hydroxide in the bath appears to give rise to the following reactions:

$$2NaOH \rightarrow Na_2O + H_2O\uparrow$$

$$4NaOH \rightarrow O_2{}^{2-} + 2Na_2{}^+ + 2H_2O\uparrow$$

$$SiO_2 + 2NaOH \rightarrow SiO_3Na_2 + H_2O\uparrow$$

Some sodium hydroxide is simultaneously volatilized. The different proportions of NaOH that take part in these reactions have been determined. A qualitative scale of acidity in the molten alkaline chlorides is established.

E. P. Mignonsin and G. Duyckaerts,
Anal. Chim. Acta, 47 (1969) 71–80

SPOT TESTS IN ORGANIC ANALYSIS

Seventh English Edition, completely revised and enlarged

by FRITZ FEIGL in collaboration with VINZENZ ANGER

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

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

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

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

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

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

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

FROM REVIEWS OF THE NEW EDITION

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

Analytica Chimica Acta

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

Bulletin de la Société Chimique de France

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

Analytical Chemistry

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

Chemistry in Britain

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DETERMINATION OF TRACES OF IRON, NICKEL AND CHROMIUM IN PLUTONIUM NITRATE SOLUTIONS, WITHOUT PREVIOUS SEPARATION OF PLUTONIUM, BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

(in French)

Rapid determinations of traces of iron, nickel and chromium in aqueous plutonium nitrate solutions, without prior separation, are described. These methods can be used in the 0.1–8 μg ml^{-1} range for plutonium nitrate solutions containing up to 100 g Pu l^{-1} with a precision better than 5%. The effect of plutonium concentration, and interference between the three elements are discussed. In order to apply atomic absorption spectrophotometry to strongly radioactive solutions, a system of glove boxes has been designed. The method can be successfully applied to the analysis of plutonium recovery solutions in fuel-reprocessing plants.

M. Ganivet and A. Benhamou,
Anal. Chim. Acta, 47 (1969) 81–90

A STUDY OF THE MOLECULAR STRUCTURE OF HYDROXYETHYLENEDIAMINETRIACETIC ACID IN AQUEOUS MEDIA BY NUCLEAR MAGNETIC RESONANCE

(in French)

The molecular structure of HEDTA in aqueous solutions at different pH values, has been studied by nuclear magnetic resonance. The different sites occupied by the protons during the successive neutralisation of the triacid have been established. Different molecular models are proposed to explain the form and the evolution of the NMR spectra as a function of pH.

E. Merciny and N. Zaman,
Anal. Chim. Acta, 47 (1969) 91–100

DIAZOCOUPLING OF AMINES AND NITROGEN HETEROCYCLES BY MEANS OF 3-METHYLBENZOTHIAZOLINE-2-ONE HYDRAZONE

(in French)

A colorimetric determination of various compounds containing amino groups is described, with 3-methylbenzothiazoline-2-one hydrazone as reagent. Primary aromatic amines, some heterocyclic amines, hexamethylenetetramine and some derivatives of pyrazol-5-one can be determined.

M. Pays, R. Bourdon and M. Beljean,
Anal. Chim. Acta, 47 (1969) 101–112

THE PHOTOMETRIC DETERMINATION OF LOW CONCENTRATIONS OF OZONE IN WATERS

(in German)

A photometric method for the determination of ozone in waters down to a 0.01 mg O_3/l level is described. Ozone reacts with the manganese(II) diphosphate complex to form the manganese(III) diphosphate complex which is then reacted with *o*-tolidine. If ozone is swept out of the sample by a stream of gas and absorbed in manganese-(II) diphosphate solution in the presence of chromium(III) as catalyst, the method can be applied to heavily polluted waters; at the 0.52 mg O_3/l level, the standard deviation was 3.1%. The method can be easily applied for the determination of ozone in gases.

P. Hofmann and P. Stern,
Anal. Chim. Acta, 47 (1969) 113–120

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^{a} matrix elements and other useful expressions for subsequent applications and future reference.

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

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

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

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

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

Elsevier Publishing Company Amsterdam London New York

ATOMIC ABSORPTION SPECTROPHOTOMETRY OF ANTIMONY

The atomic absorption of antimony in combination with extraction of the chloride complex provides a suitable determination of antimony in various materials. The effect of variables on antimony absorption and the extraction of antimony were studied. Procedures for small amounts of antimony in metallurgical products and synthetic fibers are given.

M. Yanagisawa, M. Suzuki and T. Takeuchi,
Anal. Chim. Acta, 47 (1969) 121–126

SPECTROPHOTOMETRIC DETERMINATION OF ANIONS BY SOLVENT EXTRACTION WITH CUPROIN– OR NEOCUPROIN–COPPER(I) CHELATE CATIONS

Spectrophotometric methods are proposed for the determination of anions such as perchlorate, nitrate, phthalate and tetraphenylborate. The methods are based on solvent extraction of the ion pairs formed between colored copper(I) chelate cations and the anions, into organic solvents. Perchlorate or tetraphenylborate is easily extracted with the cuproin–copper(I) chelate into chloroform or chlorobenzene, and nitrate with the neocuproin–copper(I) chelate into methyl isobutyl ketone. Either system can be used for the determination of phthalate. Potassium can be determined in the range 20–200 μg by means of the tetraphenylborate procedure. Calibration graphs were linear in the range 10^{-6}–10^{-5} M for each anion in aqueous solution. The effects of diverse ions are described; anionic interferences can be largely eliminated by addition of silver(I) or mercury(II) salts.

Y. Yamamoto, N. Okamoto and E. Tao,
Anal. Chim. Acta, 47 (1969) 127–137

NEW STUDIES ON METALLOFLUORESCENT INDICATORS

Four new metallofluorescent indicators, analogous to calcein but prepared from glycine instead of iminodiacetic acid, have been synthesized and studied by thin-layer chromatography. In addition to fluorescein itself, three isomers of dichlorofluorescein were used in the syntheses. The product obtained with 2′,7′-dichlorofluorescein, bis-4′,5′-N,N-glycinemethylene-2′,7′-dichlorofluorescein, is recommended as a fluorescent indicator for the titration of copper(II) with EDTA solutions.

F. Bermejo-Martínez and M. G. González de Lopidana,
Anal. Chim. Acta, 47 (1969) 139–144

CRITERIA FOR THE SUITABILITY OF CHEMICAL COMPOUNDS AS INDICATOR ELECTRODES FOR POTENTIOMETRIC METHODS BASED ON SIMPLE REDOX SYSTEMS

(Short Communication; in German)

E. Pungor and A. Weser,
Anal. Chim. Acta, 47 (1969) 145–148

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.

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DETERMINATION OF ANTIMONY, IRON, AND MOLYBDENUM IN NICKEL OR URANIUM BY ATOMIC ABSORPTION SPECTROSCOPY*

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(Received March 10th, 1969)

The U. S. Atomic Energy Commission has established rigid specifications to insure the purity of uranium compounds used as feed sources for the gaseous diffusion process and in various nuclear applications. To measure conformance to these specifications, uranium compounds must be analyzed for many trace elements among which are antimony, iron, and molybdenum. Particularly sensitive analytical methods are required for antimony, whose specification limit is 1 μg per gram of uranium, and molybdenum, whose limit is 1.4 μg per gram of natural uranium (*i.e.* 200 μg of molybdenum per gram of uranium-235). In addition, there is often the need to analyze nickel a common material of construction in gaseous diffusion plants, for these elements.

In the past, uranium and nickel have been analyzed for antimony, iron, and molybdenum by emission spectroscopy or colorimetry, but both techniques have inherent disadvantages. Spectrographic methods lack accuracy and sensitivity, and colorimetric methods are often subject to elemental interferences and require a separate analysis for each element.

To eliminate these disadvantages, an attempt was made to analyze uranium or nickel solutions for antimony, iron, and molybdenum directly by atomic absorption. This approach did not produce the desired analytical sensitivity; furthermore, it had the additional disadvantage that the direct aspiration of uranium solutions is undesirable since it tends to spread radioactive contamination. Thus, a separation and concentration of these elements from nickel or uranium was essential. The desired separation and concentration was achieved by the solvent extraction of antimony, iron, and molybdenum into *n*-amyl acetate from 8 *N* hydrochloric acid[1-3]. The *n*-amyl acetate extract was then analyzed directly by atomic absorption.

With this separation, the analytical sensitivity for these elements was significantly improved, both by concentrating them and by taking advantage of the increased atomic absorption sensitivity of these elements in an organic solvent. Other improvements included the elimination of both the problem of radioactive contamination and the matrix effects associated with high salt concentrations.

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* Presented in part at the 19th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Inc., Cleveland, Ohio, March 1968.

EXPERIMENTAL

Reagents

All chemicals used were reagent grade. The *n*-amyl acetate was a purified grade.

Equipment

A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a Boling burner for the antimony and molybdenum analysis and a wide-slot premix burner for the iron analysis was used.

A Beckman Model DU-2 spectrophotometer was used for comparative colorimetric analyses.

Recommended standard procedure

Dissolve nickel metal, using 30 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid for each 5 g of nickel. After dissolution, evaporate the solution to *ca.* 15 ml, add 23 ml of concentrated hydrochloric acid, and transfer the solution to a 125-ml separatory funnel, washing the beaker with about 5 ml of 8 *N* hydrochloric acid. Add 2 ml of 20% (w/v) potassium nitrite to the funnel and mix thoroughly; then add 10 ml of *n*-amyl acetate, stopper, and shake the funnel for 5 min. Allow the phases to separate for 10 min. Discard the raffinate and analyze the *n*-amyl acetate extract for the desired elements by atomic absorption.

Dissolve uranium oxides or metal with 8 *N* nitric acid (10 ml per 5 g U), and fume the solution to dryness. Add 10 ml of concentrated sulfuric acid to the residue, and fume the solution to dryness (do not bake). For water soluble compounds such as uranyl chloride, fluoride, or nitrate, add 10 ml of concentrated sulfuric acid, and fume to dryness. Dissolve the sulfated residue with 15 ml of 8 *N* hydrochloric acid, and heat the solution to boiling. Add 1 ml of 10% (w/v) sodium sulfate to the solution and mix thoroughly. Add 25 ml of concentrated hydrochloric acid to the solution, and transfer it to a 125-ml separatory funnel, washing the beaker with about 5 ml of 8 *N* hydrochloric acid. Add 2 ml of 20% (w/v) potassium nitrite to the funnel, and mix thoroughly. Proceed with the extraction and analysis as described for nickel samples.

Calibrations

Prepare four 5-g nickel or uranium standards spiked with 1, 10, 20, or 50 μg each of antimony, iron, and molybdenum. Dissolve and extract the standards as in the procedure described, using the atomic absorption results to prepare calibration curves. Calibrations for either nickel or uranium samples were found to be interchangeable.

Instrumental procedure

The instrumental conditions described apply to the Perkin-Elmer 303 Atomic Absorption Spectrophotometer[4]. Set the air flow at 9.5 with a gauge setting of 30 psi. Adjust the aspiration rate of amyl acetate at 3.5–4.0 ml/min.

For antimony, set the wavelength at 2176 Å. Using the Boling burner, adjust the burner height so that the center of the light beam is about 15 mm above the burner top. With a gauge pressure of 10 psi, set the acetylene flow at 7.5 on the gas manifold. Zero the instrument with amyl acetate. Measure the absorptions of the sample and standard extracts. Calculate the antimony content of the samples from standard data.

For molybdenum, set the wavelength at 3133 Å. Using the Boling burner, adjust the burner height to 7 mm. Set the acetylene flow at 9.0 and zero the instrument. Measure the absorption of the standard extracts before, between, and after sample absorption measurements are made. This calibration is necessary in the case of molybdenum because its absorption is extremely sensitive to flame conditions[5]. Calculate the molybdenum content from standard data.

For iron, use a standard premix or wide-slot burner and set the wavelength at 2483 Å. Adjust the burner height to 15 mm and acetylene flow to 7.5 on the gas manifold. Measure the absorption of both the sample and standard extracts; calculate the iron content from standard data.

RESULTS AND DISCUSSION

Evaluation of the extraction of antimony, iron, and molybdenum

The extractions of antimony, iron, and molybdenum into *n*-amyl acetate from hydrochloric acid at various acid concentrations were evaluated by atomic absorption and colorimetric techniques. Hydrochloric acid solutions of antimony, iron, and molybdenum at different acid concentrations of 2–11 *N* and containing 20 µg of each element per ml were equilibrated with *n*-amyl acetate for 10 min. Equal volumes of acid and solvent were used in each extraction. After phase separation, both extracts and raffinates were analyzed for metal content by atomic absorption. Iron and molybdenum in the raffinates were also analyzed colorimetrically[6]. From these analyses, extraction efficiencies for antimony, iron, and molybdenum into *n*-amyl acetate from hydrochloric acid were determined. The extraction of each element is dependent on hydrochloric acid concentration as shown in Fig. 1.

Salt concentration also increases the extraction efficiency of this system. Extractions of antimony and molybdenum are essentially complete (>99%) from 8 *N* hydrochloric acid solutions that are 1 *M* in nickel or uranium. From 8 *N* hydrochloric

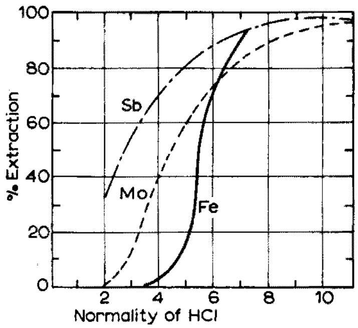


Fig. 1. Effect of hydrochloric acid on the extraction of antimony, iron and molybdenum into *n*-amyl acetate.

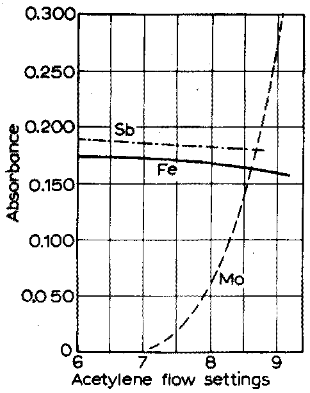


Fig. 2. Effect of acetylene flow on absorbance of antimony, iron, and molybdenum in amyl acetate.

acid alone, however, the extraction of antimony and molybdenum is only 95 and 89%, respectively.

Antimony, iron, and molybdenum are extracted into amyl acetate from hydrochloric acid in their highest valency states. For the complete extraction of antimony from dissolved uranium compounds, it must be reduced to the trivalent form and then oxidized to the pentavalent state just before extraction.

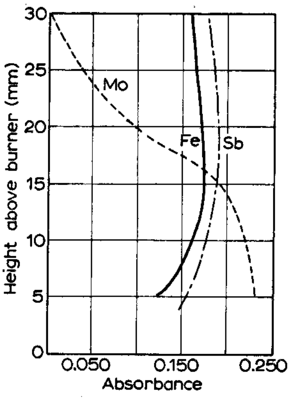
Evaluation of instrumental conditions

Effects of flame conditions, burner position, and burner types on the analysis of antimony, iron, and molybdenum were evaluated. The effects of fuel-to-air ratios on absorption were studied by maintaining the air flow at a constant manifold setting and varying the acetylene flow. Gage settings of 10 psi for acetylene and 30 psi for air were used. Aspiration rates were measured by weighing solution aspirated per unit time and were also kept reasonably constant (variations of 0.05 ml/min) for this study. The effects of fuel : air ratios on the absorbance of antimony, iron, and molybdenum are shown in Fig. 2.

The fuel-to-air ratio is critical in the determination of molybdenum and almost negligible in the analysis of antimony and iron. In the case of molybdenum, the absorbance increases as the flame becomes more fuel-rich. Control of the fuel : air ratio is essential in the determination of molybdenum, and frequent calibration is necessary to compensate for the absorption changes[5].

Fuel-to-air ratios that yielded maximum absorption for each element and stable instrument operation were adopted. These manifold settings were then used to evaluate all other instrumental variables, such as burner height and types. The height settings were measured from the top of the burner to the center of the light beam traversing the burner top. The effects of burner height on absorbance of antimony, iron, and molybdenum are shown in Fig. 3.

The height of the burner in respect to the optical beam is critical in the determination of molybdenum. For maximum absorption the beam must be kept very



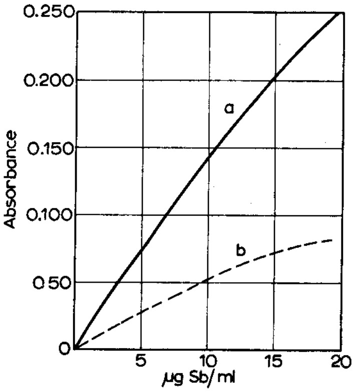


Fig. 3. Effect of burner height on absorbance of antimony, iron, and molybdenum in amyl acetate.

Fig. 4. Calibration curves for antimony. Wavelength, 2175 Å. Boling burner. (a) Amyl acetate, sensitivity 0.30 μg/ml; (b) 9 N HCl, sensitivity 0.82 μg/ml.

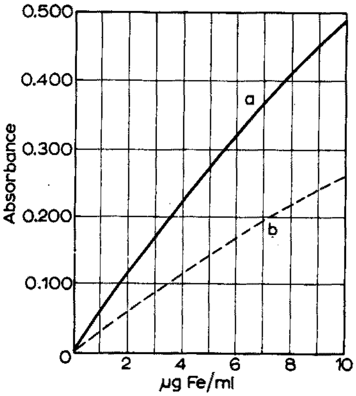
close to the burner top. Burner height is not as critical in the cases of antimony and iron; a broad operating range of 12–20 mm is usable for these two elements.

With respect to burner types, the Boling burner and wide-slot premix burner were compared for the analysis of a *n*-amyl acetate extract containing all three elements. In the iron determination, burner erosion by the *n*-amyl acetate extract which contained hydrochloric acid caused erratic iron measurements. Since this erosion was more severe with the Boling burner, the wide-slot premix burner should be used for iron.

In the determinations of antimony and molybdenum, the Boling burner was superior to the wide-slot premix burner because greater sensitivity was achieved for both elements; an increase of about 25% in sensitivity was observed for molybdenum and an increase of 15% for antimony.

Calibration curves

A series of calibration curves for antimony, iron, and molybdenum in *n*-amyl acetate, based on the established optimum instrumental parameters, are shown in Figs. 4, 5, and 6. These curves also show absorbance for each element in aqueous hydrochloric acid solutions. In every case, the presence of *n*-amyl acetate, increases the sensitivities of all three elements significantly[7].



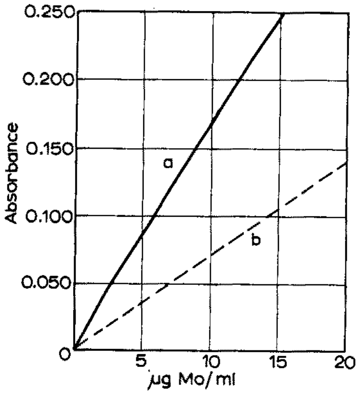


Fig. 5. Calibration curves for iron. Wavelength, 2483 Å. Wide-slot burner. (a) Amyl acetate, sensitivity 0.08 μg/ml; (b) 0.1 *N* HCl, sensitivity 0.15 μg/ml.

Fig. 6. Calibration curves for molybdenum. Wavelength, 3133 Å. Boling burner. (a) Amyl acetate, sensitivity 0.26 μg/ml; (b) 1 *N* HCl, sensitivity 0.61 μg/ml.

TABLE I

ANALYSES OF NICKEL AND URANIUM STANDARDS FOR ANTIMONY, IRON AND MOLYBDENUM

	Element		
	Antimony	*Iron*	*Molybdenum*
No. of standards	20	13	25
Range (μg/g)	1–20	1–10	1–20
% LE per analysis	± 4.3	± 9.7	± 6.3
% Bias	+ 0.65 ± 0.96	+ 2.1 ± 2.8	− 0.67 ± 1.2

Analysis of prepared standards

Several nickel and uranium standards spiked with antimony, iron, and molybdenum were analyzed by the recommended procedure. The concentration was 1–20 μg of each element per gram of either nickel or uranium with 80% of the standards containing 1 μg of the element per gram. The results of the analyses of both types of standards are shown in Table I. The analyses of these standards were made on several different days; therefore, these data represent analytical precision and accuracy obtainable with different instrumental settings and standardizations.

SUMMARY

The application of atomic absorption to the microdetermination of antimony, iron, and molybdenum in nickel and uranium is described. These elements are separated and concentrated by a single solvent extraction from 8 *N* hydrochloric acid into *n*-amyl acetate. The extract is then analyzed directly by atomic absorption techniques. For the 95% confidence interval, the limits of error per analysis at the 1-p.p.m. level are ±4, ±10 and ±6% for antimony, iron, and molybdenum, respectively. In general, the described procedure is more rapid and yields more accurate results than colorimetric procedures for these elements. Since the amyl acetate–hydrochloric acid solvent extraction system can separate antimony, iron, and molybdenum from gross quantities of nickel or uranium (*i.e.* up to 25 g), the method is capable of detecting the elements at about 0.05 μg/g.

RÉSUMÉ

On décrit une application de l'absorption atomique au microdosage de l'antimoine, du fer et du molybdène dans le nickel et l'uranium. Ces éléments sont séparés et concentrés par une simple extraction dans un solvant, l'acétate d'amyle, en milieu acide chlorhydrique 8 *N*. L'extrait est ensuite analysé directement par absorption atomique. Les limites d'erreur par analyse (dans l'ordre de 1 p.p.m.) sont respectivement ±4, ±10 et ±6% pour antimoine, fer et molybdène. D'une façon générale, ce procédé est plus rapide et fournit des résultats plus précis que les méthodes colorimétriques. L'antimoine, le fer et le molybdène pouvant être séparés de fortes quantités de nickel ou d'uranium (jusqu'à 25 g) par extraction dans l'acétate d'amyle, on peut ainsi déceler ces éléments en quantités de l'ordre de 0.05 μg/g.

ZUSAMMENFASSUNG

Die Anwendung der Flammenabsorptionsspektroskopie für die Mikrobestimmung von Antimon, Eisen und Molybdän in Nickel und Uran wird beschrieben. Diese Elemente werden abgetrennt und konzentriert durch Extraktion aus 8 *N* Salzsäure mit *n*-Amyl-Acetat. Der Extrakt wird dann direkt verwendet. Für einen Vertrauensbereich von 95% beträgt der Fehler im 1-p.p.m.-Bereich ±4, ±10 und ±6% für Antimon, Eisen bzw. Molybdän. Im allgemeinen ist das beschriebene Verfahren schneller und genauer als die kolorimetrischen. Durch die Extraktion aus grossen Mengen Nickel oder Uran ist die Methode zur Bestimmung von etwa 0.05 μg/g der Elemente geeignet.

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RAPID DETERMINATION OF COBALT AND COPPER IN AN ACETONE–HYDROCHLORIC ACID SYSTEM*

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Evaluation of aluminum alloys, which are used extensively throughout the nuclear industry, often depends on accurate determination of the alloying constituents, including the elements copper and cobalt. Standard methods for the determination of these elements are time-consuming since they usually require a preliminary separation. Copper, for example, can be accurately determined electrolytically, but the analysis requires up to 16 h per determination for some types of alloys. Most methods for cobalt require prior separations by precipitation, ion exchange, or solvent extraction.

LINDLEY[1] has determined cobalt colorimetrically as the cobalt(II) chloride complex in strong hydrochloric acid after removing copper electrolytically. SHERWOOD[2] has reported a similar colorimetric method, in which the blue cobalt(II) chloride color is developed in 11.4 N hydrochloric acid, but this procedure has the inherent disadvantage that the cobalt first must be separated from gross quantities of diverse ions by ion exchange and solvent extraction. He also reported that a variation in acid concentration of ± 0.25 N resulted in an error of 1.4% for a concentration of 0.12 mg Co/ml.

The use of strong hydrochloric acid for the colorimetric measurement of cobalt and copper is not satisfactory for several reasons: first, careful control of acidity is required for reproducible results; second, intensely colored complexes formed by some of the transition elements interfere seriously; and third, strong hydrochloric acid is difficult to work with as a colorimetric analysis medium, since it tends to lose strength rapidly by evaporation.

Since cobalt and copper halides are known to be soluble in organic solvents[3], color development of cobalt chloride in methanol, ethanol, and acetone solutions of hydrochloric acid was investigated, because use of an organic solvent should provide a greater latitude for variation in acid concentration while reducing interference from transition elements. Only acetone preserved the colorimetric sensitivity while permitting operation at overall acid concentrations down to 1.2 N. Thus, acetone was selected, and further investigations were made to determine the composition of the medium required for maximum sensitivity and color reproducibility.

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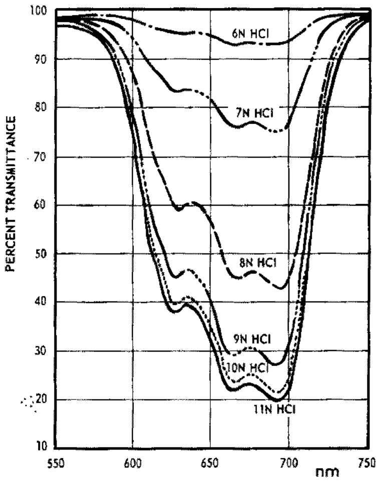
Determination of cobalt

Effect of acid concentration in aqueous media. The effect of various acid concentrations was determined by preparing spectra of cobalt chloride solutions in hydrochloric acid of various concentrations between 6 *N* and 11 *N*. The spectra, shown in Fig. 1, indicate that a high concentration of hydrochloric acid is necessary for maximum color development and that careful control of acidity is required for reproducible color development. In view of the instability of very strong hydrochloric acid solutions, 8 *N* hydrochloric acid was selected for the preliminary studies with the mixed solvents.



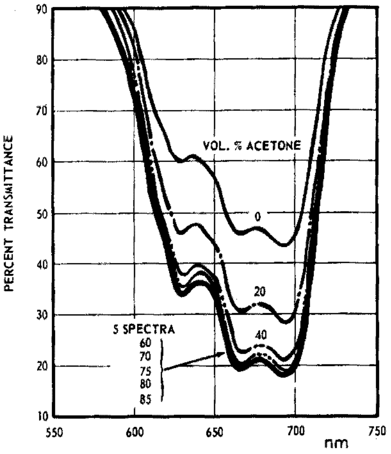


Fig. 1. Absorption spectra of cobalt in hydrochloric acid (7.5 mg Co/100 ml; 1-cm cell).

Fig. 2. Absorption spectra of cobalt in 8 *N* hydrochloric acid–acetone solutions (7.5 mg Co/100 ml; 1-cm cell).

Effect of acetone volume. Aliquots containing 7.5 mg of cobalt in 15 ml were taken from a standard solution made up with 8 *N* hydrochloric acid. Acetone and 8 *N* hydrochloric acid were added as necessary to give solutions containing from 0–85% (v/v) of acetone in a 100-ml volume. The spectra prepared from these solutions (Fig. 2) show that, at 60–85% (v/v) of acetone, the colorimetric sensitivity for cobalt is slightly better than that obtained at 11 *N* hydrochloric acid in an aqueous medium. Also, the maximum variation in color intensity at 628 nm in this same acetone range is only 4.5%. Absorbance measurements of cobalt standards containing 60–70% (v/v) acetone and 40–30% (v/v) 8 *N* hydrochloric acid were identical. Therefore, further studies were made in a 70% (v/v) acetone–30% (v/v) hydrochloric acid solution.

Effect of acid concentration in organic media. Aliquots containing 7.5 mg of cobalt were diluted to 100 ml with 70% (v/v) acetone and 30% (v/v) hydrochloric acid of varying concentrations. Figure 3 shows that the spectra for acid concentrations from 7 to 9 *N* give a variation of only 2.5% in the optical density of the solution at 628 nm. Thus, the final concentration of 70% (v/v) acetone and 30% (v/v) 8 *N* hydrochloric acid (*i.e.* an overall hydrochloric acid concentration of 2.4 *N*) was established as the standard conditions for the analysis. These parameters allow for slight variations in acid concentration that might be experienced in sample preparation without contributing significant errors in the analysis.

Study of the cobalt(II) chloride complex in acetone. The formation of the tetrahedral form of cobalt(II) chloride in a dilute acid–acetone medium was investigated by several experiments. Some were suggested by the report of DAY AND SELBIN[4], that the compound $2KCl–CoCl_2$ contains the tetrahedral ion $(CoCl_4)^{2-}$ in the crystalline solid and that when the solid dissolves in water it dissociates extensively into chloride ions, potassium ions, and hydrated cobalt(II) ions. Thus, excess of water seems to destroy the tetrahedral $(CoCl_4)^{2-}$ complex. To study the effects of dehydration, salting, and acid concentration on the color produced by the cobalt chloride ion, absorption spectra were prepared for the following solutions:

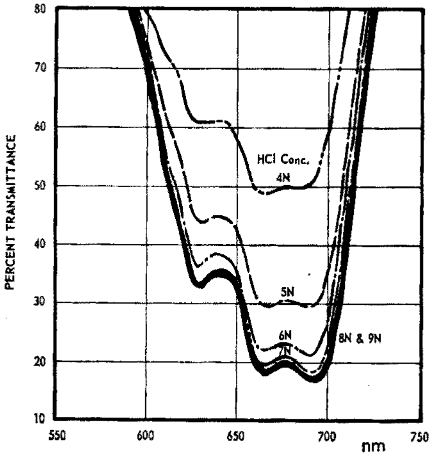


Fig. 3. Absorption spectra of cobalt in 70% acetone–30% hydrochloric acid solution (7.5 mg Co/100 ml; 1-cm cell).

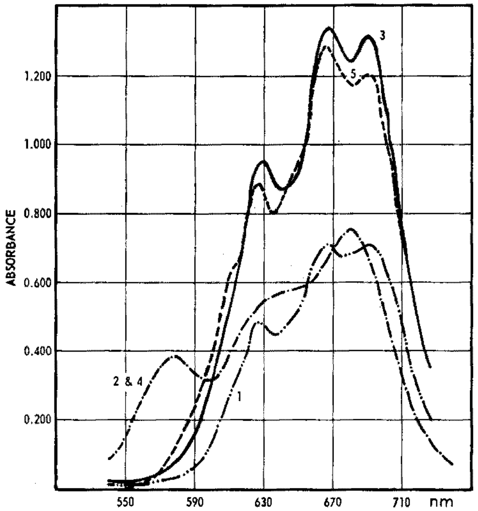


Fig. 4. Absorption spectra of cobalt in acetone and hydrochloric acid. For solution compositions relating to spectra 1–5, see text.

Solution 1: 15 mg of $CoCl_2$ in 100 ml 8 N hydrochloric acid,
Solution 2: 15 mg of dehydrated $CoCl_2$ in 100 ml of acetone,
Solution 3: 15 mg of dehydrated $CoCl_2$ in 70 ml of acetone and 30 ml of 8 N hydrochloric acid,
Solution 4: 15 mg of $CoCl_2$ dissolved in 100 ml of acetone saturated with aluminum chloride,
Solution 5: 15 mg of dehydrated $CoCl_2$ in 90 ml of acetone in which dry hydrogen chloride was absorbed to give a final volume of 100 ml.

The absorption spectra of these solutions are shown in Fig. 4. Solution 1 was run only as a reference. In solution 2, the familiar tetrahedral complex absorption peak is absent indicating that the presence of excess of chloride or hydrochloric acid is necessary to produce the complex. In solution 3, the mixture of acetone and hydrochloric acid is shown to both preserve the tetrahedral form of cobalt(II) chloride and increase the light absorption by the complex two-fold over that in 8 N hydrochloric acid alone. In solution 4, the spectrum of cobalt(II) chloride in acetone saturated with aluminum chloride is similar to that with 100% acetone. This definitely points to the fact that hydrogen ion is necessary in this system. As a final test, a spectrum was run with dry hydrogen chloride dissolved in 90% (v/v) acetone. Again, the tetrahedral form is in evidence but it does not absorb as strongly as in 70% (v/v) acetone–30% (v/v) 8 *N* hydrochloric acid. Thus, both hydrochloric acid and water are necessary for the maximum development of the tetrahedral cobaltous chloride complex in an acetone solution; the formula for the complex is probably H_2CoCl_4.

Determination of copper

During the investigation for cobalt, copper, which is quite often present as an alloying constituent along with cobalt, was also found to give an intensely colored yellow complex in the acetone–hydrochloric acid system. The distinct difference in colors produced by copper (yellow) and cobalt (blue) indicated that either could be determined in the presence of the other. The spectrum shown in Fig. 5 was obtained for 2 mg of copper and 7.5 mg of cobalt and verifies that cobalt can be measured at 628 nm and copper at 400 nm without mutual interference.

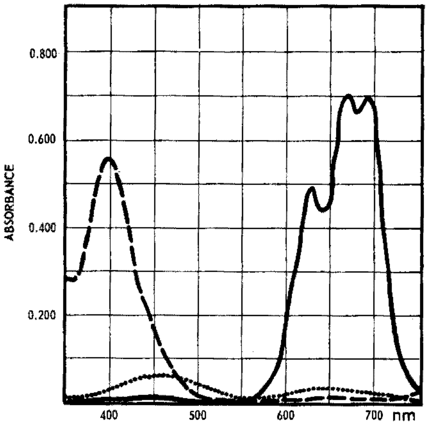


Fig. 5. Absorption spectra of copper, cobalt and chromium(III) in acetone–hydrochloric acid (70%–30% 8 *N*). (– – – –) 2.0 mg Cu; (———) 7.5 mg Co; (........) 10.0 mg Cr(III).

Standard conditions for copper. An investigation of various hydrochloric acid concentrations in 70% (v/v) acetone solution on the yellow copper–chloride complex showed that the color intensity from the complex increases with acidity and that careful control of acidity is required for accurate copper analysis. Table I shows this behavior. Since it is convenient to determine both cobalt and copper in the same sample solution, 8.0 *N* hydrochloric acid was also selected for use in the copper analysis. As a means of accurately controlling the acidity and of maintaining the integrity of the samples, samples were dissolved under reflux and then evaporated to 50 ml of constant boiling hydrochloric acid (6.1 *N*). The acidity was then adjusted to 8 *N* and final dilution made with 8 *N* hydrochloric acid.

Interferences in determination of cobalt

Table II summarizes the study of interferences in the determination of cobalt.

TABLE I

EFFECT OF ACIDITY ON THE ABSORBANCE OF 3 mg OF COPPER IN 70% ACETONE SOLUTIONS

HCl (N)	*Overall acidity (N)*	*Absorbance at 400 nm*
6.52	1.96	0.698
8.12	2.44	0.802
8.39	2.52	0.820
8.67	2.60	0.830
10.99	3.30	0.945

TABLE II

INTERFERENCES IN THE DETERMINATION OF COBALT

(Co 7.5 mg/100 ml)

Ion	*mg Present*	*Error in mg Co*	
		Blank corrected by standard procedure	*Uncorrected*
Cu(I)	100	0.00	0.00
Cu(II)	100	0.40	0.64
Cr(III)	100	0.34	5.24
Cr(VI)	100	0.00	0.00
Fe(II)	100	0.00	0.00
Fe(III)	100	0.00	0.00
Mo(VI)	100	0.00	0.00
Ni	100	0.00	0.33
V(V)	100	0.00	0.00
V(IV)	100	0.00	5.01
NO_3^-, SO_4^{2-}, PO_4^{3-}, F^-, ClO_4^-	1000	0.00	0.00

Very little interference was found from as much as 100 mg each of Fe(II) and (III), Mo(VI), V(V), Cu(I) and (II), Ni, and Cr(VI). Copper interfered slightly, but the only serious interferences were large amounts of Cr(III), V(IV), and Mo(V). The effect of 10.0 mg of chromium(III) is shown in Fig. 5.

Simple and rapid methods for eliminating these interferences were devised. The copper(II) interference was easily eliminated by reduction with tin(II) chloride as long as only small amounts of vanadium and molybdenum (less than 10 mg) were present. The tin(II) chloride was added to the sample after the addition of acetone. Chromium(III) in large concentrations presented the most serious interference; after the blank correction, 100 mg of chromium(III) was equivalent to 0.34 mg of cobalt. Chromium-bearing alloys low in copper (so that the copper(II) interference was not significant) could be oxidized with perchloric acid to eliminate any chromium(III) interference. This procedure also oxidized molybdenum and vanadium and eliminated their potential interferences. When molybdenum, which must be in its highest valency state, and copper, which must be in its lowest, were both present in quantities greater than 10 mg in the sample aliquot, the molybdenum had to be separated. A convenient molybdenum separation was provided by solvent extraction of molybdenum(VI) into amyl acetate from 8 *N* hydrochloric acid after oxidation with cerium-

(IV) ammonium nitrate to assure the proper valency state. Interference from copper could then be eliminated by reduction with tin(II) chloride.

Vanadium(IV) formed a green-colored complex that absorbed slightly at 628 nm. This interference was eliminated by either oxidizing with cerium(IV) ammonium nitrate to a yellow vanadium(V) complex that did not absorb at 628 nm, or measuring the vanadium(IV) absorbance at 760 nm (where Co, Cr, Ni, Fe and Cu(I) do not absorb) and applying a correction based on the known ratio of its absorbances at 628 and 760 nm. The blank solution containing water and the sample solutions containing 70% acetone gave different absorption ratios for vanadium(IV) at 628 and 760 nm; therefore, each had to be corrected separately. In a typical set of readings, for example, 50 mg of vanadium(IV) in 70% acetone gave a ratio of 0.69 for its absorbances at 628 and 760 nm; 50 mg of vanadium(IV) in water gave a ratio of 0.47 at the same wavelengths.

Interferences in determination of copper

The significant interferences in the analysis of copper were iron(III), which produced an intense yellow complex in the acetone–hydrochloric acid medium, and molybdenum which gave several different colors varying from orange to blue depending on which of its several unstable valency states was involved. The effect of 3 mg of iron(III), which gave an absorbance of about 0.54 under the standard conditions for the determination of copper, could not be compensated by a simple blank correction; 3 mg of molybdenum was also enough to give a serious interference.

Both iron and molybdenum, along with antimony and vanadium, can be separated rapidly by solvent extraction with amyl acetate from 8 *N* hydrochloric acid[5]. For complete extraction, the elements must be oxidized to their highest

TABLE III

ANALYSIS OF STANDARDS

Alloy		*No. of detns.*	*% Cobalt*		*Coeff. of variation (%)*
			Present	*Found*	
Cobalt					
Al–Co	prepared alloys nominal composition	2	0.50	0.50	—
Al–Co		2	1.00	0.99	—
Al–Co		2	1.50	1.52	—
Al–Co		2	2.00	2.03	—
Al–Co		8	10.	10.16	0.76
Al–Co		8	10.	9.37	0.47
NBS 153 (8.4 Mo, 4.1 Cr, 2.0 V, 1.6 W, 8.5 Co, 74 Fe)		10	8.45	8.43	0.64

NBS standard	*Composition*	*No. of detns.*	*% Copper*		*Coeff. of variation (%)*
			Present	*Found*	
Copper					
85a	Al, Cu	4	2.48	2.47	0.49
86c	Al, Cu, 0.9 Fe	4	7.92	7.85	0.68
162	Ni, Cu	6	28.93	28.96	0.17
164	22 Zn, 6 Al, 2.5 Fe, Cu	6	63.76	63.87	0.48

valency states. Cerium(IV) ammonium nitrate was used as the oxidizing agent; it gave no colorimetric interference since strong hydrochloric acid reduces it to cerium(III) which showed no absorbance at 400 nm.

Analysis of standards

To test the suitability of the methods, which were designed primarily for aluminum alloys, several aluminum alloys and NBS standards were analyzed for copper and cobalt (Table III). Based on the analyses of the NBS standards, the limit of error for a single determination of cobalt at the 95% confidence interval is ±1.3% with no bias; for copper, the corresponding value is 1.2% with no bias.

EXPERIMENTAL

Reagents and equipment

All chemicals were reagent grade, unless otherwise specified.

Hydrochloric acid 8 N. Dilute concentrated hydrochloric acid as necessary. A new bottle of concentrated acid which is normally assumed to be 12.1 *N* may vary from 11.9 *N* to 12.4 *N*. If this acid has been opened and exposed to the atmosphere on several occasions, the concentration will decrease considerably. Therefore, the concentration of the acid used to make the 8 *N* solution should be determined.

Cobalt standard solution. Dissolve 0.500 g of cobalt in 100 ml of 8 *N* hydrochloric acid. Evaporate the solution to 50 ml (this will yield 6.1 *N* hydrochloric acid), and adjust the acidity to 8 *N* hydrochloric acid with concentrated acid. Dilute the solution to 1 l with 8 *N* hydrochloric acid.

Copper standard solution. Dissolve 0.200 g of copper in 100 ml of 8 *N* hydrochloric acid. Evaporate the solution to 50 ml (6.1 *N* hydrochloric acid), and adjust the acidity to 8 *N* with concentrated acid. Dilute the solution to 1 l with 8 *N* hydrochloric acid.

Tin(II) chloride solution. Dissolve 20.0 g of tin(II) chloride in cold 8 *N* hydrochloric acid and dilute the solution to 100 ml with 8 *N* hydrochloric acid.

A Beckman DU Spectrophotometer equipped with 1-cm cuvettes was used. Separatory funnels (125 ml) had Teflon stopcocks.

Preparation of samples

With Table IV as a guide, select the proper sample weight, weigh the sample to the nearest 0.1 mg, and dissolve the sample as in either *A* or *B* below.

(*A*) For samples containing more than 5% of iron or copper, which can be lost by entrainment, place the sample in a 250-ml iodine flask fitted with a ground-glass joint. Add 100 ml of 8 *N* hydrochloric acid and attach a condenser. Reflux until the sample is in solution. If necessary, add 1–2 ml of nitric or hydrofluoric acid through the top of the condenser to promote dissolution. Alloys which react vigorously with hydrochloric acid must be dissolved slowly by adding the 8 *N* hydrochloric acid in increments through the top of the condenser.

(*B*) Samples containing only small amounts of iron or copper can be dissolved in 100 ml of 8 *N* hydrochloric acid in tall-form beakers covered with watch glasses.

After the samples are dissolved as in *A* or *B*, add 5 ml of 30% hydrogen peroxide and evaporate to 50 ml to obtain a solution 6.1 *N* in hydrochloric acid. Ad-

TABLE IV

SAMPLE PREPARATION GUIDE

Element	*Concn. (%)*	*Sample wt. (g)*	*Final dilution (ml)*	*Aliquot (ml)*
Cu	0.5	4.0	100	10
Cu	5.0	0.5	100	10
Cu	25.0	0.1	100	10
Cu	50.0	0.1	250	10
Co	0.5	1.0	Use entire sample	
Co	5.0	1.0	100	20–25
Co	25.0	1.0	100	5
Co	50.0	0.5	100	5

just the acidity to 8 *N* by adding concentrated hydrochloric acid. Then dilute to the selected volume with 8 *N* hydrochloric acid.

Determination of cobalt

Standard procedure. Pipette three aliquots containing up to 15 mg of cobalt into 100-ml volumetric flasks, and adjust their volume to 30 ml with 8 *N* hydrochloric acid. Add 65 ml of acetone to two of the aliquots and cool the solutions to room temperature. Dilute the solutions to volume with acetone and mix thoroughly. Dilute the third aliquot to 100 ml with water. This aliquot is the blank. Measure the absorbance of each solution at 628 nm against water as a reference. After subtracting the blank absorbance from the sample absorbance, convert to mg of cobalt from a previously prepared calibration curve.

Treatments for interferences. Samples low in copper (10 mg or less) and containing vanadium, molybdenum, and iron (10–100 mg). To each acidified aliquot (30 ml), add 1.0 g of solid cerium(IV) ammonium nitrate. Mix to dissolve and letst and for 5 min. Then dilute to volume with acetone, etc., as above.

Samples low in copper (10 mg or less) and containing chromium (50–100 mg). To each acidified aliquot, add 4 ml of perchloric acid and evaporate the solution to near dryness. Redissolve the residue in 30 ml of 8 *N* hydrochloric acid at room temperature and continue with the procedure.

Samples high in copper (10–100 mg) and low in vanadium, molybdenum and chromium (10 mg or less). After addition of 65 ml of acetone and cooling, add 1 ml of tin(II) chloride solution; then dilute to volume with acetone, etc., as above.

Samples high in copper (10–100 mg) and high in vanadium (10–100 mg). Proceed as described for samples low in vanadium, molybdenum and chromium, but finally measure the absorbances of the solutions at 760 nm to determine the interference of vanadium. Correct for interference with the following equation:

$$[\text{Sample OD at 628 nm} - (\text{Sample OD at 760 nm} \times 0.69)]$$
$$- [\text{Blank OD at 628 nm} - (\text{Blank OD at 760 nm} \times 0.47)]$$

Samples high in copper, iron, vanadium and molybdenum. After dissolution of the sample and adjustment of the acidity to 8 *N* hydrochloric acid, transfer the solution to a 125-ml separatory funnel, add 1 g of ammonium cerium(IV) nitrate and 50 ml of amyl acetate. Shake vigorously for 2 min and allow the layers to separate. Transfer the aqueous phase to a volumetric flask and wash the extract twice with 8 *N* hydrochloric acid. Transfer these washings to the volumetric flask and dilute to volume with 8 *N* hydrochloric acid. This extraction will remove iron, vanadium and molybdenum.

Determination of copper

Standard procedure. Pipette triplicate aliquots containing up to 2 mg of copper into 100-ml volumetric flasks. Adjust the volumes of two aliquots to 20 ml with 8 *N* hydrochloric acid, and add 75 ml of acetone. Adjust the volume of the third aliquot to be used as a blank to 19 ml with 8 *N* hydrochloric acid, and add 75 ml of acetone and 1 ml of 20% tin(II) chloride solution in that order. Cool the samples to room temperature, and adjust their volume to 100 ml with acetone. Mix the solutions thoroughly and measure, within 10 min, their optical densities at 400 nm against a water blank. Subtract the optical density of the blank from the optical density of the samples and convert the net optical density to mg of copper by reference to a previously prepared calibration curve.

Aliquots high in chromium, nickel and cobalt (50–100 mg) can be run by the above procedure. Aliquots high in iron (>3 mg) should be extracted with 50 ml of amyl acetate. Aliquots containing any molybdenum must be oxidized with cerium(IV) ammonium nitrate and extracted with 50 ml of amyl acetate; this will also extract vanadium quantitatively.

SUMMARY

Rapid methods have been developed for the direct measurement of cobalt and copper in various alloys. These spectrophotometric methods are based on measurement of the intensely colored complexes formed by cobalt and copper ions in an acetone–hydrochloric acid medium, at 628 and 400 nm, respectively. The cobalt method is highly selective; cobalt can be determined without interference from large quantities of iron, chromium, nickel, vanadium, molybdenum, and copper. In the determination of copper, only large quantities of iron, molybdenum, or vanadium interfere, but their interferences can be easily eliminated by a rapid solvent extraction procedure. The methods are sufficiently sensitive to determine 0.015% cobalt and 0.005% copper in aluminum alloys. Both elements can be determined with a limit of error of 1.2–1.3% at the 95% confidence interval.

RÉSUMÉ

Des méthodes rapides sont proposées pour des mesures directes de cobalt et de cuivre dans divers alliages. Ces procédés spectrophotométriques sont basés sur la mesure de complexes fortement colorés du cobalt et du cuivre formés en milieu acétone–acide chlorhydrique à 628 et 400 nm, respectivement. Le dosage du cobalt est très sélectif, sans interférence en présence de grandes quantités de fer, chrome, nickel, vanadium, molybdène et cuivre. Lors du dosage du cuivre, seules de grandes quantités de fer, de molybdène et de vanadium gênent; on peut éviter facilement ces interférences par une rapide extraction dans un solvant. On peut ainsi doser 0.015% de cobalt et 0.05% de cuivre dans des alliages d'aluminium, avec une limite d'erreur de 1.2–1.3%.

ZUSAMMENFASSUNG

Schnelle spektralphotometrische Methoden wurden zur direkten Bestimmung von Kobalt und Kupfer in verschiedenen Legierungen entwickelt. Die Methoden beruhen auf der Messung des intensiv gefärbten Komplexes, der vom Kobalt und Kupfer in acetonhaltiger Salzsäure bei 628 und 400 nm gebildet wird. Kobalt kann sehr empfindlich und ohne Störungen in grossen Mengen Eisen, Chrom, Nickel, Vanadin, Molybdän und Kupfer bestimmt werden. Bei der Bestimmung von Kupfer stören nur grosse Mengen Eisen, Molybdän oder Vanadin. Diese Störungen können leicht durch Flüssigextraktion eliminiert werden. Die Methoden sind geeignet, 0.015% Kobalt und 0.005% Kupfer in Aluminiumlegierungen zu bestimmen. Beide Elemente können mit einem Fehler von 1.2 bis 1.3% bei einem 95%igen Vertrauensbereich bestimmt werden.

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THE SOLVENT EXTRACTION OF THULIUM WITH ALIPHATIC MONOCARBOXYLIC ACIDS

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Some simple carboxylic acid extractions of rare-earth ions have been carried out previously. It has been shown that mixed naphthenic acids in such organic media as ethyl ether, 1-hexanol, and kerosine will extract rare-earth ions from aqueous solutions at appropriate pH values[1]. The slopes obtained for plots of the logarithm of the distribution (log D) against pH and for plots of log D against the logarithm of the naphthenic acid concentration in the organic phase (log $[HR]_o$) are *ca.* 3. The value of log D is dependent upon pH, naphthenic acid concentration, mole ratio of naphthenic acid to rare-earth ion, organic solvent, contact time, and temperature. Complexing ions such as ethylenediaminetetraacetate, diethylenetriaminepentaacetate, chloride, and sulfate shift the extraction toward higher pH.

Rare-earth mandelates have been extracted into 1-butanol, but the maximum D value is less than unity[2]. The lanthanides have been separated from thorium, scandium and uranium by extraction from a concentrated aqueous solution of ammonium nitrate into pure butyric acid; the separation is brought about by proper pH control[3]. The influence of the organic medium on the extraction of rare-earth ions with mixtures of 7-, 8-, and 9-carbon aliphatic monocarboxylic acids has been investigated[4]. The value of D decreases in the series: 1-heptanol, 1-decanol, 3-methyl-1-butyl acetate, 1,3-dimethylbenzene, dichlorodiethyl ether, carbon tetrachloride, kerosine. This series also shows a general decrease in hydrogen-bond formation potential.

The present paper reports an exploratory survey of the use of aliphatic monocarboxylic acids as extractants for rare-earth ions, thulium being taken as a representative rare earth. In addition, it sets out detailed studies on extractions with hexanoic acid which has been selected as a representative aliphatic monocarboxylic acid extractant.

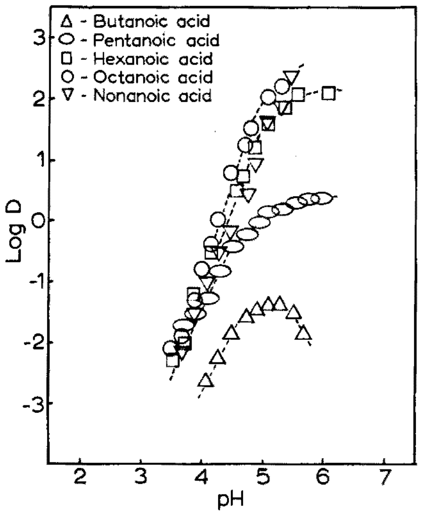
EXPERIMENTAL

In each distribution determination, a 20-ml bottle contained 8.00 ml of an aqueous phase and 8.00 ml of an organic phase. The aqueous phase was either $10^{-4.0}$ M or $10^{-8.0}$ M in thulium perchlorate labelled with thulium-170, was made up to an ionic strength of 0.10 with sodium perchlorate, and may have contained a given concentration of a water-soluble acid such as formic, acetic, or propionic acid. The organic phase consisted either of a pure carboxylic acid or of an organic solvent which may have contained a known concentration of a carboxylic acid. All aqueous phases were pre-saturated with the proper organic phase, and all organic phases were pre-saturated with a proper aqueous phase containing no thulium. The aqueous pH was adjusted with sodium hydroxide and perchloric acid solutions.

After preparation, the 20-ml bottles were rotated on a turning bar for 4 days at 27 °. This period of time was demonstrated to be quite sufficient for the attainment of equilibrium. The bottles were then centrifuged, the pH value of the aqueous phase was determined, the phases were sampled with 100-μl pipettes, the samples were dried on planchets, and the planchets were counted with conventional β-detection apparatus. Distribution coefficient (D) values were obtained by dividing the organic count by the aqueous count. Previous investigations had demonstrated that no self-absorption corrections were needed for either phase.

RESULTS

Figure 1 presents data for the extraction of $10^{-8.0}$ M thulium into 1.0 M solutions of various carboxylic acids in 4-methyl-2-pentanone. Extractions with 1.0 M formic, acetic, and propanoic acids and with pure 4-methyl-2-pentanone gave no log D values greater than -3.00, and so they are not shown in the figure. Figure 2 depicts the results obtained when chloroform was employed as the organic phase. Again, 1.0 M formic, acetic, and propanoic acids as well as pure chloroform gave log D values less than -3.00.



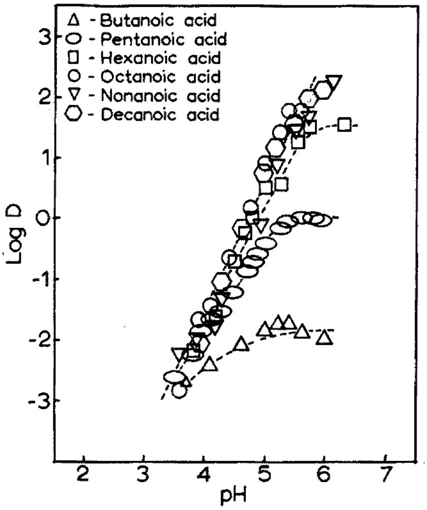
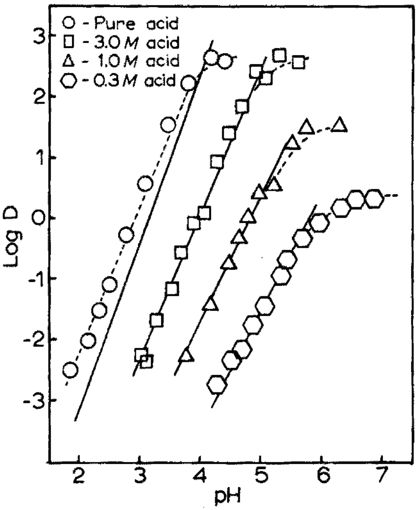


Fig. 1. Extraction of $10^{-8.0}$ M thulium into 4-methyl-2-pentanone containing 1.0 M carboxylic acid.

Fig. 2. The extraction of $10^{-8.0}$ M thulium into chloroform containing 1.0 M carboxylic acid.

Figure 3 shows the experimental data arrived at when pure hexanoic acid and various concentrations of hexanoic acid in 4-methyl-2-pentanone were used for



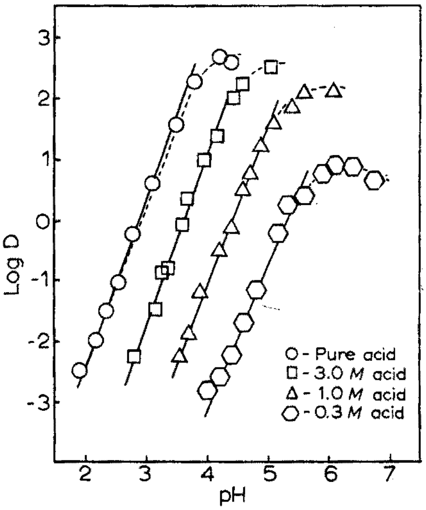


Fig. 3. Extraction of 10^{-8} M thulium into 4-methyl-2-pentanone containing hexanoic acid. (———) Theoretical curves (see text); (– – – – –) experimental curves.

Fig. 4. Extraction of 10^{-8} M thulium into chloroform containing hexanoic acid. (———) Theoretical curves (see text); (– – – – –) experimental curves.

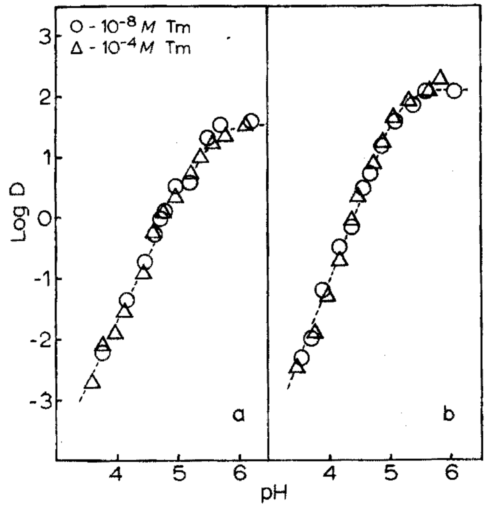


Fig. 5. Extractions of thulium into (a) 4-methyl-2-pentanone and (b) chloroform containing 1.0 M hexanoic acid.

extraction of $10^{-8.0}$ M thulium. Figure 4 shows the results obtained for similar systems with chloroform solutions of hexanoic acid. Figure 5 illustrates the effects of altering the thulium concentration. Results for both $10^{-4.0}$ and $10^{-8.0}$ M thulium extracted into 1.0 M hexanoic acid in both 4-methyl-2-pentanone and chloroform are given.

INTERPRETATION

Figures 1 and 2 illustrate the generally expected tendency as larger and larger molecular weight acids are employed. The slight differences evidenced in the higher-weight acids are probably due to variations in the organic–aqueous partition constants (P) and in the organic dimerization constants (C).

In the 4-methyl-2-pentanone systems, which are shown in Fig. 3, the hexanoic acid is essentially in the monomeric form in the organic phase as is reflected by the negligible dimerization constant (C) measured by SAWHNEY[5]. The total hexanoic acid concentration $[HR]_t$ at any given pH value is given by $[HR]_t = [HR]_o + [HR] + [R]$, where $[HR]_o$ is the monomer concentration in the organic phase, $[HR]$ is the monomer concentration in the aqueous phase, and $[R]$ is the hexanoate ion concentration in the aqueous phase. Substituting a value of $10^{4.9}$ for the association constant K of the acid[5], and a value of $10^{1.6}$ for the partition constant[5], one obtains the relation:

$$[HR]_o = [HR]_t (1 + P^{-1} + K^{-1}P^{-1}[H]^{-1})^{-1} = [HR]_t (1 + 10^{-1.6} + 10^{-6.5}[H]^{-1})^{-1}.$$

Using this equation to calculate $[HR]_o$ at various pH values, and fitting the data of Fig. 3 to the best mathematical expression, one arrives at

$$D^{-1} = 10^{13.2}\,[HR]_o^{-4}[H]^3 + 10^{9.4}\,[HR]_o^{-4}[H]^2.$$

The solid lines in Fig. 3 were obtained with this expression.

If it is assumed that the predominant species in the organic phase could be represented as $TmR_3(HR)_a$ and that the predominant species in the aqueous phase could be represented as $TmR_r(OH)_h$, then

$$D^{-1} = [TmR_r(OH)_h][TmR_3(HR)_a]_o^{-1}.$$

Making appropriate substitutions, one can write this expression as

$$D^{-1} = K^{3-r}P^{3+a-r}C_{rh}W^hK_{3a}^{-1}P_{3a}^{-1}[HR]_o^{r-3-a}[H]^{3-r-h}$$

where K is the acid association constant, P is the organic–aqueous acid partition constant, C_{rh} is the aqueous association constant of $TmR_r(OH)_h$, W is the ion product of water, K_{3a} is the association constant of $TmR_3(HR)_a$, and P_{3a} is the organic–aqueous partition constant of $TmR_3(HR)_a$. When this theoretical expression is compared with the equation derived from the curve fitting, the following may be recognized: an organic species for the first and second terms of $TmR_3(HR)$, an aqueous species for the first term of Tm^{3+}, an aqueous species for the second term of $TmOH^{2+}$, an overall equation of

$$D^{-1} = K^3P^4K_{31}^{-1}P_{31}^{-1}[HR]_o^{-4}[H]^3 + K^3P^4C_{01}WK_{31}^{-1}P_{31}^{-1}[HR]_o^{-4}[H]^2,$$

a log $K_{31}P_{31}$ value of $10^{7.9}$, and a log C_{01} value of $10^{10.2}$.

Application of the expression from the curve fitting to the pure hexanoic acid extraction produces a curve which deviates considerably from the experimental one. This is not surprising since the hexanoic acid probably exists as an acid-solvent adduct in the 4-methyl-2-pentanone but as a dimer in the pure acid. In addition, the extracting species in the 4-methyl-2-pentanone system is $TmR_3(HR)$ probably with several molecules of the solvent attached, whereas the extracting species in the pure-acid system is probably $TmR_3(HR)_a$ with an a value greater than unity.

In the chloroform systems, which are shown in Fig. 4, the hexanoic acid in the organic phase is predominantly in the dimeric form, as is indicated by the dimerization constant (C) of $10^{1.6}$ as measured by SAWHNEY[5]. The total hexanoic acid concentration $[HR]_t$ at any given pH value is expressable as $[HR]_t = 2\,[H_2R_2]_o + [HR]_o + [HR] + [R]$, where $[H_2R_2]_o$ is the dimer concentration in the organic phase and the other symbols have their previous significances. With a value of $10^{4.9}$ for the acid association constant (K), $10^{0.9}$ for the partition constant (P)[5], and $10^{1.6}$ for the dimerization constant (C)[5], the following equation can be written:

$$[HR]_t = 2\,[H_2R_2]_o + (C^{-1/2} + C^{-1/2}P^{-1} + C^{-1/2}K^{-1}P^{-1}[H]^{-1})\,[H_2R_2]_o^{1/2}$$

$$= 2\,[H_2R_2]_o + (10^{-8.0} + 10^{-1.7} + 10^{-6.6}[H]^{-1})\,[H_2R_2]_o^{1/2}.$$

This relation was used to calculate $[H_2R_2]_o$ at various pH values. Then the data of Fig. 4 were fitted to the best mathematical expression which turned out to be

$$D^{-1} = 10^{11.3}[H_2R_2]_o^{-4}[H]^3 + 10^{7.0}[H_2R_2]_o^{-4}[H]^2.$$

The solid lines in Fig. 4 were calculated from this expression.

If it is assumed that the predominant species in the organic phase could be represented as $TmR_3(HR)_a$ and that the prevailing species in the aqueous phase could be represented as $TmR_r(OH)_h$, then,

$$D^{-1} = K^{3-r}P^{3+a-r}C_{rh}W^hK_{3a}^{-1}P_{3a}^{-1}C^{(3+a-r)/2}[H_2R_2]_o^{(r-3-a)/2}[H]^{3-r-h},$$

where the symbols are as previously stated. When this theoretical expression is compared with the equation derived from the experimental data, the following may be recognized: an organic species for the first and second terms of $TmR_3(HR)_5$, an aqueous species for the first term of Tm^{3+}, an aqueous species for the second term of $TmOH^{2+}$, and an overall equation of

$$D^{-1} = K^3P^8K_{35}^{-1}P_{35}^{-1}C^4[H_2R_2]_o^{-4}[H]^3 + K^3P^8C_{01}WK_{3a}^{-1}P_{3a}^{-1}C^4[H_2R_2]_o^{-4}\,[H]^2,$$

with a $K_{35}P_{35}$ value of $10^{7.9}$, and a C_{01} value of $10^{9.7}$.

When the expression derived from curve fitting of the experimental chloroform-system data is applied to the pure hexanoic acid extraction, a curve which fits the pure hexanoic acid data very closely is obtained. This curve is shown by a solid line in Fig. 4. The fit probably indicates that the species extracting into the pure acid is similar to the species extracting into chloroform solutions of the acid, namely, $TmR_3(HR)_5$. Such a formula evidences a coordination number of at least 8. This is not unusual since rare-earth ions with coordination numbers of 8 and greater are now well known[6].

The assumption has been made in all the above considerations that no polymerization of either the predominant aqueous or organic metal-bearing species is occurring. This supposition appears to be warranted in view of the lack of dependency of extraction upon the thulium concentration as shown in Fig. 5.

The values for the first-hydrolysis constant of the thulium(III) ion obtained in these two systems, $10^{10.2}$ and $10^{9.7}$, seem to be high in comparison with other rare-earth first-hydrolysis constants. Values[7] for lanthanum(III) range from $10^{3.9}$ to $10^{8.4}$ in various aqueous media, for cerium(III) $10^{5.0}$, for praseodymium(III) $10^{5.5}$, and for lutetium(III) $10^{7.4}$. Values[7] for scandium(III) range from $10^{8.9}$ to $10^{10.2}$ and for yttrium(III) from $10^{5.0}$ to $10^{7.0}$. At first, it might be thought that the discrepancy could be assigned to slight errors in the constants K, P, and C which are magnified by raising them to higher powers. However, this cannot be maintained since the constants in the first and second terms of the empirical equations differ only by $C_{01}W$ causing everything else (for example, for the chloroform system $K^3P^8K_{35}^{-1}P_{35}^{-1}C^4$ and for the 4-methyl-2-pentanone system $K^3P^4K_{31}^{-1}P_{31}^{-1}$) to cancel out. Thus small errors in K, P, and C should not affect the results. It is possible that the presence of organic solvent in the aqueous phases could alter the constant C_{01}, this being one of the difficulties encountered in the use of solvent extraction for association ion-constant studies[8]. It is interesting to note that a higher C_{01} value for scandium(III) was also obtained by a solvent extraction method[9]. Because of the several difficulties with extraction techniques, the authors tend to trust the potentiometrically determined values more than those obtained by extraction.

SUMMARY

The extraction of 10^{-4} and 10^{-8} M thulium(III) into 4-methyl-2-pentanone and chloroform containing aliphatic monocarboxylic acids has been studied with formic through decanoic acids. Extraction tends to increase with acid molecular weight, acid concentration, and pH up to about 6. Detailed studies with hexanoic acid indicate that the species extracting into 4-methyl-2-pentanone is $TmR_3(HR)$ and the species extracting into chloroform is $TmR_3(HR)_5$. In both cases the predominant aqueous species are Tm^{3+} and $TmOH^{2+}$. From the data first hydrolysis constants of Tm^{3+} have been calculated to be $10^{10.2}$ and $10^{9.7}$, these values being larger than those expected from previous rare-earth hydrolysis data.

RÉSUMÉ

Une étude a été effectuée sur l'extraction du thulium(III) (10^{-4} et 10^{-8} M) dans la méthyl-4-pentanone-2 et le chloroforme, renfermant des acides aliphatiques monocarboxyliques. L'extraction tend à augmenter avec le poids moléculaire des acides, la concentration en acide et le pH jusqu'à environ 6. Avec l'acide hexanoïque, on extrait $TmR_3(HR)$ dans la méthyl-4-pentanone-2 et $TmR_3(HR)_5$ dans le chloroforme. Dans les deux cas les particules prédominantes dans l'eau sont Tm^{3+} et $TmOH^{2+}$. Les constantes d'hydrolyse de Tm^{3+} calculées sont $10^{10.2}$ et $10^{9.7}$. Ces valeurs sont plus grandes que prévues d'après les valeurs d'hydrolyse des terres rares.

ZUSAMMENFASSUNG

Die Extraktion von 10^{-4} und 10^{-8} M Thulium(III) mit 4-Methyl-2-pentanon and Chloroform, das aliphatische Monocarbonsäuren enthält (Ameisen- bis Dekansäure), wurde untersucht. Die Extraktion steigt mit dem Molekulargewicht der Säure, der Säurekonzentration und dem pH-Wert bis zum Wert 6. Genauere Untersuchungen mit Hexansäure zeigen, dass die Spezies, welche mit 4-Methyl-2-Pentanon extrahiert werden, $TmR_3(HR)$ und dass die Spezies, welche mit Chloroform extrahiert werden, $TmR_3(HR)_5$ sind. In beiden Fällen sind die bevorzugten wässrigen Spezies Tm^{3+} und $TmOH^{2+}$. Aus diesen Daten wurden die ersten Hydrolyse-Konstanten des

Tm^{3+} zu $10^{10.2}$ und zu $10^{9.7}$ berechnet. Diese Werte sind grösser als diejenigen, welche aus früheren Hydrolysedaten Seltener Erden ermittelt wurden.

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VOLTAMMETRY OF THE NEPTUNYL GLUTARATE COMPLEX AT THE ROTATING GLASSY CARBON ELECTRODE*

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Protactinium(V) glutarate is the only glutarate complex of the actinide rare earths that has been investigated. KOLARICH *et al.*[1] used solvent extraction for this investigation and determined that only a small percentage of the protactinium(V) present complexes with the glutaric acid. The acetate complex of the neptunyl ion has been investigated by MEFOD'EVA *et al.*[2] and the phthalic acid and 5-sulfosalicylic acid complexes by EL-EZABY[3]. In both instances, spectrophotometric methods were used. In this laboratory, several neptunyl complexes have been investigated by means of voltammetry[4–7].

This paper describes a voltammetric investigation of the neptunyl glutarate complex at the rotating glassy carbon electrode.

EXPERIMENTAL

Apparatus

All voltammograms were obtained at 25° with a Sargent Model XXI recording polarograph. The applied potential was monitored by a Hewlett Packard Model DY-2401C integrating digital voltmeter. None of the measurements were damped. The electrolysis cell, the glassy carbon electrode (G.C.E.), the electrode mounting, and the cleaning of the electrode have been described[4,8]. The pH values of the solutions were measured with a Sargent Model DR pH meter and a glass electrode. The pH was adjusted with perchloric acid or sodium hydroxide.

The conductometric titrations were performed with a YSI Model 31 (Yellow Springs Instrument Co., U.S.A.) line-operated conductivity bridge. The amperometric titrations were performed with the Sargent Model XXI recording polarograph and a 10-ml Sargent Model C automatic constant-rate burette.

A Cannon-Fenske-Ostwald viscometer (Cannon Instrument Co., U.S.A.) was used to obtain the viscosity values.

Reagents

The preparation and standardization of the neptunium(VI) and the neptunium(V) stock solutions have been described[7]. The disodium glutarate stock solution was prepared by neutralizing glutaric acid (J. T. Baker Chemical Co., U.S.A.) with an equivalent amount of sodium hydroxide. The solution was standardized by an am-

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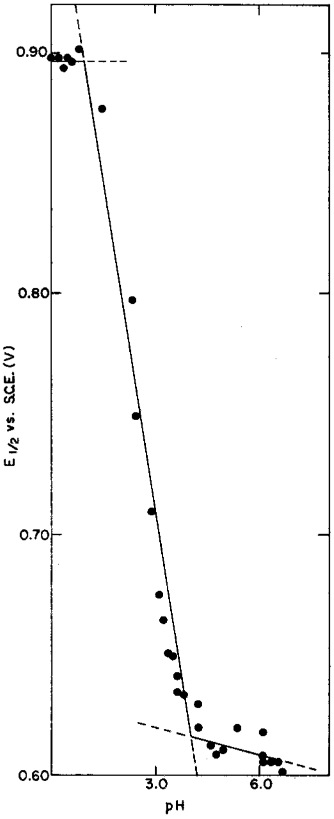
* Work performed under U. S. Atomic Energy Commission Contract AT(29-1)-1106.

perometric titration against an iron(III) solution whose concentration had been determined by controlled-potential coulometry. All other chemicals were reagent grade and prepared in the usual manner. Purified nitrogen was used to deaerate the test solutions when necessary.

DISCUSSION AND RESULTS

The effect of changes in acidity on the half-wave potential and on the limiting current of the neptunium(VI) glutarate complex was determined in solutions which were $7.00 \cdot 10^{-4}$ *M* in neptunium(VI), 0.676 *M* in disodium glutarate and 0.5 *M* in sodium perchlorate. The influence of the pH on the half-wave potential is apparent in a plot of half-wave potential *versus* pH (Fig. 1). The plot can be divided into three straight line portions, corresponding to the pH ranges 0.0–1.0, 1.0–4.0 and 4.0–6.6. In the pH range 1.0–4.0 the half-wave potential is a function of the pH, and the slope can be represented by the equation:

$$E_{\frac{1}{2}} = 0.991 - 0.093 \text{ pH}$$



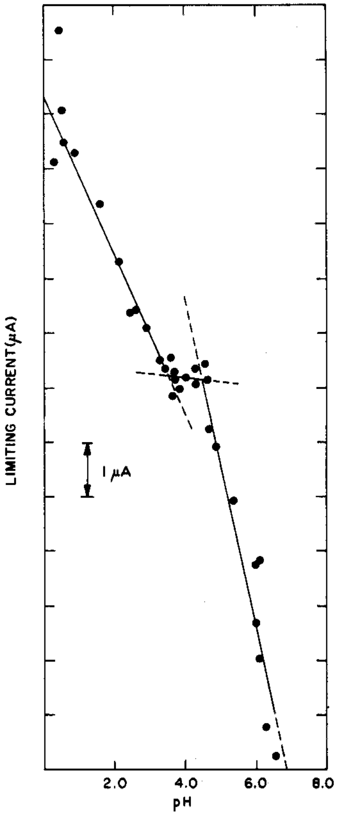


Fig. 1. Variation of the half-wave potential with pH.

Fig. 2. Variation of the limiting current with pH.

This indicates that three hydrogen ions are involved in the reduction of two neptunium(VI) ions in this pH range.

The effect of pH on the limiting current for the complex in the above solution is shown in Fig. 2. The limiting current is a function of the hydrogen ion in the pH ranges 0.0–3.5 and 4.5–6.6, indicating that complex species with changing composition exist in these pH ranges. In the pH range 0.0–3.5 the decrease in the limiting current would indicate that the ligand species is changing from the hydrogen glutarate form to the glutarate form. In the pH range 3.5–4.5 the limiting current is constant and independent of the pH, indicating that a complex species with a constant composition exists in this pH range. As the pH is increased further, the limiting current again decreases indicating the competition between the hydroxyl ions and the glutarate ions for the neptunium(VI).

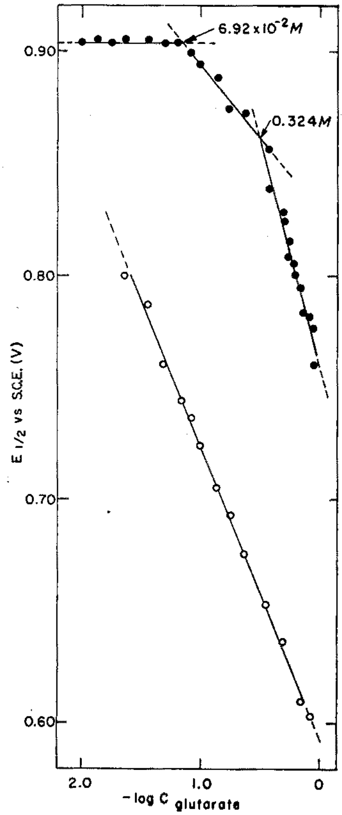


Fig. 3. Variation of half-wave potential with glutarate concentration. (●) pH 2.50; (○) pH 5.50.

Effect of glutarate concentration

The effects of changes in the disodium glutarate concentration on the half-wave potential of the neptunyl glutarate complex were determined in solutions $7.00 \cdot 10^{-4}$ *M* in neptunium(VI), and 0.5 *M* in sodium perchlorate at pH 2.50 and pH 5.50. At pH 2.50 the half-wave potential is independent of the glutarate concentration when the glutarate concentration is less than $6.92 \cdot 10^{-2}$ *M* (Fig. 3). In the glutarate concentration range from $6.92\cdot10^{-2}$ *M* to 1.01 *M*, the half-wave potential is a function of the glutarate concentration. When the concentration of the glutarate is less than $6.92\cdot10^{-4}$ *M*, the half-wave potential has an average value of 0.901 V *versus* S.C.E. which compares very favorably with the potential reported for the reduction of non-complexed neptunium(VI)[8–10]. This would indicate that either no complexation has taken place or that the dissociation constant of the neptunyl glutarate complex is equal to the dissociation constant of the neptunium(V) glutarate complex.

In the glutarate concentration range $6.92\cdot10^{-2}$–0.324 *M*, the slope of the plot is −0.066 V which indicates that neptunium(VI) has one more glutarate ligand bound to it than does neptunium(V). The slope of the plot is −0.197 V in the glutarate concentration range 0.324–1.01 *M*, which would indicate that neptunium(VI) has three more glutarate ligands bound to it than does neptunium(V).

Reversibility of the reduction of neptunium(VI) was demonstrated by the value of the slopes for the plots of $\log i/(i_l-i)$ *versus* E_{RGC}. The average value of these slopes in the glutarate concentration range $1.01\cdot10^{-2}$–$6.92\cdot10^{-2}$ *M* was 0.0639 V. This compares well with the theoretical value of 0.0591 V for a one-electron, reversible reduction. In the glutarate concentration ranges $6.92\cdot10^{-2}$–0.324 *M* and 0.324–1.01 *M*, the average values of the slopes of the plots were 0.0583 V and 0.0580 V, respectively, which agree very well with the theoretical value for a one-electron, reversible reduction.

To confirm the reversibility of the electrode reaction, solutions were prepared which were $7.00\cdot10^{-4}$ *M* in neptunium(V), and 0.5 *M* in sodium perchlorate with various concentrations of glutarate at pH 2.50. The neptunium(V) in these solutions was oxidized, and the half-wave potential of the anodic waves was compared with the half-wave potential of the cathodic waves (Table I). The anodic half-wave potential compares fairly well with the cathodic half-wave potential. This indicates that the electrode reduction of the neptunium(VI) in the glutarate concentration ranges $1.01\cdot10^{-2}$–$6.92\cdot10^{-2}$ *M*, $6.92\cdot10^{-2}$–0.324 *M*, and 0.324–1.01 *M* in the pH range 1.0–4.0 is reversible.

TABLE I

COMPARISON OF ANODIC HALF-WAVE POTENTIAL WITH CATHODIC HALF-WAVE POTENTIAL AT VARIOUS GLUTARATE CONCENTRATIONS AT pH 2.50 AND 5.50

$Na_2C_5H_6O_4$ *concn. (moles/l)*	*pH 2.50*		*pH 5.50*	
	$(E_{\frac{1}{2}})_c$ *vs. S.C.E. (V)*	$(E_{\frac{1}{2}})_a$ *vs. S.C.E. (V)*	$(E_{\frac{1}{2}})_c$ *vs. S.C.E. (V)*	$(E_{\frac{1}{2}})_a$ *vs. S.C.E. (V)*
$1.01\cdot10^{-2}$	0.904	0.908		
$2.37\cdot10^{-2}$			0.800	0.842
$3.78\cdot10^{-2}$	0.904	0.909		
$5.07\cdot10^{-2}$			0.761	0.772
0.101	0.893	0.902	0.726	0.733
0.237	0.870	0.881		
0.507	0.821	0.840	0.636	0.647
1.01	0.760	0.772	0.595	0.604

At pH 5.50 the plot of the logarithm of the glutarate concentration *versus* the half-wave potential (Fig. 3) revealed that the half-wave potential is a function of the glutarate concentration. In the glutarate concentration range $5.07\cdot10^{-2}$–1.01 *M*, the slope of the plot is -0.129 V which would indicate that neptunium(VI) has two more ligands bound to it than does neptunium(V).

Reversibility of the reduction of neptunium(VI) in the glutarate concentration range $5.07 \cdot 10^{-2}$–1.01 *M* was demonstrated by the value of the slopes for the plots of $\log i/(i_1 - i)$ *versus* E_{RGC}. The average value of these slopes was 0.0573 V. This compares fairly well with the theoretical value of 0.0591 V for a one-electron, reversible reduction. To confirm the reversibility of the electrode reaction, experiments were made as described above, but at pH 5.5 (Table I). Again, the anodic and cathodic half-wave potentials agree fairly well for higher glutarate concentrations, indicating that the electrode reaction in this range over the pH range 4.0–6.6 is also reversible. However, in the glutarate range $1.69 \cdot 10^{-2}$–$5.07 \cdot 10^{-2}$ *M*, the slope of the $\log i/(i_1 - i)$ *versus* E_{RGC} plots varied from 0.090 to 0.070 V, which are not in agreement with the theoretical value. Another indication of the irreversibility of the electrode reaction in this glutarate concentration range is the non-agreement of the anodic and cathodic half-wave potentials (Table I).

When the pH was adjusted in the range 4.0–6.6, the solutions came to equilibrium in 1–2 min. In the pH range 1.0–4.0, however, 5–15 min was required for the solutions to come to equilibrium after an addition of acid or alkali. The reason for this slowness in reaching equilibrium is not clear.

Composition of the neptunyl glutarate complex

Conductometric titrations were used to determine the metal–ligand ratio; 5.0 ml of $17.39 \cdot 10^{-3}$ *M* neptunium(VI) solution were diluted to 350 ml with water, and the resultant was titrated with $34.8 \cdot 10^{-3}$ *M* disodium glutarate solution. The titration curves (Fig. 4) show that when neptunium(VI) is in excess, the metal–ligand ratio of the complex formed is 1:1, and is 1:2 and 1:3 when the glutarate is in excess. To confirm the conductometric results, amperometric titrations were performed. The results of these titrations are shown in Fig. 5, and indicate only the maximum metal–ligand ratio. The maximum ligand ratio found confirms the conductometric results.

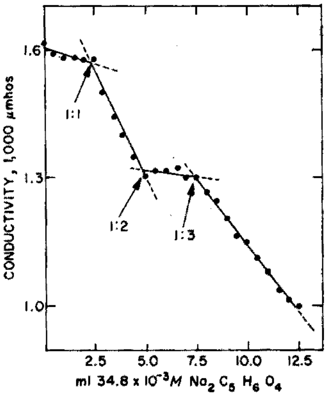


Fig. 4. Conductometric titrations.

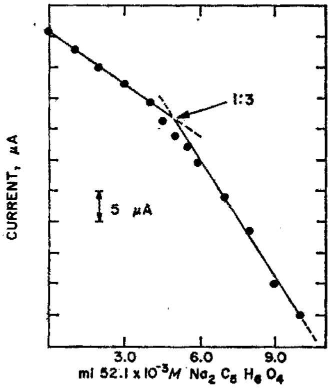


Fig. 5. Amperometric titrations. 5 ml of $17.39 \cdot 10^{-3}$ *M* neptunium(VI), 10 ml of 2.5 *M* $NaClO_4$, 10 ml water.

Electrode reactions

Based on the foregoing data and discussions, the electrode reactions are postulated as follows when the disodium glutarate concentration is greater than 0.324 *M*. The glutarate ion is designated as A^{2-}:

$\text{pH} < 0.1$

$NpO_2^{2+} + e^- \rightarrow NpO_2^+$

$\text{pH} > 1.0$, but < 3.5 and $q = p - 3$

$2\ NpO_2(HA)_3^- + 3\ H^+ + 2\ e^- \rightarrow 2\ NpO_2^+ + 3\ H_2A + 3\ HA^-$

$\text{pH} > 3.5$, but < 4.0 and $q = p - 3$

$2\ NpO_2A_3^{4-} + 3\ H^+ + 2\ e^- \rightarrow 2\ NpO_2^+ + 3\ HA^- + 3\ A^{2-}$

$\text{pH} > 4.0$, but < 4.5 and $q = p - 2$

$NpO_2A_3^{4-} + e^- \rightarrow NpO_2A^- + 2\ A^{2-}$

$\text{pH} > 4.5$, but < 6.6 and $q = p - 2$

$NpO_2(OH)A_3^{5-} + e^- \rightarrow NpO_2(OH)A^{2-} + 2\ A^{2-}$

Diffusion coefficient

The diffusion coefficient of the neptunium(VI) glutarate complex was determined at 25° in solutions which were $7.00 \cdot 10^{-4}$ *M* in neptunium(VI), 0.5 *M* in sodium perchlorate, and 0.676 *M* in disodium glutarate at pH 3.1 and pH 5.3, by means of the following equation[11]:

$$D^{\frac{2}{3}} = \frac{i_1 v^{\frac{1}{6}}}{1.500 \cdot 10^5\ n\ ACN^{\frac{1}{2}}}$$

where i_1 = limiting current (μA), v = kinematic viscosity, n = number of Faradays, A = electrode area (cm²), C = concentration (mmoles/l), N = number of revolutions/sec. The value for the diffusion coefficient was $0.21 \cdot 10^{-5}$ cm²/sec at pH 3.1 and $0.15 \cdot 10^{-5}$ cm²/sec at pH 5.3.

Stability constant

The stability constant of the neptunium(VI) glutarate complex ion can be calculated from the equation:

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{0.0591}{n} \log K_c - (p - q)\frac{0.0591}{n} \log C_x$$

The value of $(E_{\frac{1}{2}})_c$, 0.632 V *versus* S.C.E., was obtained by extrapolating the pH range 4.0–6.6 (Fig. 1) to pH zero. The value for the stability constant was found to be $1.6 \cdot 10^{-5}$.

SUMMARY

The voltammetry of the neptunyl glutarate complex was investigated over widely varying conditions of ligand concentration and pH. A reversible, one-electron wave was obtained in nearly all glutarate concentration ranges investigated over the pH range 0.0–6.6. The half-wave potential was independent of the pH in the ranges 0.0–1.0 and 4.0–6.6, but was a function of the pH in the range 1.0–4.0. The maximum metal–ligand ratio was found to be 1:3 by conductometric and amperometric titrations. The diffusion coefficient was $0.21 \cdot 10^{-5}$ cm^2/sec at pH 3.1 and $0.15 \cdot 10^{-5}$ cm^2/sec at pH 5.3. The stability constant of the neptunyl glutarate complex was determined as $1.6 \cdot 10^{-5}$.

RÉSUMÉ

La voltammétrie du complexe neptunylglutarate est examinée en fonction de la concentration de ligand et du pH. Une onde réversible à un électron est obtenue à presque toutes les concentrations pour des pH de 0.0 à 6.6. Le potentiel de demi-vague est indépendant du pH entre 0.0–1.0 et 4.0–6.6; il est fonction du pH entre 1.0 et 4.0. Le rapport maximum métal–ligand trouvé par titrages conductométrique et ampérométrique est de 1:3. Le coefficient de diffusion est de $0.21 \cdot 10^{-5}$ cm^2/sec au pH 3.1 et $0.15 \cdot 10^{-5}$ cm^2/sec au pH 5.3. La constante de stabilité du complexe neptunylglutarate est de $1.6 \cdot 10^{-5}$.

ZUSAMMENFASSUNG

Die Voltametrie des Neptunyl-Glutarat-Komplexes wurde über einen weiten Bereich der Ligandenkonzentration und des pH-Wertes untersucht. Eine reversible Einelektronenstufe wurde bei nahezu allen untersuchten Glutaratkonzentrationen im pH-Bereich von 0–6.6 erhalten. Das Halbstufenpotential war unabhängig vom pH im Bereich von 0–1.0 und 4.0–6.6. Das Maximum des Metall–Liganden-Verhältnisses wurde durch konduktometrische und amperometrische Titrationen mit 1:3 gefunden. Die Diffusionskoeffizienten betrugen 0.21×10^{-5} cm^2/sec beim pH 3.1 und 0.15×10^{-5} cm^2/sec beim pH 5.3. Die Stabilitätskonstante des Neptunyl-Glutaratkomplexes wurde mit 1.6×10^{-5} bestimmt.

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FLUORESCENCE AND METALLIC VALENCY STATES

PART II. DETERMINATION OF MANGANESE

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The chelates of paramagnetic metal ions are non-fluorescent and fluorescence methods for determining such metal ions are based on fluorescence quenching rather than upon fluorescence development. A program has been initiated to investigate the use of variable metallic valency states to form species useful in the analysis of metals through either the formation of stable, fluorescent diamagnetic chelates, or the specific oxidative action of higher valent metal ions upon selected organic molecules to give fluorescent reagent products[1]. The present paper describes the spectrofluorimetric determination of trace amounts of manganese; the method involves the oxidative reaction of permanganate, formed by catalytic oxidation of manganese(II), upon oxine-5-sulphonic acid to produce a highly fluorescent species.

The high sensitivity and selectivity which can be obtained through catalytic reactions has been known for many years[2-4]. The catalytic oxidation of manganese to permanganate, by silver(I) and persulphate, was recommended by MARSHALL[5] for the absorptiometric determination of manganese and it was included among the standard methods for iron and steel analysis in 1912; the method was later criticized for its highly erratic nature and uncertainty. A detailed study of the method was done by NYDAHL[6] and excellent results for determining traces of manganese are obtained by his procedure; with a 10-cm cell, however, the lowest limit for manganese is 55 p.p.b. and, at such concentrations, photometric readings are very low. The fluorimetric method described in this paper is at least 100 times more sensitive and 5 p.p.b. of manganese can be determined with confidence in a 1-cm cell.

EXPERIMENTAL

Apparatus, reagents and solutions

An Aminco Bowman Spectrophotofluorimeter was used for obtaining excitation and emission spectra. Intensity measurements at 485–490 nm were uncorrected.

8-Hydroxyquinoline-5-sulphonic acid was recrystallized several times from water and dried at 110°; the melting point was 320–323° with decomposition. Reagent solutions (10^{-3} *M*) were freshly prepared in doubly distilled water.

Stock silver solutions (0.1 *M*) were prepared from Analar silver nitrate and were standardized by FAJAN's method with dichlorofluorescein as indicator.

Ammonium persulphate solutions (2%) were freshly prepared from Analar ammonium persulphate.

Standard manganese solutions were prepared from $5 \cdot 10^{-3}$ *M* potassium permanganate which was standardized against sodium oxalate. Permanganate solution (10 ml) was pipetted into a beaker, the solution was acidified with 1 ml of 2 *N* sulphuric acid and a freshly prepared 1% sodium sulphite solution was added dropwise until the solution became colorless. A few drops of the sulphite solution were added in excess, the excess of sulphur dioxide was removed by boiling and the contents, after cooling, were transferred to a 100-ml volumetric flask and diluted to the mark. More dilute solutions were prepared by dilution of such stock solutions.

Procedure

To a solution aliquot containing 0.25–50 μg of manganese(II), add 2.5 ml of 10 *M* phosphoric acid, 1 ml of 10^{-4} *M* silver nitrate, and 5–10 ml of 2% ammonium persulphate, and dilute to 15–20 ml. Boil the solution for 1–2 min on a hot plate, remove from the heat and allow to stand for 1 min before cooling in ice-cold water. Transfer the sample quantitatively to a 25-ml volumetric flask. Add a 5–20 molar excess of reagent, dilute to the mark and measure the fluorescence intensity at 485–490 nm after 10 min; the excitation wavelength is 375 nm. A reagent blank should be run concurrently.

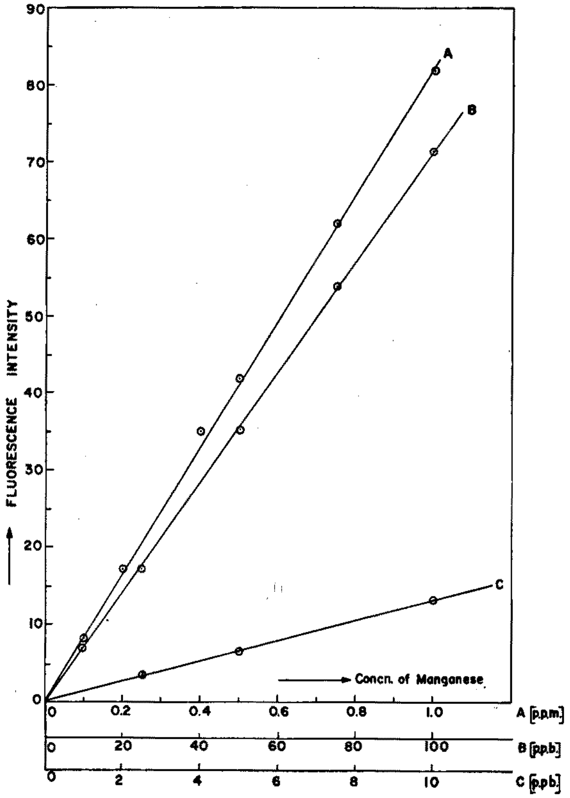

Fig. 1. Calibration curves. (A) Meter multiplier (MM) setting 0.003 and sensitivity (S) 0; (B) MM 0.003 and S 50; (C) slit arrangement #5 with MM 0.001 and S 50.

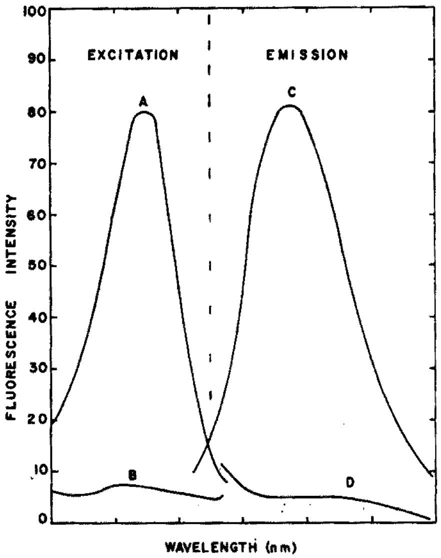

Fig. 2. Spectra. A and B are excitation spectra of product (0.1 p.p.m. Mn) and reagent respectively (emission λ, 485 nm); C and D are corresponding emission spectra (excitation λ 375 nm).

Typical calibration curves are shown in Fig. 1. Uncorrected excitation and emission spectra are shown in Fig. 2; all results, except in Fig. 2, are corrected for reagent emission.

RESULTS AND DISCUSSION

Factors affecting fluorescence intensity

The method is dependent upon two different chemical reactions: (i) oxidation of manganese(II) to permanganate by ammonium persulphate in the presence of silver(I) as catalyst, and (ii) oxidation of oxine-5-sulphonic acid by the permanganate formed in (i) to give a fluorescent product. The factors affecting the first reaction have been discussed in detail by NYDAHL[6]; he prescribed 10^{-5} *M* silver ion for the determination of manganese by permanganate and similar concentrations are recommended in the fluorimetric procedure. Although 10^{-2} *M* silver ion develops the permanganate color at room temperature, there is little difference in the fluorescent intensity of blank and sample; the blank with 10^{-4}–10^{-5} *M* silver ion, however, is negligible. The solution must be boiled to oxidize manganese to permanganate at such silver ion concentrations but complete oxidation requires boiling for only 1 min; there is no difference in fluorescence intensity on boiling for 1 or 10 min.

Plots of fluorescence intensity against metal concentration (Fig. 1) are linear through the origin for a wide range of manganese concentrations. Intensities are maximal and constant when reagent to metal mole ratios are between 5:1 and 20:1; for example, for 0.33 p.p.m. of manganese the fluorescence intensity was 56 for 1:1, 82 for 5, 10, 15 or 20:1 mole ratios, and 71 for a 25:1 reagent to metal mole ratio at the same instrument sensitivity.

The fluorescence intensity is maximal and constant in the presence of 1–10 ml of 2% ammonium persulphate solution; however, in the determination of 0.1 p.p.m. or less of manganese, 1 ml of persulphate solution is recommended to maintain a small reagent blank.

The reaction between permanganate and oxine-5-sulphonic acid is rapid; maximum fluorescence is obtained within 10 min and remains constant for 1 h.

Intensity is also constant over a wide range of acidity. Solutions 1 *M* in phosphoric acid gave the same intensity at a pH of 2 as they did in solutions up to 2 *N* in sulphuric acid. Above pH 5.0 a bathochromic shift of fluorescence maximum, similar to that previously reported[1], occurs. All measurements were made in 1 *M* phosphoric acid unless otherwise stated.

Results and interferences

Ten samples, each containing 0.1 p.p.m. of manganese, were analyzed by the above procedure; the percent standard deviation was 1.9. Four different standard steels, containing 0.52 to 1.84% manganese, were analyzed with excellent results; for example, three analyses of a steel containing a reported 0.83% manganese gave 0.829±0.005%. Dow metals, containing *ca.* 0.25% manganese, were also analyzed; excellent agreement with analyzed values was obtained.

Manganese (0.1 p.p.m.) was accurately determined in the presence of 500 p.p.m. of Ca^{2+}, Cd^{2+}, Mg^{2+}, Zn^{2+}; 200 p.p.m. of Al^{3+}, La^{3+}, Li^{+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, Zr^{4+}; 50 p.p.m. of Cu^{2+}, Ni^{2+}; 40 p.p.m. Cl^{-}; 20 p.p.m. Co^{2+}. Large amounts (10,000 p.p.m.) of sodium, potassium, ammonium, nitrate, sulphate, persulphate and phosphate had no effect on the results obtained. Thorium and cerium were precipitated as phosphates; their centrifuged solutions showed that a 3000-fold excess of thorium(IV) gave no interference but even a 50-fold excess of cerium(IV) was a positive interference. Tin(IV) enhanced the fluorescence at pH 1–2 but, in solutions 1–2 *N* in sulphuric acid, 200 p.p.m. of tin did not interfere.

Nature of reaction

The fluorescent species, like the parent reagent, is water-soluble and non-extractable by water-immiscible organic solvents. Attempts to obtain a pure reaction product by fractional crystallization, ion exchange, and thin-layer chromatography were unsuccessful; although concentration of the fluorescent species was achieved, the product was always contaminated by reagent and meaningful ultraviolet and infrared spectra were not possible.

The fluorescent oxidized product used for the determination of manganese is neither pyridine-2, 3-dicarboxylic acid nor quinoline-5, 8-quinone; both of these compounds, which were considered to be possible products, have different fluorescent spectra from the fluorescent species formed and are, of course, readily soluble in organic solvents. The usual fluorescent species was obtained on 1–2 h heating of an aqueous solution of oxine-5-sulphonic acid with a large excess of potassium persulphate; prolonged heating (4–5 h), however, gave a fluorescent solution with excitation and emission spectra similar to pyridine-2, 3-dicarboxylic acid*. These results suggest that the oxidized product responsible for fluorescence is a stable intermediate containing the initial sulphonic acid group which is changed to pyridine-2, 3-dicarboxylic

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* Anodic oxidation of an aqueous solution of oxine-5-sulphonic acid, at platinum electrodes and a potential of 5 V, produced the same fluorescent species as that produced by permanganate.

acid on further oxidation. A number of possible structures for the intermediate can be written but any such postulates are purely speculative.

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SUMMARY

Manganese is selectively and simply determined through the oxidative reaction of permanganate, formed by catalytic oxidation of manganese(II), upon oxine-5-sulphonic acid to produce a highly fluorescent product; the method is 100 times more sensitive than the conventional permanganate method. The fluorescence intensity attains a maximum after 10 min, is constant for 1 h, and is linear for 2.5 p.p.b. to 2.5 p.p.m. of manganese. Few ions interfere and manganese can be accurately determined in steels and other alloys.

RÉSUMÉ

Le manganèse peut être dosé sélectivement et simplement par oxydation catalytique du manganèse(II) et réaction du permanganate formé sur l'acide oxine-5-sulfonique pour donner un produit très fluorescent. La méthode est 100 fois plus sensible que la méthode conventionnelle au permanganate. L'intensité de fluorescence atteint son maximum après 10 minutes; elle est constante pendant une heure et linéaire pour des concentrations en manganèse de 2.5 p.p.b. à 2.5 p.p.m. Peu d'ions gênent. Le manganèse peut être dosé avec précision dans les aciers et autres alliages.

ZUSAMMENFASSUNG

Mangan kann selektiv und einfach bestimmt werden durch die oxydative Reaktion des Permanganats, welche durch katalytische Oxydation von Mangan(II) auf Oxin-5-sulphon-Säure ein sehr stark fluoreszierendes Produkt bildet. Das Verfahren ist 100mal empfindlicher als die konventionelle Permanganat-Methode. Die Fluoreszenzintensität erreicht nach 10 Min ein Maximum, das für 1 Stünde lang konstant ist und zu einer linearen Eichkurve zwischen 2.5 p.p.b. und 2.5 p.p.m. Mn führt. Einige Ionen stören, Mangan kann in Stählen und anderen Legierungen genau bestimmt werden.

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DETERMINATION OF SUBMICROGRAM AMOUNTS OF SILVER(I) BY QUENCHING OF FLUORESCENCE*

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No direct or indirect spectrofluorimetric procedure for the trace determination of silver(I) ions has been published up to this date. SAWICKI *et al.*[1,2] have described several methods for trace analysis based on quenching of fluorescence. Several reviews have summarized most of the published direct and indirect spectrofluorimetric methods[3-7]. Eosin has been used for the determination of iodide ions in aqueous and non-aqueous media[8]. BABKO *et al.*[9] have described a chemiluminescent method for the determination of silver ions down to 10^{-7} g/l, based on the catalytic action of silver ions on the reaction between lucigenin and hydrogen peroxide at pH 13.5. The method is subject to interference from several transition and noble metals. Recently, PAL AND RYAN[10] have described a method for the spectrofluorimetric determination of silver(III) ions, in aqueous media, involving the oxidation of silver(I) to silver(III) by potassium persulfate. The tervalent silver ions form a fluorescent compound with the reagent oxine-5-sulphonic acid at pH 1.5–3.5.

A molecular-absorption spectrophotometric procedure for the trace characterization of silver(I) ions in aqueous and non-aqueous media has been described[11]. This method involves the formation of the ternary complex, bis-phenanthroline–silver(I)–eosin, $\{[Ag(Phen)_2^+]_2, TBF^{2-}\}$, which has molar absorptivities of *ca.* 35,000 and 55,000 in aqueous and non-aqueous media respectively. One of the main advantages of this method over other spectrophotometric procedures is its specificity. Although its sensitivity in non-aqueous media is good, it is surpassed by other methods in aqueous media. In order to improve the sensitivity of this method in aqueous media, it was decided to make use of the fluorescence-quenching phenomenon observed with eosin. Molecular-emission spectrofluorimetry is a suitable technique because sensitivity is governed by the well-known relationship:

$$F = [I_0(2.3\,\varepsilon\,Cd)]\,[\Phi]$$

where F is the fluorescence intensity and I_0 is the intensity of the incident light. Since there is a direct relationship between the fluorescence intensity and the intensity of the incident light, the sensitivity can be increased with the use of a powerful energy source, such as a mercury or xenon lamp[4,12,13].

Preliminary investigations indicated that the fluorescence intensity of TBF

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is unchanged by the addition of silver(I) ions. On the other hand, fluorescence quenching occurs in the presence of 1,10-phenanthroline as the concentration of silver(I) ions is increased. These preliminary observations suggest that the complex formed is ternary rather than binary. BAILEY, DAGNALL AND WEST[14,15] examined in detail several dyestuffs of fluorescein and its derivatives for their reaction with silver(I) ions through the formation of ternary complexes. Since ternary complexes make possible more selective and sensitive analytical procedures than binary complexes, a selective quenching effect was to be expected. This concept has been explained by WEST[12,13] and by BABKO[16]. The bis-phenanthroline–copper(II)–tetrabromotetraiodofluorescein ternary complex was proposed by BAILEY, DAGNALL AND WEST[17,18] for the molecular-absorption spectrophotometric and molecular-emission spectrofluorimetric analysis of copper.

In view of these findings, the reaction between silver(I) ions, 1,10-phenanthroline and 2,4,5,7-tetrabromofluorescein was examined for the indirect fluorimetric determination of traces of silver(I) ions in aqueous medium.

EXPERIMENTAL

Apparatus

Emission and excitation spectra were recorded with an Aminco-Bowman spectrofluorimeter. Fluorescence measurements were made with a Turner fluorimeter, Model 110, with the primary filter 1–60 +58 (546 nm) and the secondary filter 110–819 (22) (560 nm) with sensitivity setting 30 ×. Matched glass cuvettes were employed.

Spectrophotometric measurements were carried out with a Unicam SP500 Spectrophotometer.

A Radiometer pH-meter, Model 28A, was used for all pH measurements.

Reagents

Ethylenediamine tetraacetic acid, disodium salt (Eastman Organic Chemicals) was used to prepare a 10^{-1} *M* solution.

Silver nitrate (analytical-reagent grade; Mallinckrodt Chemical Work, Montreal) was used to prepare a standard 10^{-2} *M* silver nitrate solution which was standardized against a 10^{-2} *M* sodium chloride solution with dichlorofluorescein as an adsorption indicator[19].

2,4,5,7-Tetrabromofluorescein (TBF; Aldrich Chemical Company) and 1,10-phenanthroline (Phen; Fisher Limited) were used.

Recommended procedure

A series of solutions was prepared containing 2.0 ml of 10^{-2} *M* EDTA between 1 and 10 ml of 10^{-6} *M* silver nitrate, 2.0 ml of 10^{-3} *M* Phen, 1.0 ml of aqueous 2% ammonium acetate as buffer and 1.0 ml of $1.25 \cdot 10^{-4}$ *M* TBF. The solutions were then diluted to the mark in 25-ml volumetric flasks with distilled water. After mixing the solutions thoroughly, the fluorescence measurements were made, with the filter combination which gave a wavelength as close as possible to 550 nm, against a reagent blank prepared similarly but containing no silver. No standing time was required. By plotting fluorescence readings *vs.* micrograms of silver(I), a straight line passing through a fluorescence reading of 100 was obtained.

When examining the effect of foreign ions, portions were pipetted first, followed by solutions of silver nitrate, EDTA, Phen, acetate buffer and TBF. The above procedure was then followed.

RESULTS AND DISCUSSION

Fluorescence spectra

Curves A and C of Fig. 1 show the excitation and emission spectra of a solution containing 1 ml of 10^{-2} *M* EDTA, 1 ml of 2% ammonium acetate and 2 ml of 10^{-5} *M* TBF, diluted to 10 ml. The emission and excitation peaks are at 300 and 545 nm respectively. The addition of silver(I) ions to this solution produces no change in spectra, nor does the addition of 1,10-phenanthroline to the original solution. On the other hand, when silver(I) ions (2 ml of 10^{-5} *M* Ag(I)) and 1,10-phenanthroline are added to the solution, there is a sharp decrease in the intensities of the peaks at 300 and 545 nm (Fig. 1, Curves B and D). In other words, fluorescence quenching of eosin by silver(I) ions takes place only in the presence of 1,10-phenanthroline.

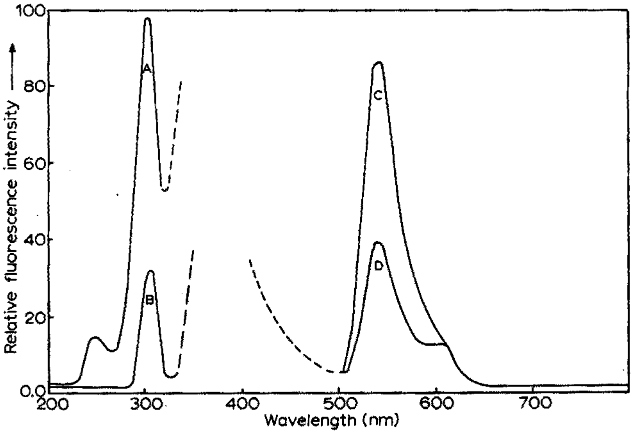


Fig. 1. Emission and excitation spectra of TBF^{2-}.

Optimum pH

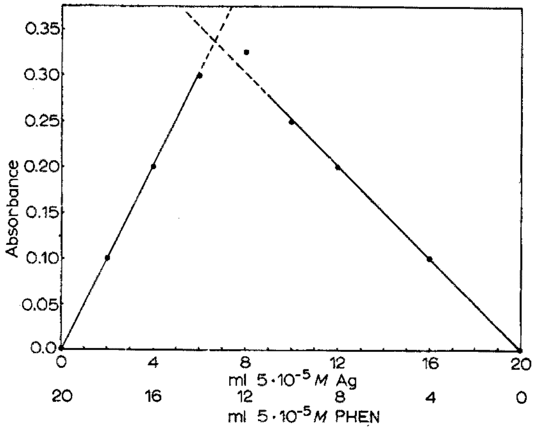
A study of pH indicated that the reaction of silver(I) ions with 1,10-phenanthroline and TBF to form a complex takes place over the pH range 3–9 with maximal quenching over the pH range 3–8. A pH of 7 was chosen for simplicity, with a buffer solution containing 2% ammonium acetate.

Optimum time

The fluorescence intensity of a solution containing 1 ml of 10^{-2} *M* EDTA, 2 ml of 10^{-5} *M* silver(I), 1 ml of 10^{-3} *M* 1,10-phenanthroline, 1 ml of 2% ammonium acetate and 2 ml of 10^{-5} *M* TBF diluted to 10 ml was measured against a reagent blank over a period of two weeks. No significant changes were observed.

Reagent to metal ratios

Several molar ratios of the complex constituents were examined. It was found that the combination which gives the best results was that which can just be set up on the fluorimeter at a sensitivity setting of 30 ×. As large a concentration as possible of TBF and a 1000-fold molar excess of 1,10-phenanthroline with respect to silver(I) would give the best results. However, a 12.5 and 200-fold molar excess of TBF and



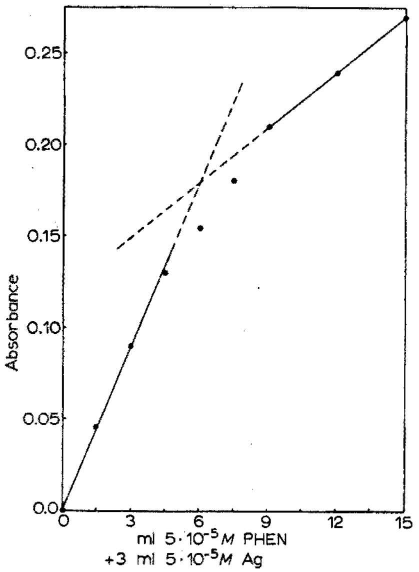
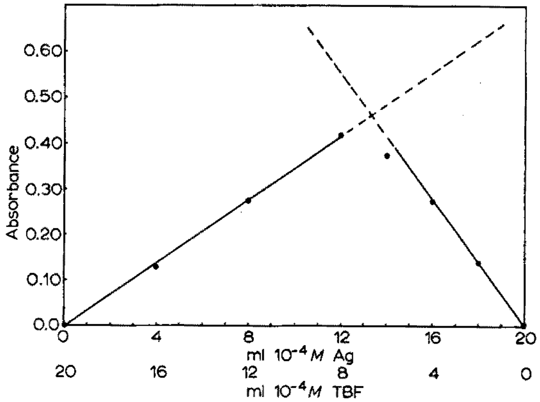


Fig. 2. Continuous variation plots. Ag : Phen ($5 \cdot 10^{-5}$ M) complex ratio, in presence of excess TBF (10^{-3} M).

Fig. 3. Mole ratio. Ag : Phen ($5 \cdot 10^{-5}$ M) complex ratio, in presence of excess TBF (10^{-3} M).



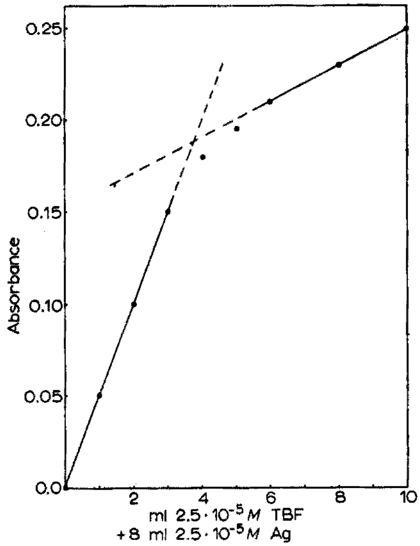


Fig. 4. Continuous variation plots. Ag : TBF (10^{-4} M) complex ratio, in presence of excess Phen (10^{-2} M).

Fig. 5. Mole ratio. Ag : TBF ($5 \cdot 10^{-5}$ M) complex ratio, in presence of excess Phen ($5 \cdot 10^{-3}$ M).

1,10-phenanthroline respectively over silver is the maximum which can be used with an instrument setting of 30 ×.

Nature of the complex

The nature of the complex, silver–1,10-phenanthroline–TBF, was examined by applying the continuous variation ("Job's plots")[20,21] and mole ratio[22] methods. The results obtained with a Unicam SP500 Spectrophotometer were as follows:

(i) *Ag : Phen ratio, in presence of excess of TBF*. Job's plots indicated a complex ratio of 6:65:13.35 or a 1:2 ratio between silver(I) and Phen (Fig. 2). This ratio was confirmed by the mole ratio plots (Fig. 3).

(ii) *Ag:TBF ratio, in presence of excess of Phen*. From Job's plots, it was deduced that the ratio between silver(I) and TBF is 13.3:6.7 or *ca.* 2:1 (Fig. 4). This ratio was confirmed by the mole ratio plot method (Fig. 5).

(iii) *Phen:TBF ratio, in presence of excess of silver(I)*. Job's plots indicated a ratio of 15.85:4.15 or *ca.* 4:1 between 1,10-phenanthroline and TBF (Fig. 6). Therefore, the overall ratio of the Ag:Phen:TBF complex is 2:4:1.

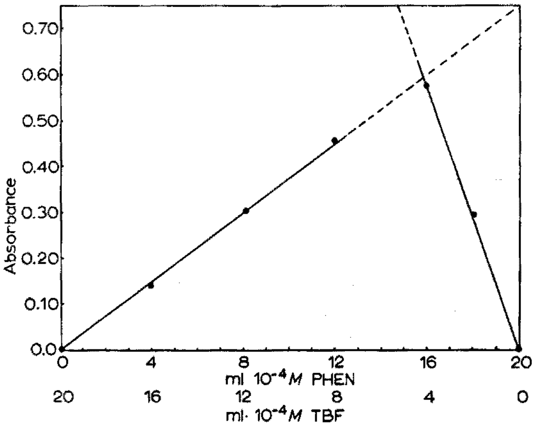
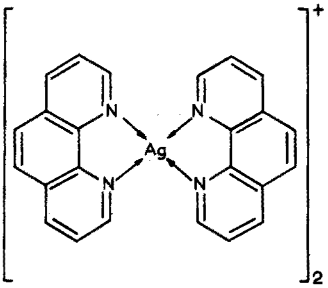
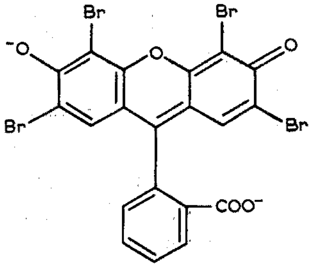


Fig. 6. Continuous variation plots. Phen : TBF (10^{-4} M) ratio, in presence of excess Ag (10^{-2} M).

It is assumed that the silver ions form a coordinated complex with the 1,10-phenanthroline ($Ag(Phen)_2^+$). This positively charged bis-phenanthroline–silver(I) complex then associates with the counter ion, which is the negatively charged fluores-





cent reagent TBF, to form the ternary and non-fluorescent complex $\{[\mathrm{Ag(Phen)_2^+}]_2, \mathrm{TBF^{2-}}\}$.

Interferences

The addition of EDTA up to 3000-fold molar excess over silver(I) ions did not affect the sensitivity of the method. Therefore, the EDTA was used as a mass-masking agent. In the presence of EDTA, the interferences of twenty cations and ten anions were examined. Table I summarizes the results obtained. The only ions which interfere seriously are palladium(II) and cyanide, which consequently must be absent if the method is to be applied successfully.

TABLE I

EFFECT OF EXTRANEOUS IONS

Cationic interferences
100-fold molar excess: Al(III), Au(III), Cu(II), Fe(II), Fe(III), K^+, Mg(II), Mn(II), Na^+, NH_4^+, Pb(II), Ru(IV), Sn(II), U(VI), Zn(II)
10-fold molar excess: Os(IV), Rh(III)
Equimolar conditions: Pt(IV), Ir(IV)
Interfering cations: Pd(II)

Anionic interferences
100-fold molar excess: Cl^-, $C_2H_3O_2^-$, F^-, NO_3^-, SO_3^{2-}, SO_4^{2-}
10-fold molar excess: I^-, S^{2-}
Equimolar conditions: Br^-
Interfering anions: CN^-

Calibration curve

A calibration curve was prepared by the recommended procedure, by plotting micrograms of silver(I) against relative fluorescence intensity. A linear relationship was obtained over the range 0.1–1 μg of silver(I) per 25 ml, corresponding to 4–40 p.p.b. in the final concentration.

Reproducibility

The reproducibility of the method was determined by analysing a set of 11 solutions, each containing 1.0 ml of 10^{-6} M silver(I) per 25 ml. A standard deviation of 2.7% was obtained.

CONCLUSIONS

With this method an analytical procedure for the indirect fluorimetric trace characterization of silver(I) ions in aqueous media has been developed, which is about twenty-five times more sensitive than the corresponding spectrophotometric method[11], with some sacrifice in reproducibility and selectivity. The sensitivity could be further increased if the measurements were made with a spectrofluorimeter equipped with a stronger source of radiation, *e.g.* a xenon lamp. The method is simple and does not require a skilled analyst. The reaction can be rendered specific for silver(I) ions in the presence of the other coinage metals and most of the noble metals and compares favourably with other spectroscopic procedures.

This work was supported by a grant of the National Research Council. M. T. E.-G. is grateful for financial support as a Post-doctoral Fellow from the same grant and a special research grant from Dalhousie University. G. W. H. gratefully acknowledges support provided through a summer research grant from the Atlantic Provinces Inter-university Committee on the Sciences.

SUMMARY

The reaction of the bis-phenanthroline–silver(I) cationic complex with the counter-ion, 2,4,5,7-tetrabromofluorescein (eosin), to form the ternary complex, $\{[\mathrm{Ag(Phen)_2}^+]_2, \mathrm{TBF}^{2-}\}$, has been studied for the determination of submicrogram amounts of silver(I) ions in aqueous media. The eosin itself is fluorescent and in the presence of 1,10-phenanthroline, its sharpest excitation and emission peaks are at 300 and 545 nm, respectively. The addition of silver(I) ions to the eosin–phenanthroline solution causes a quenching of this fluorescence. With this method, silver(I) ions can be determined down to 4 p.p.b., with a reproducibility of 2.7%, in the pH range 3–8. Reaction is instantaneous and the fluorescence remains stable for two weeks. Twenty cations, including the other coinage and most of the other noble metals, and ten anions have been tested for their interferences in the presence of EDTA. Only palladium(II) and cyanides interfere seriously.

RÉSUMÉ

On a étudié la réaction du complexe cationique bis-phénanthroline-argent(I) avec l'ion, tétrabromo-2,4,5,7-fluorescéine (éosine) pour donner le complexe ternaire $\{[\mathrm{Ag(Phen)_2}^+]_2, \mathrm{TBF}^{2-}\}$ en vue du dosage de submicroquantités d'argent(I) en solution aqueuse. L'éosine elle-même est fluorescente; en présence de 1,10-phénanthroline, ses pics d'excitation et d'émission sont respectivement 300 et 545 nm. L'addition d'argent(I) à la solution éosine–phénanthroline produit un affaiblissement de la fluorescence. On peut ainsi doser jusqu'à 4 p.p.b. d'argent(I) avec une reproductibilité de 2.7%. Entre les pH 3 et 8, la réaction est instantanée et la fluorescence est stable pendant deux semaines. L'influence de vingt cations et dix anions a été examinée en présence d'EDTA. Seuls palladium(II) et cyanures gênent sérieusement.

ZUSAMMENFASSUNG

Die Reaktion des kationischen Komplexes von Bis-phenanthrolinsilber(I) mit 2,4,5,7-Tetrabromofluorescein (Eosin) zum ternären Komplex $\{[\mathrm{Ag(Phen)_2}^+]_2, \mathrm{TBF}^{2-}\}$, wurde zur Bestimmung von Submikrogrammen Silber(I)-ionen im wässrigen Medium untersucht. Das Eosin selbst fluoresziert in Gegenwart von 1,10-Phenanthrolin. Seine schärfsten Anregungs- und Emissions-Maxima liegen bei 300 bzw. 545 nm. Die Zugabe von Silber(I)-Ionen zu der Eosin-Phenanthrolin-Lösung verursacht einen Quenching-Effekt der Fluoreszenz. Mit dieser Methode können Silber(I)-Ionen bis hinab zu 4 p.p.b. mit einer Reproduzierbarkeit von 2.7% beim pH-Bereich von 3–8 bestimmt werden. Die Reaktion erfolgt sofort, und die Fluoreszenz bleibt 2 Wochen lang stabil. 20 Kationen und 10 Anionen wurden auf ihre Störungen in Gegenwart von AeDTE untersucht. Nur Palladium(II) und Cyanide stören ernsthaft.

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APPLICATIONS OF THE FLUORIDE-SENSITIVE ELECTRODE TO THE STUDY OF METAL–FLUORIDE ION ASSOCIATION CONSTANTS

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FRANT AND ROSS[1] have described a fluoride-sensitive membrane electrode, the essential component of which is a single crystal of lanthanum fluoride doped with europium(II), and which is now commercially available. The electrode gives a Nernstian response over a wide range of fluoride ion activity, and common anions, such as chloride, nitrate, acid carbonate and sulphate do not interfere[1,2]. LINGANE[3] in a study of its application to end-point detection in the titration of fluoride ion with thorium, lanthanum and calcium, has shown that phosphate and acetate are without effect. The electrode also responds satisfactorily in acidic media up to 0.25 *M* in hydrogen ion at ionic strengths of 1 maintained with sodium nitrate[4]. The electrode has been used for the measurement of the association of hydrogen ion with fluoride in a sodium perchlorate[5] medium at an ionic strength of 1 providing evidence that high ionic strength and the perchlorate ion do not interfere with the electrode response.

In the work to be described, the application of the electrode, incorporated in the cell

$$\mathrm{Ag|AgCl|Na^+Cl^-, F^-|La(Eu(II))F_3|test\ soln|NaCl_{(sat)}|Hg_2Cl_2|Hg}$$

has been examined for the measurement of association constants for metal ion–fluoride interactions in aqueous solution. The metal ion systems investigated are, in the main, those for which association constants have previously been measured by other methods. They cover a range of metal ions (magnesium, calcium, scandium, iron(III), yttrium, europium(III), and gadolinium) sufficient to indicate any limitations arising from the extent of ion–ion interaction. The yttrium–fluoride and hydrogen–fluoride systems were examined at 15, 25 and 35° and enthalpy and entropy changes were obtained, applicable to the conditions of measurement.

EXPERIMENTAL

Chemicals

Common chemical substances used were of reagent grade. The trivalent oxides of scandium, yttrium, europium and gadolinium (Koch-Light, Colnbrook, England, all of 3N quality or better) were heated to remove any carbonate before dissolution in perchloric acid to give standard solutions. The rare-earth metal content of each was also checked by EDTA titration[6]. Iron of high purity, in the form of granules (British Chemical Standard No. 149/2, Bureau of Analysed Samples, Ltd., Newham

Hall, Middlesbrough) was dissolved in dilute perchloric acid and converted to the trivalent state with a little nitric acid. The solution was standardised by chromium-(VI) and EDTA titrations[6]. Calcium and magnesium perchlorate solutions were prepared by dissolution of "Specpure" calcium carbonate and magnesium oxide (Johnson, Matthey and Co. Ltd., Hatton Garden, London) in perchloric acid. The source of fluoride ion was analytical reagent-grade sodium fluoride.

Stock solutions about 10^{-2} M in metal ion (except calcium which was 0.15 M) were made up to an ionic strength, μ, of 0.500 with sodium perchlorate.

Apparatus

An Orion Model 94-09 fluoride indicator electrode was used, with a calomel electrode immersed in saturated sodium chloride as reference electrode. The e.m.f. was measured with a Derritron pH meter (Derritron Instruments Ltd., Stroud, Gloucester, England), fitted with an external spot galvanometer for improved null-point detection.

The cell, constructed of polypropylene, had a total capacity of about 250 cm^3 and was thermostatted at 25.00±0.05°. Measurements were carried out in a cell atmosphere of nitrogen and all surfaces (electrode, stirrer, etc.) in contact with the cell solution were constructed from substances substantially inert to fluoride.

Method

The metal ion solution (100 ml) in perchlorate at the required ionic strength and pH was placed in the cell and a series of e.m.f. measurements made with the addition of known volumes (0.1–1 ml aliquot parts) of fluoride solution at the same ionic strength and pH.

Any change in the pH of the solution at the end of a series of measurements was noted and, if warranted, the change over the range of addition of fluoride ion was determined in a subsidiary experiment.

The cell was calibrated for direct fluoride ion measurement by determining the e.m.f. for various known fluoride concentrations at the required ionic strength and pH. The effect of hydrogen ion activity on the fluoride ion activity as determined by the electrode was also checked for the perchlorate solution.

The method in which free fluoride is determined in a metal ion–fluoride system by the iron(III)–iron(II) half-cell potential was applied as described by LATIMER *et al.*[7] without modification except that nitrogen gas was used over the test solution instead of carbon dioxide, and glass was avoided in the construction of the cell.

RESULTS AND DISCUSSION

A linear relation was observed between the cell e.m.f. plotted against log [F$^-$], where [F$^-$] is the fluoride ion concentration, in the range 10^{-2}–10^{-5} M, at an ionic strength of 0.500 at 25°. The slopes of the curves obtained by least squares were in the range 58.5–59.2 mV, *i.e.*, somewhat lower than the theoretical value (59.16) but in agreement with the findings of VANDERBORGH[5]. The cell e.m.f. proved to be quite stable and reproducible to within a few tenths of a millivolt over several hours but changes of several mV were observed over 2 or 3 months. The "drift" in e.m.f.

may depend on the nature of the cations present, *e.g.* alkaline earth ions appeared to cause a reduction in e.m.f. when immersed for several hours. (Subsequent immersion in thorium perchlorate solution seemed to lead to rapid restoration of performance.)

Titration of the chosen metal ion with sodium fluoride solution was carried out at constant hydrogen ion activity. The total fluoride, $[F^-]_t$, added, the measured free fluoride, $[F^-]_f$, from the cell e.m.f., and the calibration curve then permitted the calculation of the average number of ligands, $\bar{n}$, per metal ion from

$$\bar{n} = ([F^-]_t - [F^-]_f)/[M]_t$$

where $[M]_t$ is the total metal concentration. The quantities $[F^-]_t$ and $[M]_t$ were corrected for the small volume changes introduced by addition of the standard fluoride solution. $\bar{n}$ is related to successive formation constants $\beta_j = [MF_j^{(x-j)+}]/[M^{x+}][F^-]^j$ by

$$\bar{n} = \frac{\beta_1[F^-]_f + 2\beta_2[F^-]_f^2 + 3\beta_3[F^-]_f^3 + \ldots}{1 + \beta_1[F^-]_f + \beta_2[F^-]_f^2 + \beta_3[F^-]_f^3 + \ldots}$$

β_j was calculated by well-established methods[8,9].

The hydrogen ion–fluoride system

The association constants for hydrogen and fluoride ion interaction were determined by potentiometric titration at 15.00, 25.00 and 35.00° with the results recorded in Table I. Agreement with the previously recorded values is good. The enthalpy and entropy changes accompanying "protonation" are in satisfactory agreement with published values (Table II).

TABLE I

ASSOCIATION CONSTANTS FOR YTTRIUM FLUORIDE AND HYDROGEN FLUORIDE SYSTEMS IN AQUEOUS $NaClO_4$ (0.500 *M*) AT DIFFERENT TEMPERATURES

($[Y^{3+}] = 4.94 \cdot 10^{-4}$ *M*; pH = 3.60)

Temp. (°)	*Yttrium ion*		*Ref.*	*Hydrogen ion*	*Ref.*
	$\beta_1 \cdot 10^{-3}$	$\beta_2 \cdot 10^{-6}$		$\beta_H \cdot 10^{-2}$	
15.00 ± 0.05	7.61 ± 0.06[a]	15.5 ± 0.7	p.w.[b]	6.97 ± 0.04	p.w.
	7.41	5.24	10	7.08	11
25.00 ± 0.05	8.22 ± 0.06	14.4 ± 0.7	p.w.	8.14 ± 0.10	p.w.
	8.51	13.49	10	8.13	11
35.00 ± 0.05	8.72 ± 0.06	14.3 ± 0.7	p.w.	9.70 ± 0.16	p.w.
	9.80	47.86	10	10.00	11

[a] Errors quoted here and elsewhere are standard errors of the means.

[b] p.w. = present work.

Gadolinium and europium–fluoride systems

Three main experimental runs were attempted with gadolinium at different metal ion concentrations (Fig. 1). At the highest metal ion concentration chosen, $\bar{n}$ was small and its range of values narrow so that only β_1 could be obtained. The limitations were imposed by the tendency for the change in e.m.f. to diminish with successive incremental additions of titrant and by the ultimate appearance of a metal fluoride precipitate. (Throughout the work described in this paper separate

TABLE II

FREE ENERGY, ENTHALPY AND ENTROPY CHANGES FOR YF^{2+}_{aq}, $YF^{+}_{2\,aq}$ AND HF FORMATION FROM Y^{3+}_{aq}, H^{+}_{aq} AND F^{-}_{aq} AT $\mu = 0.500$ ($NaClO_4$) AND 25.00 ± 0.05°

Cation	*Method*[a]	ΔH_1[b]	ΔG_1	ΔS_1	ΔH_2	ΔG_2	ΔS_2	*Ref.*
Y^{3+}	FE	1.205	−5.34	22.0	−1.20	−4.43	11.0	p.w.[c]
	Red	2.37	−5.34	26.6	—	—	—	10
	Cal (μ = 1.00)	8.32 ± 0.08	−4.91 ± 0.44	44.5 ± 1.5	—	—	—	12
Sc^{3+}	Red	0.40	−8.36	29.4	−1.23	−7.19	19.9	13
H^{+}	FE	3.11 ± 0.09	−3.97	23.75	—	—	—	p.w.
	Sp	3.06	−3.97	22.0	—	—	—	11
	Cal	2.6	−3.96	22.0	—	—	—	14

[a] FE = fluoride electrode; Red = potentiometric with Fe(III)–Fe(II) halfcells; Cal = calorimetric value for ΔH; Sp = spectrophotometric.

[b] ΔH was calculated from the van 't Hoff isochore.

[c] p.w. = present work.

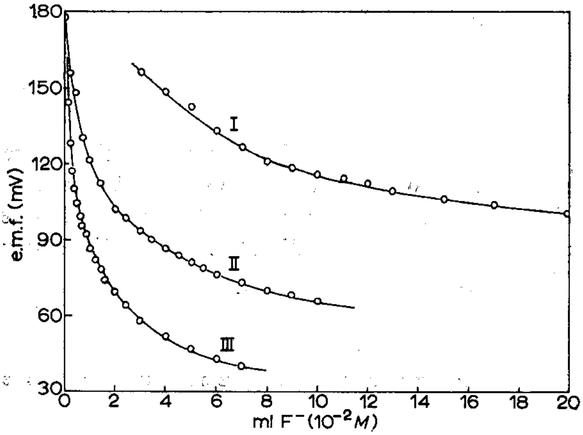

Fig. 1. Titration of 100 ml of gadolinium(III) with 10^{-2} *M* fluoride ion each at pH = 3.60, $\mu = 0.500$ ($NaClO_4$) and 25.00 ± 0.05°. The initial gadolinium concentrations were $2.021 \cdot 10^{-2}$ *M* (curve I), $2.021 \cdot 10^{-3}$ *M* (curve II) and $2.021 \cdot 10^{-4}$ *M* (curve III).

experiments were always performed in order to determine the point in a titration at which precipitation occurred and e.m.f. data near or beyond it were not subsequently used.) The lowest gadolinium concentration gave the largest range for $\bar{n}$ (0.01–0.37). However, there are unlikely to be advantages in attempting to use appreciably lower $[M]_t$ since this would entail addition of smaller increments of $[F^-]$ to accumulate adequate data near the beginning of the titration. Already the aliquot portions of $[F^-]$ are near the limit in providing e.m.f. changes which can be measured reliably. For a lanthanoid, the metal ion concentration would have to be appreciably greater than the concentration of lanthanum ion derived from solution of the membrane. The two titration curves lowest in $[M]_t$ gave β_1 and β_2 only (Table III) and it was concluded that no more than two steps in gadolinium complex ion formation can be investigated quantitatively by this electrode system. The β values obtained are in fair agreement with the previously published values (Table III).

A limited study of europium(III) gave β_1 in good agreement with the value obtained from liquid–liquid partition studies[16].

BLE III

SOCIATION CONSTANTS FOR SOME METAL FLUORIDES AT AN IONIC STRENGTH $\mu = 0.500$ (UNLESS OTHERWISE CORDED) AND $25.00 \pm 0.05°$

tal	*Method*[a]	β_1	β_2	β_3	β_4	*Ref.*
$^{3+}$	FE,	$(2.46 \pm 0.05)10^3$	—	—	—	p.w.
		$(2.39 \pm 0.04)10^3$	$(2.73 \pm 0.38)10^6$	—	—	p.w.
		$(2.29 \pm 0.05)10^3$	$(4.16 \pm 0.48)10^6$	—	—	p.w.
	Dis	$(2.67 \pm 0.30)10^3$	$(5.17 \pm 0.32)10^6$	—	—	15
$^{3+}$	FE	$(2.54 \pm 0.05)10^3$	—	—	—	p.w.
	Dis	$2.48\cdot10^3$	$3.01\cdot10^6$	—	—	16
$^{+}$	FE	$(8.22 \pm 0.06)10^3$	$(14.4 \pm 0.7)10^6$	—	—	p.w.
	Red	$(8.20 \pm 0.21)10^3$	$(13.8 \pm 0.6)10^6$	$(19.5 \pm 0.8)10^9$	—	p.w.
	Red	$8.51\cdot10^3$	$13.49\cdot10^6$	$21.3\cdot10^9$	—	10
	Dis	$(7.70 \pm 0.21)10^3$	$(12.8 \pm 0.3)10^6$	$20.0\cdot10^9$	—	17
$^{3+}$	FE	$(1.66 \pm 0.08)10^6$	$(2.16 \pm 0.10)10^{11}$	$(1.7 \pm 0.2)10^{15}$	—	p.w.
	Red	$1.51\cdot10^6$	$2.82\cdot10^{11}$	$3.31\cdot10^{15}$	$2.34\cdot10^{18}$	13
	Dis	$(1.47 \pm 0.11)10^6$	$(2.77 \pm 0.07)10^{11}$	$(2.91 \pm 0.14)10^{15}$	$(3.06 \pm 0.12)10^{18}$	17
$^{3+}$	FE	$(1.46 \pm 0.02)10^5$	$(1.17 \pm 0.16)10^9$	$\sim 1\cdot10^{12}$ [b]	—	p.w.
	Red	$1.54\cdot10^5$	$1.31\cdot10^9$	$1.13\cdot10^{12}$	—	p.w.
	Red	$1.50\cdot10^5$	$1.26\cdot10^9$	$1.02\cdot10^{12}$	—	18
	Red	$1.53\cdot10^5$	$1.29\cdot10^9$	$0.61\cdot10^{12}$	—	19
$^{2+}$	FE	20.7 ± 0.2	—	—	—	p.w.
	Red	20.0	—	—	—	11
	FE ($\mu = 1.00$)	20.8 ± 1.0	—	—	—	20
$^{2+}$	FE	4.97 ± 0.15	—	—	—	p.w.
	Red	$\leqslant 3$	—	—	—	11
	FE ($\mu = 1.00$)	4.3 ± 0.3	—	—	—	20

Dis = liquid–liquid distribution; for other abbreviations see Table II.
Estimated graphically.

The yttrium–fluoride system

Three experimental runs at 25.00° each starting with the same concentration of yttrium gave the β_1 and β_2 recorded in Table III. The reproducibility of e.m.f. data in these runs was very good. However, to study higher association species the iron(III)–iron(II) method had to be used. Three runs at different initial yttrium concentrations ($1.98\cdot10^{-4}$, $4.90\cdot10^{-4}$ and $1.98\cdot10^{-3}$ M) gave β_1 to β_3 (Table III). Both methods of measurement gave results in good agreement with those already published.

The fluoride membrane electrode system was used to determine β_1 and β_2 at various temperatures (Table I). From the data, the enthalpy, ΔH_1, and entropy, ΔS_1, changes appropriate to the conditions of measurement were calculated. ΔH_1 and ΔS_1 thus obtained are in reasonable agreement with the results obtained by PAUL *et al.*[10] (Table II) from e.m.f. studies with the iron(III)–iron(II) electrode at different temperatures. ΔH_1 is, however, considerably at variance with the recent calorimetric measurement of WALKER AND CHOPPIN[12]. This largely accounts for the wide discrepancy in ΔS_1 even although there is a factor of two separating the β_1 values from which ΔG_1 were calculated. It is hardly conceivable that the difference in ionic strengths (0.5 and 1) of the media in which these measurements were made can account for the differences in ΔH_1 and ΔS_1. Clearly, additional work is needed to resolve the discrepancy and establish proper data.

ΔH_2 and ΔS_2 calculated from results from the present work should be regarded as no more than very rough estimates in view of the uncertainties in the β_1 and β_2 values. They are nevertheless approximately in line with those published[13] for scandium (Table II).

Scandium and iron(III)-fluoride systems

For both metal ion systems the formation of the first three fluoro complexes was observed. Values of β_1 and β_2 are in reasonable agreement with values obtained by other methods (Table III); β_3 is less certain. Again, the ion-membrane electrode is more limited than the iron(III)–iron(II) electrode in investigations of chemical equilibria.

Magnesium and calcium-fluoride systems

The value obtained for the formation constant for MgF^+_{aq} is in good agreement with that of CONNICK AND TSAO[11]; only an approximate value was available for CaF^+_{aq} for comparison purposes (Table III). It would appear that β_1 for magnesium or calcium is not greatly influenced by the ionic strength of the medium in the 0.5–1 range although such an effect may become more evident at lower ionic strengths. As with the lanthanoid systems, the ratios of $[F^-]$ to $[M]_t$ are restricted by precipitation.

CONCLUSIONS

The membrane electrode is very convenient for the measurement of free fluoride; it is, however, less sensitive than the iron(III)–iron(II) electrode and so is of more limited application in the measurement of equilibrium constants. For potentiometric studies leading to the calculation of reliable values for such constants, $[F^-]_f$ needs to be at least 10^{-6} M so that reasonably useful measurements will be restricted to metal ion systems where β_1 is about 10^6 l M^{-1} or less. Thus, satisfactory values were not obtainable for thorium, for which $\beta_1 = 3.6 \cdot 10^7$ (DODGEN AND ROLLEFSON[19]).

The insolubility of metal fluorides also tends to restrict the range of the $[F^-]_t$ to $[M]_t$ ratio accessible to study in a homogeneous aqueous solution. Conditions need to be chosen so that competition between lanthanum ion from dissolution of the membrane crystal and the metal ion being studied can be neglected. Likewise, for measurement of formal fluoride in water samples, fluoride bound to metal ions (calcium, magnesium, iron, etc.) is released by addition of EDTA and other ligands[21]. Care would be needed, particularly at low $[F^-]_t$, because of the possible solubilising effect of the ligand particularly EDTA, on the lanthanum fluoride membrane.

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SUMMARY

An "Orion" fluoride-sensitive membrane electrode has been examined critically for the measurement of metal–fluoride ion association in aqueous solutions of constant ionic strength, with a calomel reference electrode and sodium chloride salt bridge. Measurements were made with magnesium, calcium, scandium, iron(III), europium(III) and gadolinium ions at 25°; yttrium and "protonation" of $[F^-]$ were studied at 15, 25 and 35° and enthalpy and entropy changes calculated. The electrode is limited to solutions 10^{-6} *M* or greater in free $[F^-]_{aq}$, with a consequent limitation on the magnitude of the first association constant to $\leqq 10^6$. Further limitations are imposed by the insolubility of most metal fluoride salts. The electrode is less sensitive than the iron(III)–iron(II) electrode system, but is much more convenient. Good agreement with previous results was obtained from measurements at various temperatures.

RÉSUMÉ

On a examiné l'utilisation d'une électrode à membrane du type "Orion" fluorure pour des mesures métal–fluorure en solution aqueuse de force ionique constante avec électrode de référence au calomel et pont de chlorure de sodium. Des essais ont été faits avec magnésium, calcium, scandium, fer(III), europium(III) et gadolinium à 25°; yttrium et $[F^-]$ "proton" à 15, 25 et 35°; les variations d'enthalpie et d'entropie ont été calculées. On a examiné également les limites de l'électrode dues à la solubilité de sa membrane et à l'insolubilité de la plupart des fluorures métalliques. Cette électrode est moins sensible que le système fer(III)–fer(II) mais elle convient beaucoup mieux. Les mesures à diverses températures correspondent bien aux résultats précédents.

ZUSAMMENFASSUNG

Eine fluoridempfindliche "Orion"-Membranelektrode wurde auf ihre Eignung zur Messung von Metallfluoridionenassoziationen in wässrigen Lösungen konstanter Ionenstärke kritisch geprüft. Verwendet wurde eine Kalomel-Bezugselektrode und eine Natriumchloridbrücke. Messungen wurden mit Magnesium-, Calcium-, Scandium-, Eisen(III)-, Europium(III)- und Gadolinium-Ionen bei 25° durchgeführt. Yttrium und die Protonisierung von $[F^-]$ wurden bei 15, 25 und 35° bestimmt und der Enthalpie- und Entropie-Wechsel berechnet. Die Elektrode eignet sich für Lösungen von 10^{-6} *M* oder mehr an freiem $[F^-]_{aq}$, wahrscheinlich wegen der Löslichkeit der Membran als Begrenzung auf die Grösse der ersten Assoziationskonstanten von $\leqq 10^6$. Eine weitere Begrenzung ist durch die Unlöslichkeit der meisten Metallfluoride gegeben. Die Elektrode ist weniger empfindlich als das Eisen(III)–Eisen(II)-Elektrodensystem, aber sie ist bequemer zu handhaben. Gute Übereinstimmung mit früheren Ergebnissen wurden bei Messungen bei verschiedenen Temperaturen erhalten.

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INTERPRETATION OF TITRATION CURVES BY MEANS OF THE COMPUTER PROGRAM HALTAFALL

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Considerable attention has been focused on the calculation of the form of titration curves and many papers have been published on this subject, not least in recent years. Titrations have been classified as, for example, acid–base, precipitation, compleximetric or redox. This mode of classification originates from practical aspects rather than from differences in the way in which the various types of curves have been calculated. Acid–base equilibria are those which have been the most thoroughly discussed. General expressions have, for instance, been derived for the dependence of pH on the total concentration of protolyte, on dilution effects, on the stability constants for the proton complexes, on ionic strength and on the ionic product of water[1–14]. Great attention has also been given to the conditions which must be fulfilled in order that inflexion points may be obtained and on the position of such points in relation to the position of the half-titration and equivalence points[15–17]. This is of importance in the determination of the systematic titration errors and in the choice of methods for evaluating the equivalence points[18–26]. Similar aspects have also been considered for simple compleximetric[27–37], redox[38–41] and precipitation reactions[42,43]. Some of the problems dealt with previously are listed in Table I.

The analytical chemist is, however, mainly interested in the calculation of a specific titration curve with stability constants, dilution effects, interferences etc. pertaining to his particular problem. It is very often difficult to find those expressions in the literature which are most suitable for the particular problem at hand. Moreover, because of the complexity of the calculations, these expressions are often based on approximations whose relevance to the specific problem may be difficult to appraise. In order to calculate the form of a titration curve with as few approximations as possible, a computer must almost always be used. A few computer programs dealing with specific problems in the calculation of ionic equilibria have been written in recent years[44,45]. However, since the mathematical expressions for the calculation of chemical equilibria are all based on the equations for mass balance, it has been possible to construct more general programs covering all sorts of titration procedures. Among the computer programs so far published the program most suited to the calculation of titration curves is, without doubt, HALTAFALL[46]. By means of equations for mass balance this program is able to compute the *free* concentrations of each of the species formed during the titration directly from *total* concentration data and the values of the stability constants for the possible complexes in solution. Since two-phase systems can also be included it is possible to compute all kinds of titration problems involving, for example, precipitation or extraction equilibria.

TABLE I

PREVIOUS CONTRIBUTIONS TO THE TREATMENT OF THEORETICAL TITRATION CURVES

Reference no.	*Chemical problem*
1	Calculation of unsymmetrical titration curves avoiding the use of cubic equations.
2	Expressions relating the pK_a value, the degree of neutralisation and intermolecular forces for polymeric poly-acids.
3	Titration of mono- and diprotic acids with strong base.
4	Derivation of equations to calculate pH in acid–base titrations.
5	Acid–base titrations in acetic acid medium.
6	pH dependence of poly-acids in different oxidation states.
7	Potentiometric titration of poly-electrolytes involved in precipitation.
8	Calculation of acid–base titration curves.
9	Equations for acid–base titrations including dilution effects and discussion of inflexion points.
10	Interpretation of potentiometric data in the neighbourhood of the equivalence point and the derivation of protonisation constants.
11	Potentiometric acid–base titration curves.
12	Simple equations for titration curves of monoprotic acids.
13	Errors in calculating hydrogen ion concentration.
14	Interpretation of titration curves for monoprotic and diprotic acids.
15	Acid–base titrations. Location of the points for which pH = pK_a.
16	Method for the location of inflexion points on sigmoid curves.
17	Precipitation and strong acid–strong base titration curves. Points of minimum slope.
18	Extrapolation method for the evaluation of the equivalence point in the photometric titration of weak bases.
19	Methods for evaluating the equivalence points in potentiometric titrations by means of a least squares procedure.
20	Linear extrapolation of the end-point in photometric titrations.
21	A graphical method to evaluate the equivalence point in symmetrical potentiometric titrations. Influence of dilution.
22	Systematic errors in visual titrations.
23	Method to evaluate the end-point in potentiometric acid–base titrations.
24	Straight line regression to determine the volume of titrand added in the inflexion point and its relation to the equivalence volume.
25	Straight line regression to evaluate the equivalence point in potentiometric acid–base titrations introducing the concept of conditional constants.
26	Simple graphical method to evaluate the end-point in potentiometric titrations.
27	Calculation of visual compleximetric titrations without the use of indicator.
28	End-point detection by linear extrapolation in compleximetric titrations.
29	Theoretical relations for the pH dependence in the potentiometric titration of silver with EDTA.
30	Theories for the evaluation of stability constants for the potentiometric titration of vanadium.
31	Theoretical expressions for compleximetric titration curves. Effect of pH.
32	Expressions for the inflexion point in photometric indicator titrations.
33	Use of conditional constants to predict optimal conditions in compleximetric titrations.
34	Photometric end-point detection for the simultaneous compleximetric titration of several metal ions.
35	Mathematical expressions for the titration of several metal ions with one ligand.
36	Inflection points in potentiometric chelometric titration curves.
37	Position of the inflexion point in photometric indicator titrations. Evaluation of titration errors.
38	The concentration dependence of the potential in a redox titration.
39	Calculation of the potential at the equivalence point in redox titrations.
40	General equations for symmetrical homogeneous redox titration curves. Effect of concentration. Conditions for a sharp end-point. Inflection points in symmetrical redox titration curves.
41	Straight line regressions in redox titrations.
42	End-point errors in the precipitation titration of halides.
43	Inflection points in potentiometric titration curves.

Two examples, involving complicated titration curves, are given below to illustrate the redundancy of general expressions and approximate methods in the calculation of titration curves. The first example is concerned mainly with redox equilibria while the second deals with acid–base, compleximetric and precipitation reactions.

EXAMPLE I

Calculate the titration curve for the titration of 100 ml of 0.00005 M As_2O_3 with v ml of 0.001 M I_2 either in the presence of 0.00035 M sodium hydroxide or at constant pH values of 5.7 or 9

The many different ways of expressing equilibrium constants has caused much confusion in the calculation of redox titrations. By introducing [e^-], the concentration of the electron, in the same manner as [H^+] much of this confusion is eliminated. For this reason e^- is given as a ligand by SILLÉN AND MARTELL in their compilation of stability constants[47]. The selection of a particular value for a given stability constant can be a delicate matter, since there is often poor agreement between values found by different authors. With the HALTAFALL program it is, however, simple to test different values or eliminate certain complexes and study the effect on the calculated titration curve. The HALTAFALL program uses constants that apply to a certain ionic medium and does not correct these constants for changes in ionic strength during the titration. It is advisable that the constants chosen are relevant to the particular ionic strength under consideration.

Since the choice of possible complexes with their stability constants expressed with the minimum set of suitable components causes some trouble, a detailed treatment of the selection of the stability constants used in this Example is perhaps of interest.

The standard electrode potential for the formation of iodide ion from iodine is 0.624 V. This corresponds to the equilibrium

$$I_2 + 2e^- \rightleftharpoons 2I^-;\ \log K = 21.10$$

The equilibrium constant, K, is calculated from the relation

$$\log K = zE^0/(RTF^{-1}/\ln 10) = 2 \times 0.624/0.059155$$

where the number of electrons involved in the reaction is denoted by z according to the accepted nomenclature[47].

It is also well established that iodine and iodide form triiodide according to the reaction:

$$I_2 + I^- \rightleftharpoons I_3^-;\ \log K = 2.90$$

The stability constant for the formation of iodate from iodide is more uncertain, and a constant calculated by LAITINEN ($E^0 = 0.26$ V) given in *Stability Constants*[47] has been chosen:

$$IO_3^- + 3H_2O + 6e^- \rightleftharpoons I^- + 6OH^-;\ \log K = 26.37$$

Since iodic acid, HIO_3, is a fairly strong acid its presence can be neglected at pH values greater than 5.

Hypoiodite can be formed by the disproportionation of iodine in alkaline solutions

$$I_2 + 2OH^- \rightleftharpoons I^- + IO^- + H_2O$$

and a constant determined by SIGALLA[48], and given in *Stability Constants*, has been chosen for the reaction

$$I_3^- + H_2O \rightleftharpoons IO^- + 2I^- + 2H^+; \quad \log K = 25.69$$

SIGALLA suggests, furthermore, that I_2OH^- is formed by a substitution reaction

$$I_3^- + OH^- \rightleftharpoons I_2OH^- + I^-$$

and has determined a constant for the equilibrium

$$I^- + HIO \rightleftharpoons I_2OH^-; \quad \log K = 2.00$$

The acidity constant for HIO (or protonization constant for IO^-) is also rather uncertain and the value $pK_a = \log K = 11$ has been chosen:

$$H^+ + IO^- \rightleftharpoons HIO; \quad \log K = 11$$

As this titration is carried out at weak ionic strength an ionization product of water close to $pK_w = 14$ has been selected:

$$H^+ + OH^- \rightleftharpoons H_2O; \quad \log K = 13.90$$

In the mass balance equations $[I^-]$, $[H^+]$ and $[e^-]$ have been chosen as components and, consequently, for data input purposes the concentrations of all complexes must be expressed in terms of constants (and corresponding equilibria) containing these components only, *i.e.*

$$[I_2] = 10^{-21.10}\,[I^-]^2[e^-]^{-2}$$

$$[I_3^-] = 10^{-18.20}\,[I^-]^3[e^-]^{-2}$$

$$[IO^-] = 10^{-43.89}\,[I^-]\,[e^-]^2[H^+]^{-2}$$

$$[HIO] = 10^{-32.89}\,[I^-]\,[e^-]^2[H^+]^{-1}$$

$$[IO_3^-] = 10^{-109.77}\,[I^-]\,[e^-]^{-6}[H^+]^{-6}$$

Arsenic(III) oxide dissolves in water to form either protonated or unprotonated arsenite according to

$$\tfrac{1}{2}\,As_2O_3(s) + \tfrac{1}{2}\,H_2O \rightleftharpoons HAsO_2 \rightleftharpoons H^+ + AsO_2^-$$

A value for the stability constant for the reaction

$$H^+ + AsO_2^- \rightleftharpoons HAsO_2; \quad \log K = 9.24$$

has been chosen from *Stability Constants*[47]. Because of the low total concentration of arsenic, polynuclear complexes have not been taken into consideration. Arsenates are formed according to the reaction

$$AsO_2^- + 2H_2O \rightleftharpoons AsO_4^{3-} + 4H^+ + 2e^-; \quad \log K = 32.7$$

and the value for the equilibrium constant has been recalculated from *Stability Constants* as $\log K = +4 \times 13.9 - 22.9 = 32.7$, where the constant -22.9 applies to the equilibrium

$$AsO_4^{3-} + 2H_2O + 2e^- \rightleftharpoons AsO_2^- + 4OH^-$$

and 13.9 is the value used for pK_w. Arsenate forms proton complexes according to

$$AsO_4^{3-} + H^+ \rightleftharpoons HAsO_4^{2-}; \quad \log K = 11.50$$

$$HAsO_4^{2-} + H^+ \rightleftharpoons H_2AsO_4^-; \quad \log K = 6.94$$

$$H_2AsO_4^- + H^+ \rightleftharpoons H_3AsO_4; \quad \log K = 2.19$$

all constants having been taken from *Stability Constants*[47].

TABLE II

INPUT DATA REQUIRED BY THE HALTAFALL PROGRAM TO CALCULATE THE TITRATION OF 100 ml OF 0.00005 M As_2O_3 WITH v ml OF 0.001 M I_2 AFTER ADDITION OF 0.00035 M NaOH

(Information in parentheses is not included on the data tape)

4	(number of components, AsO_4^{3-}, H^+, I^- and e^-)
12	(number of complexes)
5.00 32 1 4 0 2	($[AsO_2^-] = 5.00 \times 10^{32}[AsO_4^{3-}][H^+]^4[e^-]^2$)
9.80 41 1 5 0 2	($[HAsO_2] = 9.80 \times 10^{41}[AsO_4^{3-}][H^+]^5[e^-]^2$)
3.16 11 1 1 0 0	($[HAsO_4^{2-}] = 3.16 \times 10^{11}[AsO_4^{3-}][H^+]$)
2.76 18 1 2 0 0	($[H_2AsO_4^-] = 2.76 \times 10^{18}[AsO_4^{3-}][H^+]^2$)
4.27 20 1 3 0 0	($[H_3AsO_4] = 4.27 \times 10^{20}[AsO_4^{3-}][H^+]^3$)
7.95 −22 0 0 2 −2	($[I_2] = 7.95 \times 10^{-22}[I^-]^2[e^-]^{-2}$)
6.31 −19 0 0 3 −2	($[I_3^-] = 6.31 \times 10^{-19}[I^-]^3[e^-]^{-2}$)
1.29 −44 0 −2 1 −2	($[IO^-] = 1.29 \times 10^{-44}[H^+]^{-2}[I^-][e^-]^{-2}$)
1.29 −33 0 −1 1 −2	($[HIO] = 1.29 \times 10^{-33}[H^+]^{-1}[I^-][e^-]^{-2}$)
1.29 −31 0 −1 2 −2	($[I_2OH^-] = 1.29 \times 10^{-31}[H^+]^{-1}[I^-]^2[e^-]^{-2}$)
1.70 −110 0 −6 1 −6	($[IO_3^-] = 1.70 \times 10^{-110}[H^+]^{-6}[I^-][e^-]^{-6}$)
1.26 −14 0 −1 0 0	($[OH^-] = 1.26 \times 10^{-14}[H^+]^{-1}$)
0	(number of solid phases)
16	(number of printing orders)
0 0	(print v ml titrant added)
−1 2	(print log $[AsO_4^{3-}]$, component *No.* 1)
−2 2	(print log $[H^+]$, component *No.* 2)
−3 2	(print log $[I^-]$, component *No.* 3)
−4 2	(print log $[e^-]$, component *No.* 4)
1 2	(print log $[AsO_2^-]$, complex *No.* 1)
1 1	(print $[AsO_2^-]$, complex *No.* 1)
−1 3	(print log $([AsO_4^{3-}]/[As]_{tot})$, component *No.* 1)
4 2	(print log $[H_2AsO_4^-]$, complex *No.* 4)
5 2	(print log $[H_3AsO_4]$, complex *No.* 5)
6 2	(print log $[I_2]$, complex *No.* 6)
7 2	(print log $[I_3^-]$, complex *No.* 7)
8 2	(print log $[IO^-]$, complex *No.* 8)
9 2	(print log $[HIO^-]$, complex *No.* 9)
10 2	(print log $[I_2OH^-]$, complex *No.* 10)
11 2	(print log $[IO_3^-]$, complex *No.* 11)
1	(number of titrations)
0.1	(*stegbyt*[46])
25	(number of titration points)
4	(*hur*-number[46] for the first component AsO_4^{3-})
−10	(estimated value of ln $[AsO_4^{3-}]$ at the first titration point $v = 15$ ml)
−0.001	(tolerance for the first component $\lvert [As]_{tot} - [As]_{tot\cdot calc} \rvert < 0.001[As]_{tot}$, *i.e.* the accuracy of the calculation is 0.1%)
0.0001	($[As]_{tot}$ in the titration vessel $= 2[As_2O_3]_{tot}$)
0	($[As]_{tot}$ in the buret)
4 10 −0.001 0.00015 0	*hur*-number[46], tolerances and total concentrations for components H^+, I^- and e^- respectively
4 −10 10^{-8} 0 0.002	
−4 −10 10^{-8} 0.0002 −0.002	
100	(initial volume in ml)
15 14 13 12 11.5 11 10.75 10.5 10.25 10 9.75 9.5 9 8.5 8 7 6 5 4 3 2 1 0.5 0.25 0	(ml titrant added)

The stability constants for the arsenic(III) and (V) systems expressed in terms of the components $[AsO_4^{3-}]$, $[e^-]$ and $[H^+]$ are thus

$$[AsO_2^-] = 10^{32.70} [AsO_4^{3-}] [H^+]^4 [e^-]^2$$

$$[HAsO_2] = 10^{41.99} [AsO_4^{3-}] [H^+]^5 [e^-]^2$$

$$[HAsO_4^{2-}] = 10^{11.50} [AsO_4^{3-}] [H^+]$$

$$[H_2AsO_4^-] = 10^{18.44} [AsO_4^{3-}] [H^+]^2$$

$$[H_3AsO_4] = 10^{20.63} [AsO_4^{3-}] [H^+]^3$$

In the order to be able to use the program it is only necessary to know the proper order in which the data should be fed into the computer. Thus even a chemist inexperienced in computing techniques can use the program once it has been adapted to the particular computer available. The form of the input data for Example 1 is illustrated in Table II. Comments are given in parentheses. Further information concerning the order in which the data should be introduced can be obtained from SILLÉN *et al.*[46] and from a recent textbook[49].

It must be stressed that in the execution of the calculations, there is one important difference between redox equilibria and, for instance, acid–base equilibria, since, even if the activity of the electron is well defined, there is no corresponding electron concentration. For this reason, the free electron concentration is not included

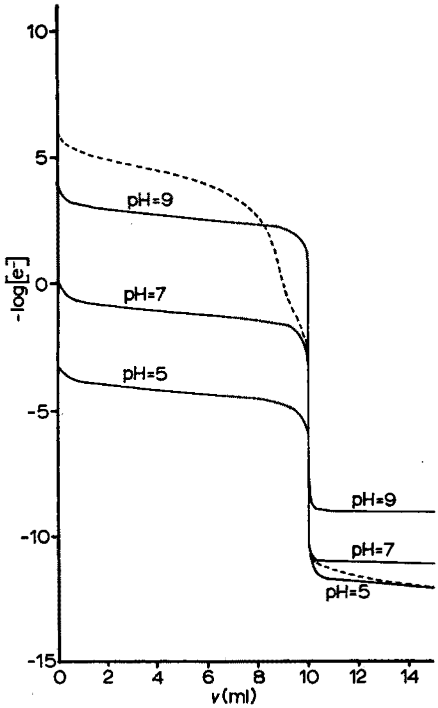

Fig. 1. pE (−log [e⁻]) plotted against ml of titrant added for the titration of 100 ml of 0.00005 *M* As_2O_3 with *v* ml of 0.001 *M* I_2 at constant pH values of 5, 7 and 9 and for the addition of excess 0.00035 *M* NaOH before the titration (dashed curve).

in the mass balance equation for the electron. From a mathematical point of view this is the only difference between the calculation of redox and of acid–base equilibria.

The results of the calculations are illustrated in Figs. 1–3 by three types of diagram, which are all, for different reasons, of interest to the analytical chemist. The first plot is that of pE ($-\log [e^-]$) against v ml of titrant added which illustrates the theoretical relationship between the measurable variables (pE with an inert electrode and v directly from the buret). It is, for instance, evident from Fig. 1 that the inflexion points coincide with the equivalence point for all pH values. The value of the first derivative is, moreover, in all cases very large in the immediate vicinity

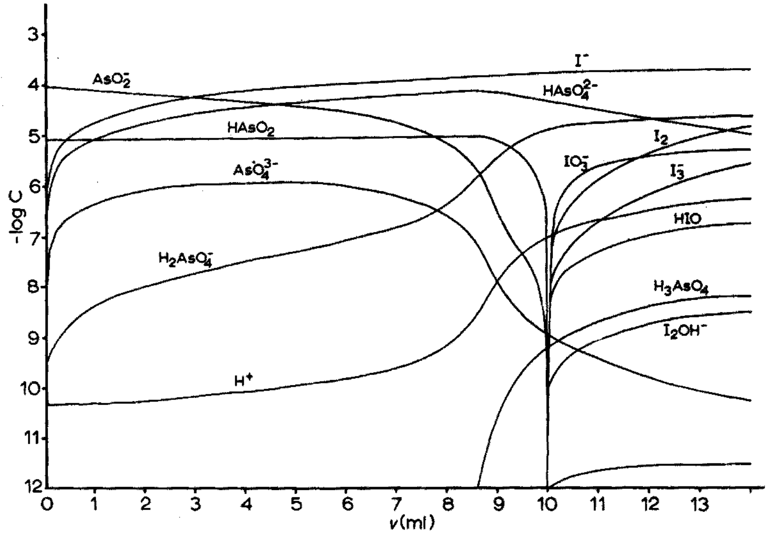

Fig. 2. Logarithmic diagram for the titration of 100 ml of 0.00005 M As_2O_3 with v ml of 0.001 M I_2 after the addition of 0.00035 M NaOH.

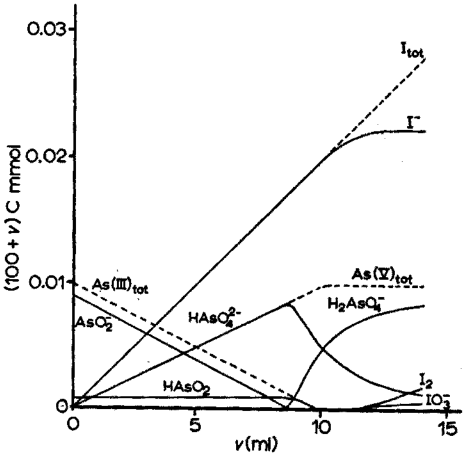

Fig. 3. Diagram to illustrate the main reactions occurring in the different parts of titration curve for the titration of 100 ml of 0.00005 M As_2O_3 with v ml of 0.001 M I_2 after the addition of 0.00035 M NaOH. The amounts of the dominating species (mmol), calculated by multiplying their concentrations with the total volume ($100 + v$) ml, have been plotted against v ml.

of this point *i.e.* there is a large "mV jump" around the equivalence point. Furthermore, it is apparent that a slightly better titration is obtained at pH 9 than at pH 5 or 7.

The irregularity in the pE *vs.* v ml curve for $v = 8.7$ ml in the case in which pH was not held constant, is explained by the consumption of the excess of sodium hydroxide at this v value. A corresponding irregularity will, of course, also be found in the pH *vs.* v ml curve (*cf.* Fig. 2).

The second way by which the titration curve may be illustrated is by means of a logarithmic concentration diagram such as that shown in Fig. 2 for the case in which 0.00035 M sodium hydroxide was added to the solution. From this type of curve it is possible to see which complexes contribute most to the form of the titration curve. Furthermore, such diagrams can be used to estimate the maximum concentrations of, for example, buffering and masking agents which can be tolerated without unfavourably changing the form of the titration curve.

Probably the most interesting way of illustrating the titration curve for the analytical chemist is by means of a diagram in which the amounts of the dominating species, that is the free concentrations multiplied by the dilution factor $(v_0 + v)$ ml, where v_0 ml is the initial volume of each species, are plotted against v ml of titrant added, since this type of diagram shows which reactions dominate in the different parts of the titration curve. Figure 3 illustrates the case in which 0.00035 M sodium hydroxide was added. It is seen, for instance, from the linearity of the plot $(100 + v)$ $[I^-]$ for $v < 10$ that the predominating reduction in this volume interval is

$$I_2 + 2e^- \rightleftharpoons 2I^-$$

The corresponding oxidation is, for $v < 8$ ml,

$$2H_2O + AsO_2^- \rightarrow HAsO_4^{2-} + 3H^+ + 2e^-$$

as is seen from the linearity of the $(100 + v)$ $[AsO_2^-]$ and $(100 + v)$ $[HAsO_4^{2-}]$ plots in this volume interval. For v values greater than 8 ml, the pH of the solution has decreased so much (*cf.* Fig. 2) that the formation of $H_2AsO_4^-$ from both AsO_2^- and $HAsO_4^{2-}$ dominates for $8 < v < 10$ ml. In the whole volume region $v < 10$ ml there occur, as can also be seen from Fig. 3, minor side-reactions such as the formation of AsO_4^{3-} and the oxidation of $HAsO_2$ rather than of AsO_2^-.

At v values greater than 10 ml, part of the iodine reacts with iodide to form I_3^- while part disproportionates into I^- and IO_3^-. The dominating reaction in the region $10 < v < 12$ ml (see Fig. 3) seems to be the formation of IO_3^- according to

$$3I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$$

For $v > 12$ ml, this reaction is hampered by the continually decreasing pH(see curve for log $[H^+]$ in Fig. 2). Likewise the formation of $H_2AsO_4^-$ according to

$$HAsO_4^{2-} + H^+ \rightleftharpoons H_2AsO_4^-;\ pK_a = 6.94$$

increases constantly for $v > 8$ ml.

Once the main reactions occurring in the different parts of the titration curve are known, all the information needed to determine the best way of evaluating the equivalence points is available. The different methods (*cf.* DYRSSEN *et al.*[49]) by which this may be done will not, however, be taken into consideration here.

EXAMPLE 2

Calculate the titration curve for the titration of 100 ml of 0.02 M DTPA (diethylenetriaminepentaacetic acid = H_5L) in 0.1 M sodium chloride solution with v ml of 0.2 M sodium hydroxide

Calculations of titration curves have been done for the following cases:

(i) no metal ion,

TABLE III

STABILITY AND SOLUBILITY CONSTANTS USED FOR THE CALCULATION OF THE TITRATION CURVES IN EXAMPLE 2

(All constants are taken from WÄNNINEN[50])

Reaction	*Logarithm of constant*	*Reaction*	*Logarithm of constant*
$H^+ + L^{5-} \rightleftharpoons HL^{4-}$	10.48	$Mg^{2+} + H^+ + L^{5-} \rightleftharpoons MgHL^{2-}$	16.19
$2H^+ + L^{5-} \rightleftharpoons H_2L^{3-}$	18.49	$Mg^{2+} + L^{5-} \rightleftharpoons MgL^{3-}$	9.34
$3H^+ + L^{5-} \rightleftharpoons H_3L^{2-}$	22.78	$Ca^{2+} + H^+ + L^{5-} \rightleftharpoons CaHL^{2-}$	16.88
$4H^+ + L^{5-} \rightleftharpoons H_4L^-$	25.57	$Ca^{2+} + L^{5-} \rightleftharpoons CaL^{3-}$	10.60
$5H^+ + L^{5-} \rightleftharpoons H_5L$	27.42	$H_2O \rightleftharpoons H^+ + OH^-$	−13.90
$Ba^{2+} + H^+ + L^{5-} \rightleftharpoons BaHL^{2-}$	14.12	$H_5L(s) \rightleftharpoons 5H^+ + L^{5-}$	−29.775
$Ba^{2+} + L^{5-} \rightleftharpoons BaL^{3-}$	8.78		

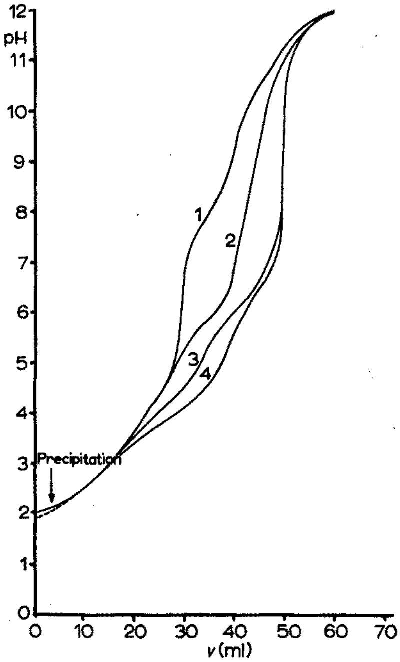

Fig. 4. pH plotted against ml of titrant added for the titration of 100 ml of 0.02 *M* DTPA in 0.1 *M* NaCl with *v* ml of 0.2 *M* NaOH in the presence of: no divalent metal ion (curve 1); 0.09 *M* Ba^{2+} (curve 2); 0.01 *M* Ba^{2+} and 0.01 *M* Mg^{2+} (curve 3); 0.01 *M* Ba^{2+}, 0.01 *M* Mg^{2+} and 0.01 *M* Ca^{2+} (curve 4). The dotted line indicates the form that the titration curve would have if all DTPA dissolved at the beginning of the titration.

(ii) 0.01 M Ba^{2+},
(iii) 0.01 M Ba^{2+} and 0.01 M Mg^{2+},
(iv) 0.01 M Ba^{2+}, 0.01 M Mg^{2+} and 0.01 M Ca^{2+}.

The stability constants used in this Example have all been taken from the same author[50] and are listed in Table III. The solubility product for $H_5L(s)$ has been estimated from data[50] on the total solubility of DTPA (4 g/l). By means of the HALTAFALL program, the pH value and the free concentration of L^{5-} in a saturated DTPA solution can be calculated. The solubility product for $H_5L(s)$ is then given by

$$[H^+]^5[L^{5-}] = 10^{-27.42}$$

The data set fed into the computer for case (i) (no metal ion present) is given in Table IV. The main difference between these and the data given in Table III is that a solid phase has been included in the data of Table IV.

The results of the calculations are illustrated in Figs. 4 and 5. In Fig. 4 pH has been plotted against v ml of titrant added. This curve corresponds to measurable units (*e.g.*, pH with a glass electrode) and it is apparent that if no metal ion is present there are only two distinguishable inflexion points, namely at $v=30$ and $v=40$ ml. The point of inflexion at $v=30$ ml exhibits the highest value of the first derivative and it should thus be possible to estimate the amount of H_5L by titration with

TABLE IV

INPUT DATA REQUIRED BY THE HALTAFALL PROGRAM TO CALCULATE THE TITRATION OF 100 ml OF 0.02 M DTPA WITH v ml OF 0.2 M NaOH

2				(number of components, H^+ and L^{5-})
6				(number of complexes)
3.02	10	1	1	($[HL^{4-}] = 3.02 \times 10^{10}[H^+][L^{5-}]$)
3.10	18	2	1	($[H_2L^{3-}] = 3.10 \times 10^{18}[H^+]^2[L^{5-}]$)
6.03	22	3	1	($[H_3L^{2-}] = 6.03 \times 10^{22}[H^+]^3[L^{5-}]$)
3.72	25	4	1	($[H_4L^{-}] = 3.72 \times 10^{25}[H^+]^4[L^{5-}]$)
2.70	27	5	1	($[H_5L] = 2.70 \times 10^{27}[H^+]^5[L^{5-}]$)
1.26	−14	−1	0	($[OH^-] = 1.26 \times 10^{-14}[H^+]^{-1}$)
1				(number of solid phases)
3.80	−30	5	1	($[H^+]^5[L^{5-}] = 3.80 \times 10^{-30}$)
8				(number of printing orders)
0	0			(print v ml titrant added)
−1	2			(print log $[H^+]$, component *No.* 1)
−2	2			(print log $[L^{5-}]$, component *No.* 2)
1	−2			(print $[HL^{4-}]/[L]_{tot}$, component *No.* 2 and complex *No.* 1)
2	−2			(print $[H_2L^{3-}]/[L]_{tot}$, component *No.* 2 and complex *No.* 2)
3	−2			(print $[H_3L^{2-}]/[L]_{tot}$, component *No.* 2 and complex *No.* 3)
4	−2			(print $[H_4L^{-}]/[L]_{tot}$, component *No.* 2 and complex *No.* 4)
5	−2			(print $[H_5L]/[L]_{tot}$, component *No.* 2 and complex *No.* 5)
1				(number of titrations)
0.2				(*stegbyt*[46])
25				(number of titration points)
4	−5	10^{-8}		(*hur*-number[46], estimated value of ln $[H^+]_{init}$ and tolerance for component *No.* 1 H^+)
0.1		−0.2		($[H^+]_{tot}$ in titration verssel and buret 0.1 and −0.2 M ($[OH^-] = 0.2$ M), respectively)
4	−20	-10^{-4}		(*hur*-number[46], estimated value of ln $[L^{5-}]$ and tolerance for component *No.* 2 L^{5-})
0.02		0		($[L]_{tot}$ in titration verssel and buret, respectively)
100				(initial volume in ml)
0	2.5	5	7 … 60	(v ml titrant added)

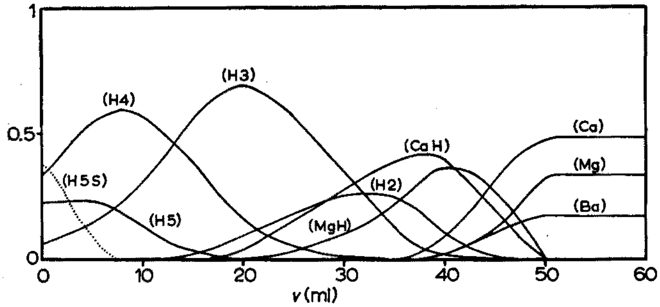

Fig. 5. Diagram illustrating the main reactions occurring in the different parts of the titration curve for the titration of 100 ml of a solution containing 0.02 M DTPA (H_5L), 0.01 M Ba^{2+}, 0.01 M Mg^{2+} and 0.01 M Ca^{2+} with v ml 0.2 M NaOH. Notations: (H5S) = mmol of solid $H_5L/(v_0+v)$ $[L]_{tot}$, (H5) = $[H_5L]/[L]_{tot}$, (H4) = $[H_4L^-]/[L]_{tot}$, (H3) = $[H_3L^{2-}]/[L]_{tot}$, (H2) = $[H_2L^{3-}]/[L]_{tot}$, (Ba) = $[BaL^{3-}]/[L]_{tot}$, (Mg) = $[MgL^{3-}]/[L]_{tot}$, (Ca) = $[CaL^{2-}]/[L]_{tot}$, (MgH) = $[MgHL^{2-}]/[L]_{tot}$, (CaH) = $[CaHL^{2-}]/[L]_{tot}$.

sodium hydroxide in three steps to H_2L^{3-}. Addition of metal ion leads to a lowering of the pH in the region $20 < v < 50$ ml and the appearance of a sharp inflexion at $v = 50$ ml (curves 3 and 4 in Fig. 4), but the disappearance of the inflexion at $v = 30$ ml.

It should be noted that the HALTAFALL program can also be used to confirm the validity of the stability constants derived from an experimental curve by fitting a titration curve calculated with these constants to the experimental curve[51]. For example, the curves computed in Fig. 4 are in good agreement with the experimental curves used by WÄNNINEN[50] to evaluate the constants given in Table III.

The main reactions occurring in this system are illustrated by plotting the curves $[H_nL^{5-n}]/[L]_{tot}$, $[MHL^{2-}]/[L]_{tot}$ and $[ML^{3-}]/[L]_{tot}$ against v ml of titrant added, as in Fig. 5 for case (iv), where M denotes any one of the ions Ba^{2+}, Mg^{2+} or Ca^{2+}. The amount of $H_5L(s)$ is included in $[L]_{tot}$. Since none of the plots in Fig. 5 is linear no reaction predominates in any part of the titration curve. For $v < 10$ ml the reaction

$$H_5L(s+aq) + OH^- \rightleftharpoons H_4L^-$$

contributes most to the form of the curve. In the volume region $10 < v < 20$ ml the formation of H_3L^{2-} from H_4L^- and H_5L is the dominating reaction. For $20 < v < 40$ ml there is competition between several reactions such as the formation of H_2L^{3-}, $CaHL^{2-}$ and $MgHL^{2-}$. In the interval $40 < v < 50$ ml reactions of the type

$$MHL^{2-} + OH^- \rightarrow ML^{3-}$$

where M^{2+} is mainly calcium and magnesium, dominate and for $v > 50$ ml, excess sodium hydroxide will only increase the free hydroxyl ion concentration.

CONCLUSIONS

These two examples show that, by using the computer program HALTAFALL, titration curves can be calculated and fully understood without the complexity of the mathematical expressions concealing the chemical nature of the problem. In fact, the main difficulty in performing these calculations lies in selecting relevant species and their formation (stability) constants, and, in expressing these species (complexes) in terms of a minimum of components. Previous work on the calculation of theoretical titration curves has been limited to special cases involving very much simpler chemical equilibria than those of the two examples given here.

It has been found that this method of calculating titration curves enables students to comprehend easily the relevance of the often very detailed instructions for the execution of titration procedures. They are, moreover, more capable of making constructive use of the data they obtain.

The HALTAFALL program is now available in Algol 60 for the Algol compilers of SAAB D21, CDC 3200, CDC 3600 and IBM 360/50 in Göteborg, Stockholm and Uppsala, and Elliot 800 at Chelsea College of Science and Technology, London. Furthermore, the program has recently been translated into Fortran IV for the IBM 360/50[52].

We should like to thank the head of this department, Professor DAVID DYRSSEN, for valuable discussions, and Mrs. SUSAN JAGNER M.A., fil.lic. for revising the English text of this paper.

SUMMARY

By the rigorous calculation of two titration curves, the use of the computer program HALTAFALL in the interpretation of titration procedures is exemplified. General expressions of the type often found in the literature are, moreover, shown to be redundant.

RÉSUMÉ

Le calcul rigoureux de deux courbes de titrage a permis d'illustrer l'application du programme computer HALTAFALL pour l'interprétation de procédés titrimétriques. Des expressions générales, rencontrées dans la littérature, semblent alors superflues.

ZUSAMMENFASSUNG

Durch die genaue Berechnung zweier Titrationskurven konnte die Eignung des Computerprogramms HALTAFALL für die Interpretation von Titrationsverfahren gezeigt werden. Es ergab sich, dass Ausdrücke des Typs, wie sie oft in der Literatur gefunden werden, überdies überflüssig sind.

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COMPORTEMENT DE L'EAU ET DE LA SOUDE DANS LES CHLORURES ALCALINS FONDUS

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La solubilité de l'eau dans l'eutectique LiCl–KCl fondu a été déterminée par BURKHARD ET CORBETT[1]. A 480°, pour un eutectique LiCl:KCl=6:10, ce phénomène obéit à la loi de Henry tant que la pression d'eau est inférieure ou égale à 18 mm de mercure avec une constante égale à $11.3 \cdot 10^{-6}$ mole d'eau par mole de LiCl et par mm. Selon ces auteurs, seul l'ion Li^+ est responsable de l'absorption d'eau. Aux pressions plus élevées, le caractère acide de Li^+ provoque l'hydrolyse de l'eau et il s'observe un dégagement d'acide chlorhydrique ($2 \cdot 10^{-4}$ mole par mole de LiCl à 26 mm de mercure).

Les mesures électrochimiques effectuées dans un bain de KHF_2 à 250° et contenant en solution des quantités variables d'eau (entre 0.1 et 1.8% en poids) ont conduit PIZZINI *et al.*[2] à admettre l'existence, dans le bain, d'espèces H_3O^+ formées selon la réaction:

$$H_2O + HF \rightarrow H_3O^+ + F^- \qquad (1)$$

D'après DELARUE[3], les ions HO^- n'existeraient pas en quantité notable dans un bain d'eutectique LiCl–KCl (59 moles de LiCl pour 41 moles de KCl) par suite de l'équilibre

$$2HO^- \rightleftarrows H_2O + O^{2-} \qquad (2)$$

qui serait très déplacé vers la droite. Les solutions de potasse ou de soude devraient donc se comporter comme des solutions de K_2O ou de Na_2O. Pourtant, WRENCH[4] a montré que dans un bain d'eutectique LiCl–KCl à 400°, la potasse n'était pas complètement décomposée. Par ailleurs, l'hypothèse de la formation de l'ion peroxyde (O_2^{2-}) a permis à PIZZINI ET MORLOTTI[5] d'expliquer les résultats des mesures électrochimiques effectuées dans un bain de fluorures fondus. Ces auteurs suggèrent la formation anodique de cet ion selon la réaction électrochimique:

$$2HO^- + 2F^- \rightarrow O_2^{2-} + 2HF + 2e \qquad (3)$$

Nous avons étudié, par spectrométrie d'absorption IR et par l'analyse des différents produits de réaction, le comportement de l'eau et de la soude dans un bain d'eutectique NaCl–KCl à 800°.

PARTIE EXPÉRIMENTALE

Le solvant est préparé dans une boîte à gants à atmosphère inerte et sèche selon la méthode mise au point précédemment[6]. Les conditions expérimentales relatives à la mesure des spectres d'absorption IR ont été décrites[7].

Réactifs

Eau distillée et pastilles de soude "Baker Analysed Reagent". Ce dernier réactif a, d'après nos analyses, une pureté de $(98.0 \pm 0.5)\%$. Il contient environ 1% de carbonate. On n'y décèle pas de quantité mesurable de silicate ou de peroxyde. Avant emploi, les pastilles de soude sont dégazées sous vide à la température ordinaire pendant 2 h et déshydratées à 250° pendant 2 h sous pression atmosphérique d'azote pur et sec.

COMPORTEMENT DE L'EAU

Deux techniques d'introduction dans le bain ont été utilisées: (*a*) entraînement par un courant d'azote pur; (*b*) injection de quantités déterminées.

Résultats expérimentaux

Titrimétrie. Le dégagement gazeux provoqué par l'introduction du réactif est recueilli dans une cellule contenant de l'eau pure. Dans la solution ainsi obtenue, nous avons pu titrer jusqu'à $(7.8 \pm 0.2) \cdot 10^{-5}$ équivalents d'acide. Le bain ayant donné lieu à un tel dégagement de vapeurs acides contient en moyenne $(8.0 \pm 0.4) \cdot 10^{-5}$ équivalents de base et $(4.0 \pm 1.0) \cdot 10^{-6}$ moles de silicates (SiO_3^{2-}); ces derniers étant titrés par la colorimétrie à 420 nm du complexe silicimolybdique[8].

Spectrométrie d'absorption IR. Selon les conditions expérimentales, deux types de résultats sont obtenus:

(*a*) les spectres IR des pastilles correspondant aux prélèvements effectués alors que le barbotage (N_2, H_2O) dans le bain n'est pas arrêté sont représentés dans la Fig. 1. Ils sont caractérisés, dans un premier stade, par des absorptions dont les maxima se situent à $\simeq 3400$ et $\simeq 1637$ cm^{-1}. Ces bandes disparaissent dans les prélèvements effectués après 60 min de barbotage (N_2, H_2O).

(*b*) les spectres mesurés après introduction d'une quantité déterminée d'eau ne contiennent aucune bande d'absorption.

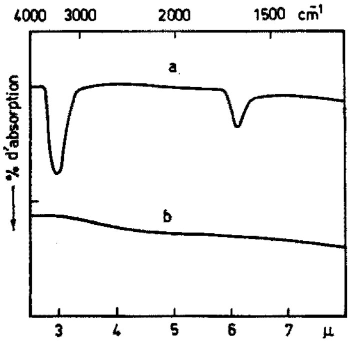


Fig. 1. Spectrométrie d'absorption IR: (a) eutectique NaCl–KCl à 800° + H_2O (entraînement par N_2). Prélèvement après 31 min de barbotage; (b) eutectique NaCl–KCl à 800° + H_2O (entraînement par N_2). Prélèvement après 60 min de barbotage.

Interprétation des résultats

Le dégagement d'acide que nous avons observé pourrait résulter des réactions:

$$H_2O + Cl^- \rightleftarrows HCl\uparrow + HO^- \tag{4}$$

$$HO^- + Cl^- \rightleftarrows HCl\uparrow + O^{2-} \tag{5}$$

soit au total

$$H_2O + 2Cl^- \rightleftarrows 2HCl\uparrow + O^{2-} \tag{6}$$

Quant aux bandes d'absorption IR observées pendant un certain temps lors du barbotage (N_2, H_2O) à 3400 et 1637 cm^{-1}, elles peuvent être dues:

soit à l'eau contenue dans la pastille au moment du prélèvement[9]: eau dissoute dans l'eutectique fondu ou eau contenue dans le courant d'azote et adsorbée sur le prélèvement.

soit aux ions HO^- issus de la réaction (4).

Mais la disparition ultérieure de toute bande d'absorption dans le cas du barbotage ininterrompu de (N_2, H_2O), l'absence complète de toute absorption dans celui de l'introduction d'une quantité déterminée d'eau prouvent, d'une part que les absorptions antérieurement observées sont dues à l'eau qui n'a pas réagi avec le solvant et accidentellement adsorbée sur les prélèvements, d'autre part que l'équilibre (6), somme de (4) et (5), est très déplacé vers la droite.

COMPORTEMENT DE LA SOUDE

L'équilibre (6) suggère l'instabilité des ions HO^- dans le bain. Pour vérifier cette hypothèse, les analyses suivantes ont été effectuées.

Résultats expérimentaux

Fusion sous vide. Lorsque la soude traitée selon les conditions décrites au début de cette étude est portée très rapidement à 800°, on observe une vive effervescence à la fusion. Les gaz recueillis, analysés par spectrométrie de masse, contiennent essentiellement de l'eau. Dans la cellule ayant servi à recueillir les dégagements gazeux, on peut titrer, sous forme d'hydroxyde, jusqu'à 2% de la quantité de soude introduite avant la fusion. Dans la masse de soude fondue, on ne décèle pas de peroxyde.

Analyse des vapeurs dégagées après introduction de NaOH dans les chlorures alcalins fondus. Les essais sont effectués sous vide: un vif dégagement gazeux est observé lors de la dissolution des pastilles de NaOH. Après la dissolution, le bain reste toujours constitué par une seule phase liquide. Deux techniques d'analyse du dégagement gazeux ont été utilisées: la spectrométrie de masse et la titrimétrie.

(a) Spectrométrie de masse. Les résultats obtenus par cette méthode montrent que l'eau est le constituant majeur des vapeurs dégagées.

(b) Titrimétrie. Lorsque l'introduction est effectuée sous vide, les gaz recueillis contiennent 1 à 2% de la quantité de soude ajoutée dans le bain. Si, par contre, juste après addition — effectuée sous pression atmosphérique d'azote pur et sec — on recouvre la cellule de réaction par une tête hermétique et que l'on laisse les gaz au contact du bain pendant quelques minutes, on ne détecte plus d'alcalinité dans le condensat. Dans ce dernier, on peut titrer, dès lors, jusqu'à $(5.0 \pm 1.0) \cdot 10^{-5}$ équivalents d'acide.

Analyse des produits de réaction contenus dans le bain. Trois méthodes ont été utilisées; ce sont la titrimétrie, la spectrométrie IR et la colorimétrie.

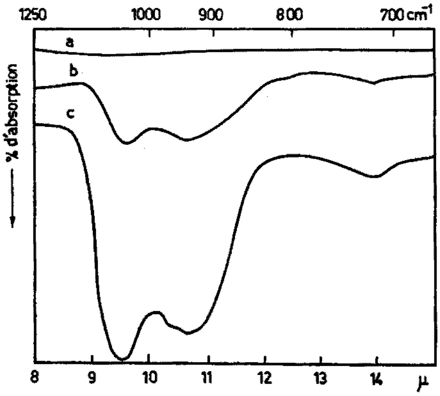
(a) Titrimétrie. Nous avons titré l'alcalinité totale du bain. La moyenne des résultats correspondant à quatre essais est de $(77 \pm 6.0)\%$ de la teneur de NaOH introduite au départ. On ne retrouve donc pas, dans le bain, toute la quantité de soude ajoutée.

(b) Spectrométrie d'absorption IR. Les spectres des échantillons correspondant à différentes concentrations de soude sont identiques à celui de la Fig. 2b et leurs caractéristiques sont les suivantes:

ν (cm⁻¹)	*Concentration NaOH (M)*	*Intensités et caractéristiques*
1040	$6.85 \cdot 10^{-2}$	Forte } et larges
940	à	Forte } et larges
715	$3.46 \cdot 10^{-1}$	Faible

Les caractéristiques du spectre de NaOD mesuré dans les mêmes conditions (Fig. 2c) sont les suivantes:

ν (cm⁻¹)	*Concentration NaOD (M)*	*Intensités et caractéristiques*
1050		Très forte
960 ↔ 935	$2.37 \cdot 10^{-1}$	Forte et large
720		Faible et large



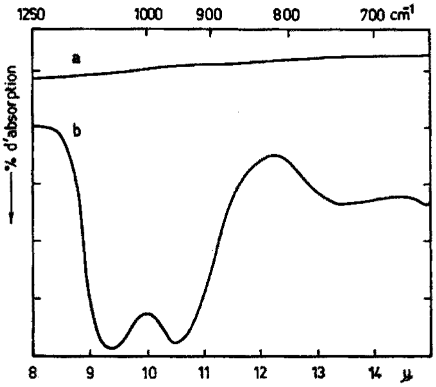


Fig. 2. Spectrométrie d'absorption IR: (a) eutectique NaCl–KCl purifié; (b) eutectique NaCl–KCl à 800° + NaOH ($6.85 \cdot 10^{-2}$ *M*): prélèvement quelques secondes après addition; (c) eutectique NaCl–KCl à 800° + NaOD ($2.37 \cdot 10^{-1}$ *M*): prélèvement après introduction.

Fig. 3. Spectrométrie d'absorption IR: (a) eutectique NaCl–KCl purifié; (b) eutectique NaCl–KCl à 800° + Na_2O_2 ($1.47 \cdot 10^{-1}$ *M*).

Les intensités des bandes observées au cours des différentes expériences décrites ci-dessus décroissent lorsqu'un barbotage d'azote pur et sec est assuré dans le bain. A 800°, les bandes finissent par disparaître complètement lorsque, après 5 h de barbotage d'azote, le bain est laissé pendant 15 h à cette température. En se référant aux maxima d'absorption, on ne remarque aucune différence importante, ni — compte tenu de la résolution de l'appareillage de mesure utilisé — aucun déplacement de bandes lorsque NaOH est remplacé par NaOD. Par ailleurs, les spectres IR mesurés après introduction de ces composés dans le bain sont analogues à celui des peroxydes (Fig. 3)*.

Nous avons donc recherché dans l'eutectique refroidi, par la méthode colorimétrique, la présence des peroxydes et aussi des silicates qui auraient pu se former par réaction à haute température des hydroxydes avec le quartz.

(c) Colorimétrie. Recherche des peroxydes par la colorimétrie à 410 nm du complexe orange formé avec le titan(IV) en milieu sulfurique 4 *N*[11]. Notons que les silicates ne donnent aucune coloration avec la solution sulfurique du titan(IV). Les résultats des dosages sont les suivants:

Concentration NaOH (M)	*Teneur de Na_2O_2 trouvée en % de NaOH introduit (moyenne de 2 mesures)*	*Moyenne*
$2.17 \cdot 10^{-1}$	10.7	
$3.5 \cdot 10^{-1}$	11.2	≃ 11.0

Il ressort qu'à 800°, (11.0 ± 1.0)% de la concentration de soude introduite sont transformés en Na_2O_2. Dans LiCl–KCl à 585°, cette teneur apparente tombe à (3.2 ± 0.2)%.

Recherche des silicates par la colorimétrie à 420 nm du complexe silicimolybdique jaune[8]. Toutes les préparations sont effectuées dans des béchers en polyéthylène. Les ions O_2^{2-} donnant la même coloration, il est nécessaire, lorsqu'ils sont présents dans la solution, de détruire les peroxydes par ébullition en milieu sulfurique 1 *N* pendant quelques minutes. Les teneurs apparentes de silicates trouvées après addition de NaOH dans le bain d'eutectique NaCl–KCl à 800°, sur la base de l'unique réaction

$$SiO_2 + 2HO^- \rightarrow SiO_3^{2-} + H_2O \qquad (7)$$

sont consignées comme suit:

Poids de NaOH introduit (mg)	*Concentration de SiO_3^{2-} (moles)*	*Quantité correspondante NaOH (moles)*	*% de la quantité de NaOH introduite*
153.5	$2.84 \cdot 10^{-4}$	$5.68 \cdot 10^{-4}$	14.7
162.5	$3.60 \cdot 10^{-4}$	$7.20 \cdot 10^{-4}$	17.75
186.9	$3.81 \cdot 10^{-4}$	$7.62 \cdot 10^{-4}$	16.0

soit en moyenne (16.0 ± 2.0)% de soude transformée.

---

* Le mélange à température ordinaire et sous atmosphère inerte et sèche de peroxyde de sodium (produit Merck) et de l'eutectique NaCl–KCl purifié, a un spectre d'absorption IR analogue à celui de la Fig. 3. Or, le nombre d'onde de vibration calculé à partir de la longueur de la liaison O–O dans Na_2O_2 se situe[10] vers 877 cm^{-1}. A défaut d'autres études et étant donné que, dans nos conditions expérimentales, ces spectres sont différents de celui des carbonates[6] dont on pouvait supposer la présence dans le peroxyde utilisé, nous admettrons le spectre représenté à la Fig. 3 comme étant celui des peroxydes.

Interprétation des résultats et discussion

Le dégagement de vapeur d'eau observé après introduction de la soude dans le bain proviendrait de la transformation:

$$2HO^- \rightarrow H_2O\uparrow + O^{2-} \qquad (8)$$

Lorsqu'un contact forcé est maintenu entre le bain et la vapeur d'eau formée, celle-ci réagit avec les ions chlorure du solvant selon:

$$H_2O + 2Cl^- \rightleftarrows 2HCl\uparrow + O^{2-} \qquad (9)$$

La réaction globale qui rend compte de la formation des peroxydes à partir de l'hydroxyde dissout dans l'eutectique NaCl–KCl serait la suivante:

$$4NaOH \rightleftarrows O_2^{2-} + 2Na_2^+ + 2H_2O\uparrow \qquad (10)$$

Cette réaction suppose, d'une part l'existence de l'ion Na_2^+ dans le solvant utilisé, d'autre part sa stabilité dans l'eutectique utilisé vis-à-vis du peroxyde de sodium.

La dissolution de sodium métallique dans un bain d'eutectique NaCl–KCl purifié à 800° s'accompagne d'une intense coloration rouge-vermillon dû à la formation d'un composé de valence inférieure[12]: Na_2^+. L'existence d'une telle espèce a été mise en évidence par des études électrochimiques de solutions de métaux dans leurs sels fondus et par des études de diagrammes de phases[13,14].

Par ailleurs, les résultats des calculs de chaleur de formation montrent que les métaux alcalins et alcalino-terreux peuvent former de tels composés par réaction avec leurs sels fondus[15].

Si au bain d'eutectique NaCl–KCl purifié à 800° et contenant une quantité déterminée de peroxyde de sodium, on ajoute une quantité de sodium métallique telle que l'on ait les proportions de Na_2O_2 et Na_2^+ produits par la réaction (10), le bain se colore de façon intense en rouge-vermillon. Le spectre d'absorption IR du prélèvement est identique à celui des peroxydes. Ces derniers ne sont donc pas détruits par addition de sodium métallique. Cette constatation rend plausible la réaction (10).

Dans les spectres IR des prélèvements effectués, on ne remarque pas des bandes d'absorption dues à la liaison H–O.

D'après BUSING[16], le nombre d'onde de la vibration asymétrique de valence s'observe à $\simeq 3637$ cm^{-1} dans la soude solide à la température ordinaire et correspond à une structure où les ions HO^- sont très faiblement associés. Dans le cas où l'effet d'association par liaison hydrogène est important, la distance H–O augmente et cela se traduit par une diminution de sa fréquence de vibration de valence. FEILCHENFELD[17], LIPPINCOTT ET SCHROEDER[18] ont déterminé, en supposant que les liaisons O–H---O sont linéaires, les déplacements de la fréquence de vibration de la liaison O–H en fonction de la distance O---O séparant les deux atomes d'oxygène liés de façon asymétrique à l'atome d'hydrogène. D'après LIPPINCOTT ET SCHROEDER, lorsque R_{O---O} passe de 2.40 à 3.10 Å (ou r_{O-H} de 1.163 à 0.975 Å), le déplacement du nombre d'onde peut varier de 1510 à 90 cm^{-1} avec un maximum à 1900 cm^{-1} lorsque R_{O---O} est égal à 2.45 Å. L'absence de bandes d'absorption correspondant aux vibrations de la liaison H–O, dans les spectres IR mesurés après introduction de la soude dans un bain de NaCl–KCl à 800° traduit:

soit l'épuisement du bain en NaOH par le jeu des équilibres (8) à (10);

soit la superposition au spectre IR observé et attribué aux peroxydes, de bandes dues à la vibration de valence de HO. Dans ce cas, le maximum d'absorption serait déplacé de plus de 2000 cm^{-1}. A titre d'exemple, pour l'eau, le passage de l'état solide à l'état gazeux entraîne une variation[19] de l'ordre de 400 cm^{-1}.

Pour vérifier la dernière hypothèse, nous avons introduit de la soude deutérée dans le bain. Mais nous n'avons observé aucun déplacement apparent des bandes d'absorption IR; ce qui confirme la première hypothèse.

En titrant l'alcalinité totale du solvant après introduction de la soude, nous avons trouvé une valeur correspondant à environ 77% de la quantité de NaOH introduite. Même en supposant que les silicates ne soient pas quantitativement dosés à cause de leur solubilité plus ou moins partielle dans les conditions du titrage, on obtient, dans le cas le plus défavorable, une teneur en NaOH égale à $77+16=93\%$.

Des essais identiques effectués avec Na_2CO_3 (pureté d'après titrage $(97\pm2)\%$) introduit dans un bain de NaCl–KCl à 800° donnent les résultats suivants:

Composés recherchés	*Teneur en % de Na_2CO_3 (moyenne de 2 essais)*
O_2^{2-}	$= 0$
SiO_3^{2-}	$(5 + 1)$
Alcalinité totale	(96 ± 2)

Aux erreurs de mesure près, l'alcalinité totale correspond à la quantité de Na_2CO_3 introduite et les silicates formés ont été titrés en même temps que les carbonates.

La différence entre les résultats des titrages effectués avant et après introduction de NaOH dans le bain pourrait s'expliquer par la vaporisation partielle de la soude. L'élimination d'une partie de cette vapeur serait favorisée par le dégagement important de l'eau issue des réactions (8) et (10). La proportion ainsi transformée serait à 800°, si l'on se réfère aux résultats des titrages $(21\pm6)\%$.

CONCLUSIONS GÉNÉRALES

La solubilité de l'eau dans un bain d'eutectique NaCl–KCl fondu à 800° est très faible. L'introduction de l'eau dans un tel milieu entraîne plutôt la formation d'acide chlorhydrique selon la réaction:

$$H_2O+2Cl^- \rightarrow 2HCl\uparrow+O^{2-}$$

Les résultats de titrage et de spectrométrie d'absorption IR montrent que la quasi totalité de cet acide se dégage en même temps qu'il se forme une faible quantité de silicates.

La soude dégazée et déshydratée, introduite dans un bain de chlorures alcalins fondus, donne lieu aux réactions suivantes:

$$2NaOH \rightarrow Na_2O+H_2O\uparrow$$

$$4NaOH \rightarrow O_2^{2-}+2Na_2^{+}+2H_2O\uparrow$$

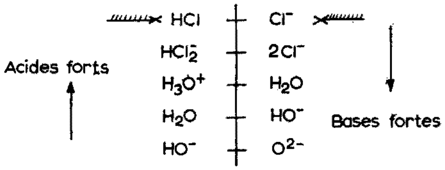
$$SiO_2+2NaOH \rightarrow SiO_3Na_2+H_2O\uparrow$$

Parallèlement, une partie de NaOH se vaporise. Les proportions moyennes des différents composés ainsi formés sont les suivantes:

Espèces	*Teneurs en % de NaOH introduit*
O_2^{2-}	(11.0 ± 1.0)
SiO_3^{2-}	(16.0 ± 2.0)
"Vapeurs de NaOH"	(21 ± 6)[a]

[a] Estimation.

Les résultats rapportés ci-dessus ainsi que ceux obtenus avec l'acide chlorhydrique[20], permettent d'établir une échelle qualitative d'acidité dans les chlorures alcalins fondus.



Bien que nous n'ayons pas observé l'espèce H_3O^+, probablement à cause de l'élimination quasi totale dans les conditions expérimentales de l'eau du couple H_3O^+/H_2O, il est possible de la situer sur cette échelle qui montre le caractère amphotère de l'eau et des ions hydroxyde.

Nous remercions vivement l'Institut Interuniversitaire des Sciences Nucléaires pour les subsides accordés au laboratoire.

RÉSUMÉ

Le comportement de l'eau et de la soude dans l'eutectique NaCl–KCl à 800° a été étudié par spectrométrie d'absorption IR et par l'analyse des différents produits de réaction. Il en ressort que la solubilité de l'eau dans le bain est très faible. La réaction principale qui a lieu est: $H_2O + 2Cl^- \rightarrow 2HCl\uparrow + O^{2-}$. Quant à la soude dégazée et déshydratée, son introduction dans le bain donne lieu aux réactions suivantes:

$$2NaOH \rightarrow Na_2O + H_2O\uparrow$$

$$4NaOH \rightarrow O_2^{2-} + 2Na_2^+ + 2H_2O\uparrow$$

$$SiO_2 + 2NaOH \rightarrow SiO_3Na_2 + H_2O\uparrow$$

Une certaine quantité de NaOH est, en outre, vaporisée. Les différentes proportions de NaOH participant aux réactions ci-dessus ont été déterminées. En conclusion, une échelle qualitative d'acidité dans les chlorures alcalins fondus a été établie.

SUMMARY

The behaviour of water and sodium hydroxide in molten NaCl–KCl eutectic at 800° has been examined by means of IR spectrometry and titrimetry. The solubility of water is very small. The main reaction that takes place is $H_2O + 2Cl^- \rightarrow 2HCl\uparrow + O^{2-}$. The introduction of sodium hydroxide in the bath appears to give rise to the following reactions:

$$2NaOH \rightarrow Na_2O + H_2O\uparrow$$

$$4NaOH \rightarrow O_2^{2-} + 2Na_2^+ + 2H_2O\uparrow$$

$$SiO_2 + 2NaOH \rightarrow SiO_3Na_2 + H_2O\uparrow$$

Some sodium hydroxide is simultaneously volatilized. The different proportions of NaOH that take part in these reactions have been determined. A qualitative scale of acidity in the molten alkaline chlorides is established.

ZUSAMMENFASSUNG

Das Verhalten von Wasser und Natronlauge im Eutektikum NaCl–KCl wurde durch Infrarotspektroskopie und Massanalyse der verschiedenen Reaktionsprodukte bei 800° untersucht. Die Löslichkeit des Wassers ist sehr niedrig. Die Reaktion $H_2O + 2Cl^- — 2HCl\uparrow + O^{2-}$ ist vorherrschend. Wird entwässerte Natronlauge der Schmelze zugefügt, so finden folgende Reaktionen statt:

$$2NaOH — Na_2O + H_2O\uparrow$$

$$4NaOH — O_2^{2-} + 2Na_2^+ + 2H_2O\uparrow$$

$$SiO_2 + 2NaOH — SiO_3Na_2 + H_2O\uparrow$$

Eine gewisse Menge Natronlauge wird gleichzeitig verdampft. Die verschiedenen Anteile NaOH, die an diesen Reaktionen teilnehmen, wurden bestimmt. Es wird eine qualitative Säureskala für Alkalichloridschmelzen vorgeschlagen.

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DOSAGE DE TRACES DE FER, DE NICKEL ET DE CHROME DANS LES SOLUTIONS DE NITRATE DE PLUTONIUM SANS SEPARATION PREALABLE PAR SPECTROPHOTOMETRIE D'ABSORPTION ATOMIQUE

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Les impuretés provenant de la corrosion des installations en acier inoxydable utilisées pour le retraitement chimique des déchets de fabrication d'éléments combustibles à base de plutonium ou le traitement des combustibles irradiés sont généralement déterminées dans les solutions de nitrate de plutonium par spectrophotométrie d'absorption. C'est le cas notamment pour le fer, le nickel et le chrome[1,2]. Ces méthodes ont l'inconvénient de nécessiter soit une séparation (cas du nickel et du chrome) soit l'ajout de nombreux réactifs entraînant un temps de mise en oeuvre assez long et un traitement des effluents compliqué.

On a cherché à mettre en oeuvre une méthode rapide permettant de doser avec une précision suffisante le fer, le nickel et le chrome.

L'analyse par spectrophotométrie d'absorption atomique sans séparation préalable du plutonium permet de concilier rapidité, précision et facilité de retraitement des effluents.

GRAFF ET MULLIN[3] ont par ailleurs appliqué une méthode semblable avec succès aux solutions de nitrate d'uranyle.

Principe de la méthode

La solution de nitrate de plutonium contenant les impuretés à doser est ajustée à une acidité comprise entre 1 et 5 N nitrique et à une teneur en plutonium comprise entre 5 et 100 g l^{-1} de plutonium. On détermine successivement le fer, le nickel et le chrome en vaporisant la solution dans la flamme et en effectuant les mesures d'absorption pour chaque élément en utilisant comme source lumineuse la lampe à cathode creuse correspondant à l'élément à doser et en réglant le spectrographe à la longueur d'onde correspondant à un pic d'absorption de cet élément. La quantité d'élément est déterminée en rapportant la densité optique sur une courbe d'étalonnage établie dans les mêmes conditions.

PARTIE EXPÉRIMENTALE

Appareillage

L'appareil utilisé est un spectrophotomètre d'absorption atomique Jarrell-Ash

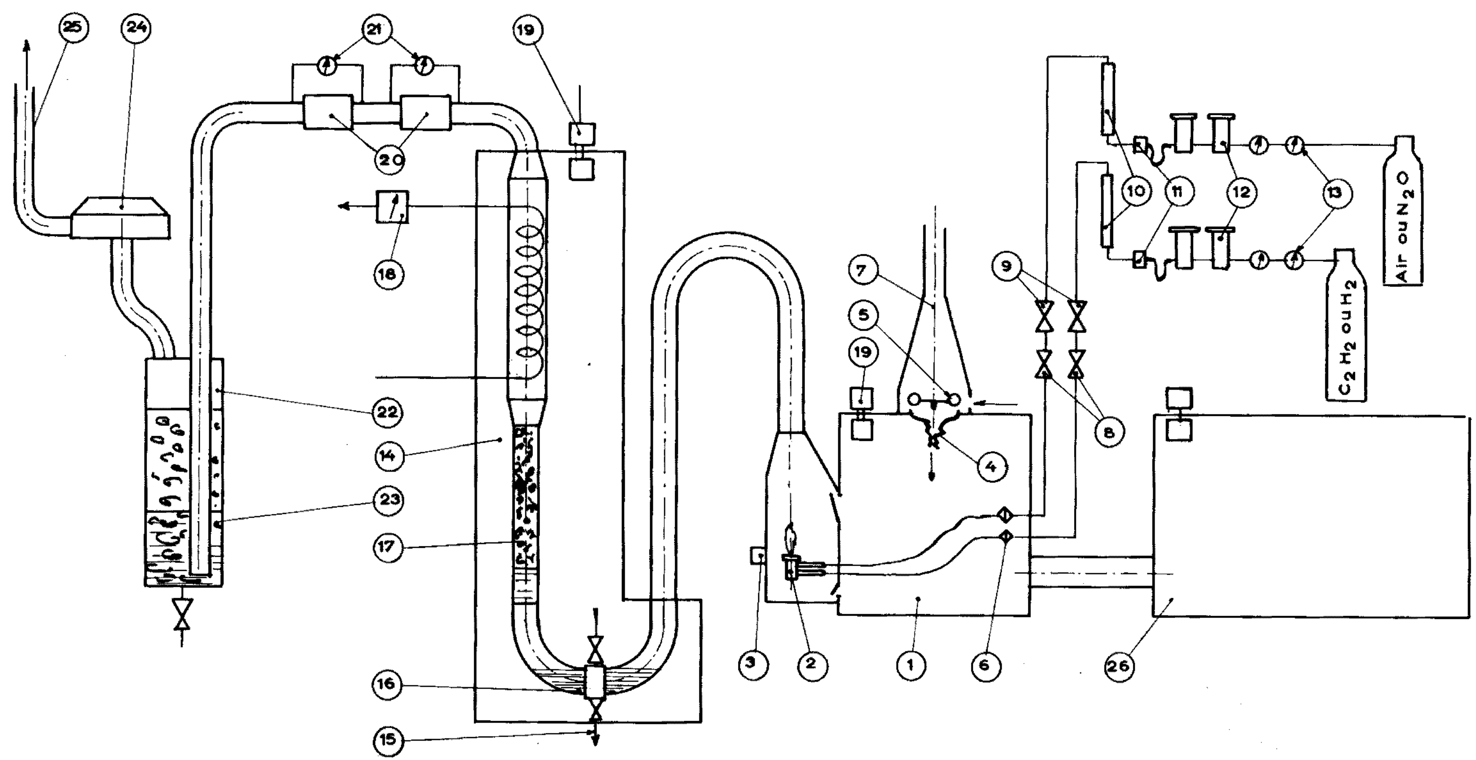

Fig. 1. Schéma de l'installation réalisée en vue de l'utilisation d'un spectrophotomètre d'absorption atomique pour l'analyse des solutions radioactives-α. (1) B.A.G. de vaporisation, (2) compartiment brûleur, (3) cellule photo-électrique, (4) obturateur s'ouvrant sous l'effet de la dépression, (5) anémomètre, (6) filtres en acier inoxydable fritté, (7) hotte, (8) électrovannes de sécurité, (9) vannes manuelles rapides, (10) débitmètres, (11) raccords rapides non interchangeables, (12) filtres épurateurs, (13) détendeur double détente, (14) B.A.G. échange thermique, (15) récupération matières radioactives, (16) acide sulfurique normal, (17) remplissage anneaux "Raschig", (18) sécurité de débit d'eau, (19) extraction B.A.G., (20) filtres, (21) manomètres différentiels, (22) colonne de neutralisation, (23) anneaux "Raschig", (24) ventilateur, (25) extraction, (26) B.A.G. préparation.

type 82 500 dont le brûleur a été placé en boîte à gants. Un brûleur laminaire est utilisé dans tous les cas.

Description de l'adaptation en boîte à gants du spectrophotomètre d'absorption atomique. Le montage réalisé a eu pour but, d'une part de placer dans une boîte à gants le brûleur, d'autre part d'évacuer la chaleur dégagée et éventuellement de récupérer les matières radioactives vaporisées dans la flamme (Demande de brevet CEA no. PV 168 284. Ensemble réalisé sous licence par la Société Barras-Provence).

Les problèmes de sécurité posés par la présence d'une flamme, l'utilisation de gaz tels que l'acétylène, l'hydrogène et le protoxyde d'azote en boîte à gants et par la vaporisation de quantités importantes d'émetteurs-α ont pu être résolus.

La mise en boîte à gants du brûleur a été facilitée par la disposition des différents éléments du spectrophotomètre 82 500. En effet, ses trois parties sont alignées sur un banc optique et il est facile de placer le brûleur dans un compartiment particulier, la continuité du chemin optique au niveau des parois de boîte à gants étant assurée par des hublots de silice transparente "Suprasil".

L'évacuation de la chaleur (4500 kcal h^{-1} au maximum) est assurée par un échangeur à serpentin en verre industriel. Les gaz sont refroidis de cette manière, après dilution par un courant d'air de 100 m^3 h^{-1}, jusqu'à 50°. De façon à améliorer l'échange thermique et à favoriser l'absorption des poussières, on opère à un pré-refroidissement par barbottage des gaz dans l'acide sulfurique dilué dans l'eau. De cette façon, l'échange thermique se fait en phase vapeur avec ruissellement et non en gaz sec. L'expérience confirme l'efficacité d'un tel système de réfrigération.

L'utilisation de solutions contenant des matières radioactives entraîne la nécessité de débarrasser les gaz de combustion des poussières d'oxydes qu'ils contiennent. Le piégeage est réalisé à trois niveaux: par barbottage des gaz de combustion dans une solution d'acide sulfurique normal, par contact intime entre les gaz et l'eau de condensation dans une colonne garnie d'anneaux Raschig, et par passage des gaz refroidis à travers des filtres "absolus".

Dans le cas du plutonium, l'expérience a montré que plus de 99.99% du plutonium est retenu dans la solution sulfurique. Il suffit alors de vidanger périodiquement la solution de lavage pour récupérer une solution de sulfate de plutonium contenant en suspension des boues d'oxyde de plutonium. Ces solutions boueuses sont traitées en milieu nitrique–fluorhydrique pour dissoudre l'oxyde de plutonium. On peut attendre d'avoir vaporisé l'équivalent de quelques dizaines de grammes de plutonium pour renouveler la solution de lavage. Des contrôles de contamination des filtres montrent que seul le premier filtre se contamine. La sécurité présentée par le deuxième filtre est dont suffisante.

Schéma d'ensemble de l'installation. L'installation qui vient d'être décrite est représentée sur le schéma de la Fig. 1. L'implantation des différents éléments est réalisée selon la Fig. 2. Trois boîtes à gants sont utilisées: une boîte à gants de préparation des échantillons, la boîte à gants abritant le brûleur, et une boîte à gants de réfrigération et de décontamination des gaz de combustion.

La boîte à gants de préparation des échantillons permet de réaliser les opérations chimiques préliminaires au dosage.

La boîte à gants de vaporisation des solutions est fabriquée en acier inoxydable et comporte deux compartiments: le premier contient le brûleur et est isolé du compartiment principal par une porte comportant deux volets d'entrée d'air; ce

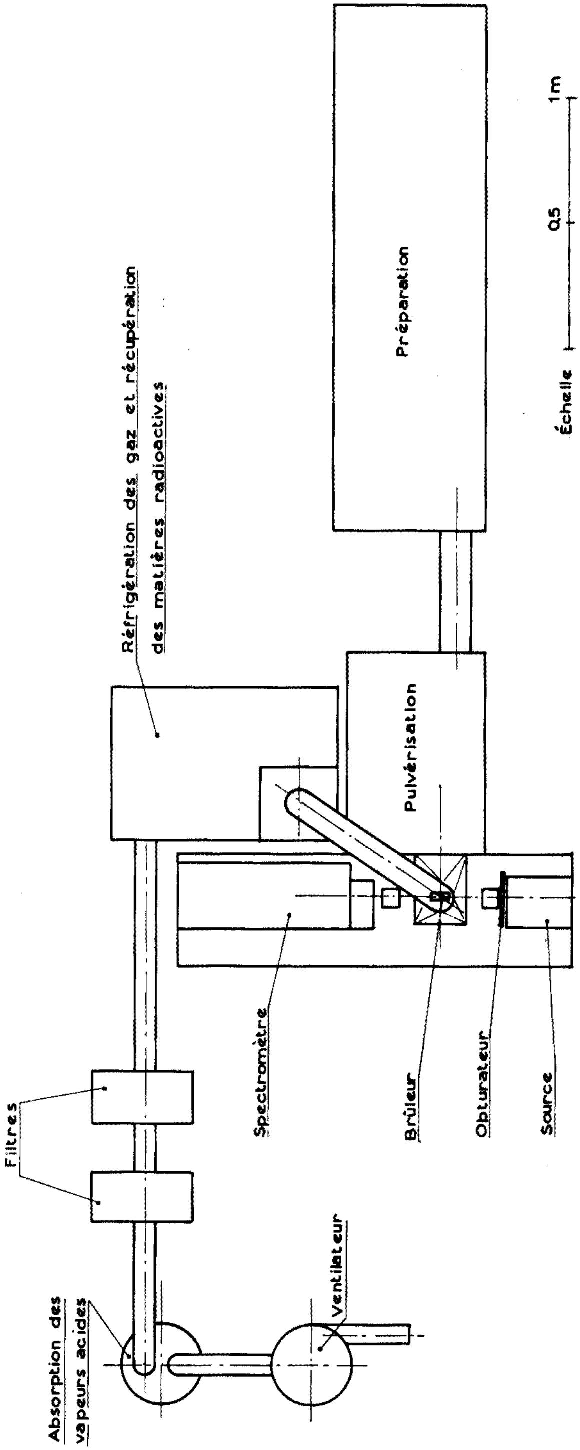

Fig. 2. Schéma "d'implantation" des différentes parties de l'installation.

compartiment possède deux fenêtres en silice Suprasil, destinées au passage du faisceau lumineux. Le second compartiment permet d'alimenter le brûleur en solution à analyser. Le capillaire y débouche et le remplissage des coupelles avec les solutions à analyser y est réalisé. L'entrée d'air dans cette boîte à gants est fait directement par une manche en caoutchouc auto-obturante qui présente l'avantage de permettre un débit d'air très important sans perte de charge. Lors de l'arrêt du débit d'air principal, cette manche se referme et laisse passer uniquement la ventilation normale de la boîte à gants. En outre, en cas d'explosion dans la boîte à gants, cette manche, en s'ouvrant au maximum, permettrait d'évacuer la surpression en éliminant ainsi le risque de bris des panneaux de plexiglas. Une hotte placée au-dessus de la manche limiterait dans ce cas la contamination résultante.

La boîte à gants d'échange thermique et de récupération du plutonium, est réalisée en acier inoxydable et contient l'ensemble de réfrigération des gaz et d'absorption des fumées chargées.

L'ensemble de filtration–neutralisation–extraction des gaz de combustion comporte deux filtres Schneider-Poëlman à grande efficacité, une tour de neutralisation en PVC garnie d'anneaux Raschig et remplie d'une solution de soude et un ventilateur d'extraction à forte hauteur manométrique et d'un débit de 100 $m^3 h^{-1}$. Les gaz rejetés par le ventilateur sont évacués dans le réseau général de ventilation des boîtes à gants.

Sécurité de l'installation. Le risque principal dont il convient de se protéger est la formation d'un mélange détonnant combustible–comburant qui présenterait de graves risques pour le personnel et le matériel. Ce mélange pourrait se réaliser à la suite de fuite de carburant, avec ou sans arrêt de ventilation.

On a pris comme hypothèse pessimiste une fuite de la totalité des gaz combustibles dans la boîte à gants. Deux cas peuvent être envisagés: fuite en présence de la ventilation et fuite en cas d'arrêt de ventilation d'une minute. Dans ces deux cas, la teneur de l'atmosphère de la boîte à gants en combustible est inférieure à la limite inférieure d'explosibilité. On a également considéré le risque d'explosion dans le brûleur dû à un mauvais réglage du rapport des débits combustible/comburant, particulièrement dans le cas où le protoxyde d'azote est utilisé. C'est un risque peu grave, compte-tenu de la faible quantité de gaz mise en oeuvre. Des essais ont montré qu'il en est bien ainsi.

Afin de tenir compte de ce qui précède, on a été amené à mettre en place les systèmes de sécurité suivants:

(*a*) contrôle du bon fonctionnement de l'extraction des gaz par un manomètre différentiel permettant de surveiller le colmatage des filtres. En cas d'arrêt du ventilateur d'extraction, des électrovannes antidéflagrantes coupent l'arrivée des gaz. Réciproquement, l'arrivée des gaz ne peut se faire que lorsque le ventilateur est en service.

(*b*) surveillance de la flamme par une cellule photo-électrique agissant sur les électrovannes si la flamme s'éteint accidentellement.

(*c*) avant tout allumage, la teneur en gaz combustible de l'atmosphère de la boîte à gants est estimée à l'aide d'une pompe Drager (test colorimétrique).

Mode opératoire

Les solutions de nitrate de plutonium provenant soit de la mise en solution d'oxyde ou de métal, soit des différents niveaux de prélèvement d'échantillons de l'installation de retraitement chimique sont ajustées à une acidité comprise entre 1 et 5 N par ajout d'acide nitrique. Les solutions obtenues sont vaporisées dans la flamme air–acétylène du brûleur laminaire. Les conditions de réglage des débits gazeux et du spectromètre sont indiquées, pour chacun des trois éléments analysés, dans le Tableau I. La courbe d'étalonnage est tracée à l'aide de solutions préparées par ajout de quantités connues des éléments à doser à une solution purifiée de nitrate de plutonium dont la concentration est voisine de celle de la solution analysée. Les Figs. 3 et 4 montrent ces courbes d'étalonnage dans la gamme 0.1–1 μg ml^{-1} et 1–8 μg ml^{-1}.

TABLEAU I

CONDITIONS OPÉRATOIRES

	Fer	*Nickel*	*Chrome*
Brûleur: laminaire	10 cm	10 cm	10 cm
Combustible: C_2H_2 pression (bar)	0.8	0.8	0.8
débit (l/min)	2.5	3	2.7
Comburant: air pression (bar)	4	4	4
débit (l/min)	7.9	7.9	7.3
Haute tension (V)	500	550	400
Lampe Westinghouse type	45455	45457	45454
Courant lampe (mA)	16	26	12
Longueur d'onde (Å)	2485	2322	3579
Amortissement	1	1	3
Gain	10 à 15%	10 à 15%	10 à 15%
Fentes: Entrée (μ)	100	100	100
Sortie (μ)	150	150	150
Photomultiplicateur	R 106	R 106	R 106
Réseau (traits/mm)	1200	1200	1200
Sensibilité enregistreur (mV)	10 ou 2	10 ou 2	10 ou 2

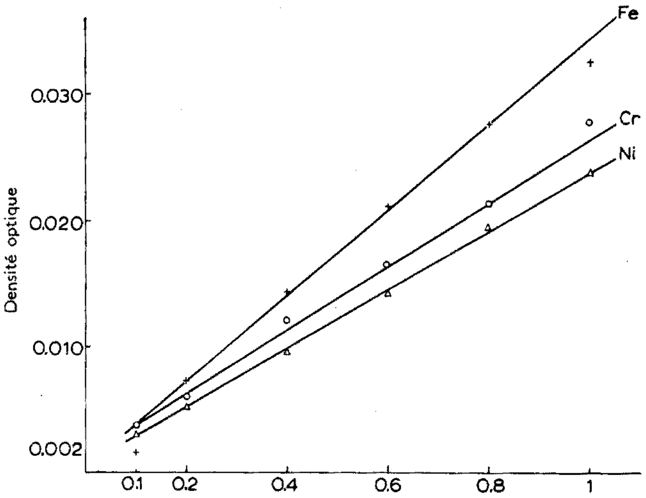

Fig. 3. Courbe d'étalonnage (domaine 0.1–1 μg ml^{-1}). 5.9 mg Pu ml^{-1}. (+) Fe, (○) Cr, (△) Ni.

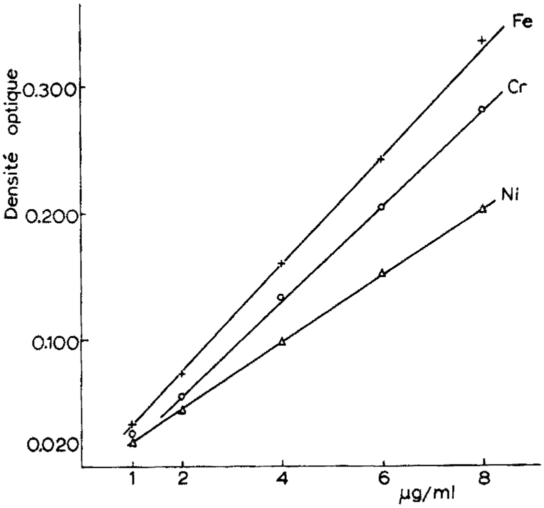

Fig. 4. Droites d'étalonnage (domaine 1 à 8 μg ml^{-1}). (+) 5.9 mg Pu ml^{-1} + Fe + 4 μg Ni ml^{-1} + 4 μg Cr ml^{-1}, (△) 5.9 mg Pu ml^{-1} + Ni + 4 μg Fe ml^{-1} + 4 μg Cr ml^{-1}, (○) 5.9 mg Pu ml^{-1} + Cr + 4 μg Fe ml^{-1} + 4 μg Ni ml^{-1}.

DISCUSSION

On a examiné successivement l'influence des anions nitrates et sulfates, de la teneur en plutonium et de la teneur en impuretés de la solution.

Influence des ions nitrates et sulfates

Les essais réalisés ont montré qu'une variation de concentration en ions nitrates entre 1 et 5 *M* entraîne une variation de densité optique de l'ordre de 1% par mole/l de nitrates dans le cas du fer et du chrome, et inférieure à 0.5% par mole/l dans le cas du nickel.

Les essais réalisés ont montré que l'effet des ions sulfates est plus important puisque la variation de densité optique est de 8% par mole/l d'ions sulfates dans l'intervalle de 0.2 à 3 *M* dans le cas du nickel. Cette variation est de 13% par mole/l d'ions sulfates dans le cas du chrome, pour le même intervalle; toutefois, cette variation n'est que de 5% dans l'intervalle 0.2 à 1.7 *M*. Dans le cas du fer, la variation de densité optique atteint 20% par mole/l d'ions sulfates dans l'intervalle 0.2 à 3 *M*. Toutefois, cette variation est ramenée à 13% par mole/l d'ions sulfates dans l'intervalle 0.7 à 2 *M*. D'une façon générale, si l'on est amené à utiliser la méthode en présence d'ions sulfates, on se limitera à une concentration de 1.5 *M* sulfates, l'acidité totale de la solution ne devant pas dépasser 5 *N*.

Influence de la teneur en plutonium

La présence de plutonium dans la solution a un effet dépressif sur le fer et le chrome tandis que l'absorption du nickel se trouve peu modifiée. Les courbes de la Fig. 5 montrent que les meilleurs résultats peuvent être obtenus dans l'intervalle 2 à 20 g l^{-1} en plutonium pour le fer et le nickel et dans l'intervalle 20–75 g l^{-1} pour chrome et nickel. Toutefois, en déterminant la courbe d'étalonnage dans des conditions de concentration en plutonium voisine de celle de la solution à analyser, il est possible de travailler à n'importe quelle concentration en plutonium—au moins jusqu'à 100 g l^{-1}—les limites de détection des éléments restant tout à fait satisfaisantes ainsi que le montre le Tableau II.

Interférences réciproques du fer, du nickel et du chrome

La Figure 6 montrant les courbes de dosage du fer, du nickel et du chrome en présence de plutonium et en présence d'un, de deux ou des trois éléments, met en évidence l'absence d'interférence entre les trois éléments au moins jusqu'au niveau 8 $\mu g\ ml^{-1}$. On note cependant dans le cas du chrome une dispersion plus importante dûe à l'extrême importance des conditions de réglage de la flamme sur l'absorption du chrome. Les meilleurs résultats sont obtenus à l'aide d'une flamme réductrice, riche en acétylène.

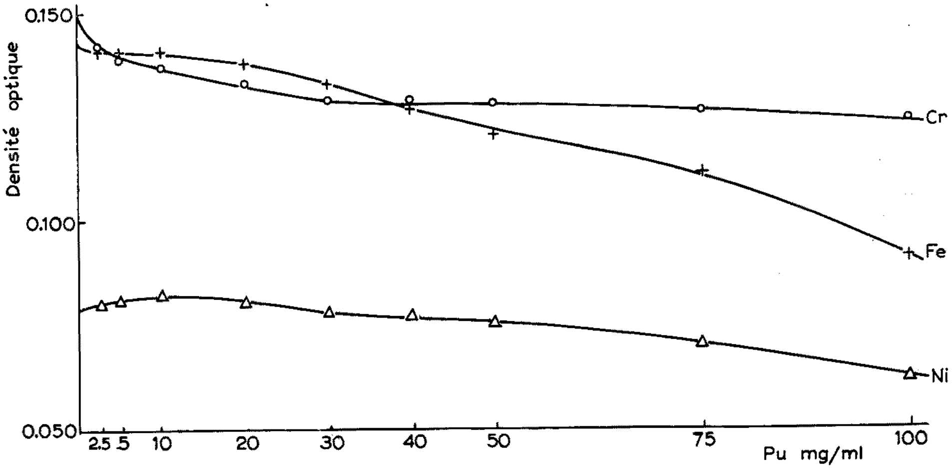

Fig. 5. Influence de la concentration en plutonium sur le dosage du fer, nickel et chrome (concentration 4 $\mu g\ ml^{-1}$).

TABLEAU II

LIMITES DE DÉTECTION (POUR 1% D'ABSORPTION)

Pour une concentration en Pu de: (mg ml^{-1})	*Fe ($\mu g\ ml^{-1}$)*	*Ni ($\mu g\ ml^{-1}$)*	*Cr ($\mu g\ ml^{-1}$)*
100	0.20	0.30	0.25
20	0.13	0.20	0.23
0	0.10	0.20	0.20

Précision de la méthode

La reproductibilité des mesures à l'intérieur d'une même série est meilleure que 0.5% pour le fer et le nickel et 0.8% pour le chrome (en valeur relative).

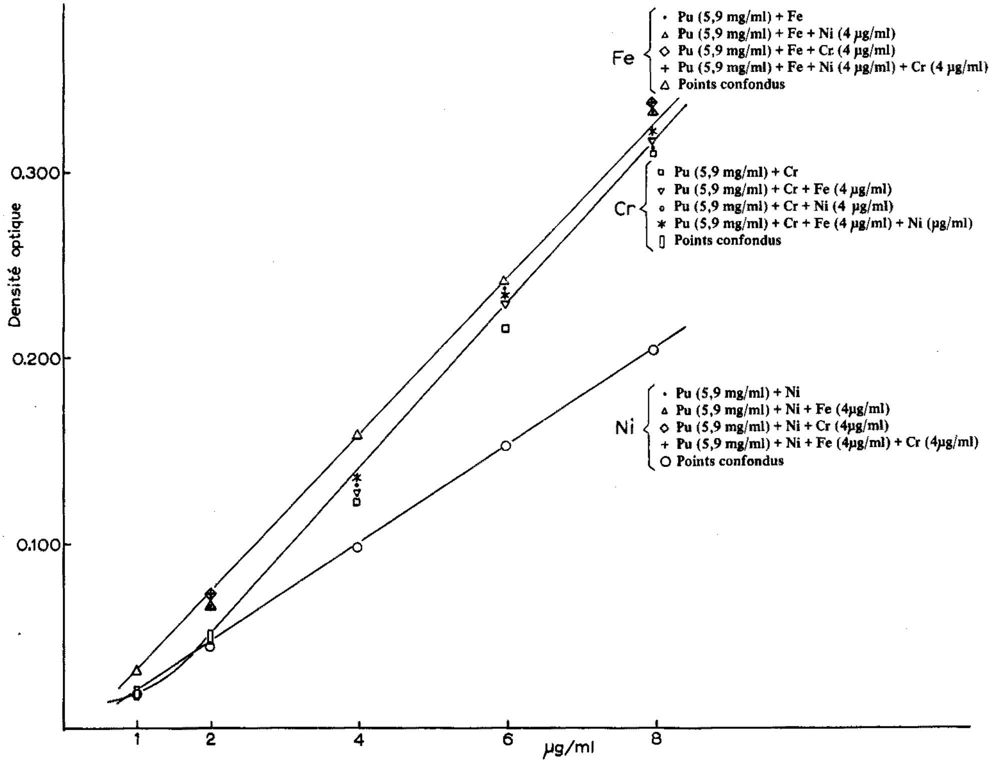

Fig. 6. Interférences réciproques entre le fer, le nickel et le chrome en présence de plutonium.

TABLEAU III

PRÉCISION DE LA MÉTHODE

(Comparaison entre les quantités d'éléments ajoutées et les quantités trouvées pour une série de six déterminations. Quantité mise Fe, Ni ou Cr = 3.5 μg ml^{-1})

	Quantité trouvée (μg ml^{-1}) Moyenne					
	Fe		*Ni*		*Cr*	
	$\bar{X}$	*Ecart*	$\bar{X}$	*Ecart*	$\bar{X}$	*Ecart*
	3.51	+0.01	3.44	−0.06	3.47	−0.03
$\sigma = \sqrt{\frac{\Sigma(X-\bar{X})^2}{n-1}}$	0.04		0.12		0.06	
$\sigma\% = \frac{\sigma \cdot 100}{\bar{X}}$	1.50		3.50		1.75	

Le Tableau III montre les résultats obtenus sur une série de six déterminations effectuées sur la même solution. Les essais réalisés ont montré que l'écart type relatif est inférieur à 3.5% dans le cas le plus défavorable (détermination du nickel) et à 2% dans le cas du fer ou du chrome.

RÉSUMÉ

Une méthode pour le dosage rapide de traces de fer, de chrome et de nickel dans les solutions aqueuses de nitrate de plutonium, sans séparation préalable du plutonium est décrite. Ces déterminations sont réalisables dans le domaine 0.1–8 μg ml^{-1} dans des solutions de nitrate de plutonium jusqu'à 100 g l^{-1} avec une précision meilleure que 5%. Des informations sont données sur l'influence de la concentration en plutonium ainsi que sur les interférences entre les trois éléments analysés. En vue d'appliquer la spectrophotométrie d'absorption atomique aux solutions présentant une forte radioactivité-α, on a été amené à adapter un spectrophotomètre d'absorption atomique à une boîte à gants. Le principal intérêt de la méthode est l'absence de séparation avant analyse des impuretés entraînant un gain de temps important.

SUMMARY

Rapid determinations of traces of iron, nickel and chromium in aqueous plutonium nitrate solutions, without prior separation, are described. These methods can be used in the 0.1–8 μg ml^{-1} range for plutonium nitrate solutions containing up to 100 g Pu l^{-1} with a precision better than 5%. The effect of plutonium concentration, and interference between the three elements are discussed. In order to apply atomic absorption spectrophotometry to strongly radioactive solutions, a system of glove boxes has been designed. The method can be successfully applied to the analysis of plutonium recovery solutions in fuel-reprocessing plants.

ZUSAMMENFASSUNG

Schnelle Bestimmungen von Spuren Eisen, Nickel und Chrom in wässrigen Plutoniumnitratlösungen mit Hilfe der Flammenabsorptionsspektroskopie ohne vorherige Trennung werden beschrieben. Die Methoden können verwendet werden in in dem Bereich von 0.1–8 μg ml^{-1} in Lösungen, die bis zu 100 g l^{-1} Pu enthalten mit einer Genauigkeit von besser als 5%. Der Einfluss der Plutoniumkonzentration und die Störungen zwischen diesen 3 Elementen werden diskutiert. Um die Flammenabsorptionsanalyse auch für stark radioaktive Lösungen verwenden zu können, wurde die Apparatur in eine Glove-Box eingebaut. Dadurch kann die Methode erfolgreich für die Analyse von Plutoniumlösungen aus der Wiederaufarbeitung verwendet werden.

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ETUDE PAR RESONANCE MAGNETIQUE NUCLEAIRE DE LA STRUCTURE MOLECULAIRE DE L'ACIDE HYDROXYETHYLENEDIAMINETRIACETIQUE EN SOLUTION AQUEUSE

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(Reçu le 3 mai, 1969)

Dans une série de publications précédentes[1-4] consacrées à l'étude de la séparation chromatographique des lanthanides et des actinides trivalents par élution sur échangeurs d'ions, nous avons pu mettre en évidence la formation de complexes du type $MeH_nY_2^{(3-n)-}$ entre ces éléments et le HEDTA.

Certains phénomènes cinétiques, en rapport probable avec l'existence de ces complexes, se sont manifestés au cours de ces élutions sans que nous puissions les interpréter sur la seule base des expériences de chromatographie.

Dans le but d'interpréter ces particularités cinétiques, nous nous proposons d'étudier la structure moléculaire du complexant et de ses différents complexes, en solution aqueuse, à différents pH et forces ioniques.

Cette première publication rend compte des résultats obtenus par l'étude NMR de la structure moléculaire du complexant en solution aqueuse, à différents pH.

TECHNIQUES EXPÉRIMENTALES

Préparation des solutions

Nous avons préparé une solution 0.50 *M* en HEDTA à partir d'eau désionisée, redistillée sur quartz et de HEDTA tricristallisé; son pH est amené à 13 au moyen d'une solution concentrée de potasse décarbonaté. Des parties aliquotes de cette solution sont amenées à différentes valeurs de pH (entre 13 et 0) en y faisant barboter de l'acide chlorhydrique gazeux; la dilution due à l'ajoute d'acide est ainsi négligeable et la concentration des différentes solutions reste constante (0.50 mole/l).

Les valeurs de pH sont déterminées, au centième d'unité près, à 25° au moyen d'un pH mètre Beckman, type ,,expendomatic'' étalonné aux pH 4.00 et 9.00.

Notons enfin qu'il est nécessaire de dépoussièrer très soigneusement les solutions (filtration non-forcée sur fritté G.4) afin d'en éliminer tout germe de cristallisation et de maintenir la sursaturation des solutions acides.

Enregistrement des spectres

Les spectres NMR ont été enregistrés au moyen d'un appareil Varian HA 100 suivant deux techniques:

tout d'abord en HR, par balayage de champ, sans référence; cette technique permet un très grand étalement du spectre et par conséquent une étude plus précise de la configuration des pics.

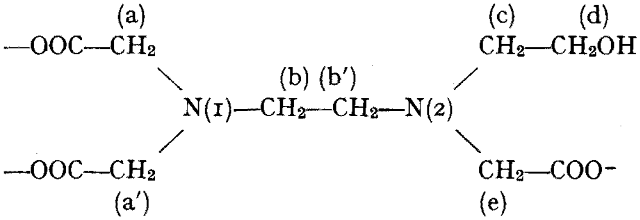
ensuite en HA (lock sur l'eau) avec référence externe; on peut ainsi mesurer le déplacement chimique des pics par rapport à une référence externe, le T.M.S. en l'occurrence.

La vitesse de rotation de l'échantillon est réglée de façon à éliminer les bandes de rotation de l'eau, très intenses, dues à la forte viscosité de la solution et qui risquent de masquer une grande partie du spectre. C'est également la raison pour laquelle nous retirons le tube capillaire contenant le T.M.S. dès le repérage du pic de ce dernier sur le papier d'enregistrement: en présence du capillaire, les bandes de rotation de l'eau sont impossibles à éliminer, quelle que soit la vitesse de rotation.

La température des échantillons est maintenue à 25° par balayage d'air refroidi sur glace.

RÉSULTATS ET DISCUSSION

Attribution des différents pics NMR



La formule de structure montre — 4 protons acétiques équivalents (a) et (a′) adjacents à N(1),
— 2 protons acétiques équivalents (e) adjacents à N(2),
— 4 protons méthyléniques (b) et (b′) compris entre les deux azotes,
— 2 protons méthyléniques (c) adjacents à l'azote (2),
— 2 protons (d) du groupement alcoolique —CH_2OH.

Des considérations sur l'électronégativité des groupes fonctionnels de la molécule et par conséquent sur l'environnement électronique des différents groupes de protons, la possibilité de couplage spin–spin entre les deux groupes de protons (c) et (d) non-équivalents et très proches les uns des autres et enfin l'intégration de la surface des bandes, permettent d'attribuer, sans ambiguité, les différents pics NMR à des groupes de protons bien définis, comme le montre le premier enregistrement (Fig. 1).

Il peut paraître étonnant de ne trouver qu'un pic, résolu en un singulet, pour les protons (b) et (b′) alors qu'ils ne paraissent pas équivalents. Il faut cependant noter que l'asymétrie de la molécule est faible, que la distance qui sépare les protons (b) et (b′) des groupes COO^- et CH_2OH respectivement est fort importante et qu'enfin la proximité des atomes d'azote, riches en électrons, peut provoquer un écran électronique suffisamment important pour empêcher la manifestation des champs magnétiques faibles des couplages spin–spin.

Influence du pH sur le spectre NMR de HEDTA

Sur la Fig. 2, nous avons porté en graphique, en fonction du pH, les déplacements chimiques des différents groupes de protons de l'acide tribasique considéré, déplacements mesurés en p.p.m. par rapport au T.M.S.

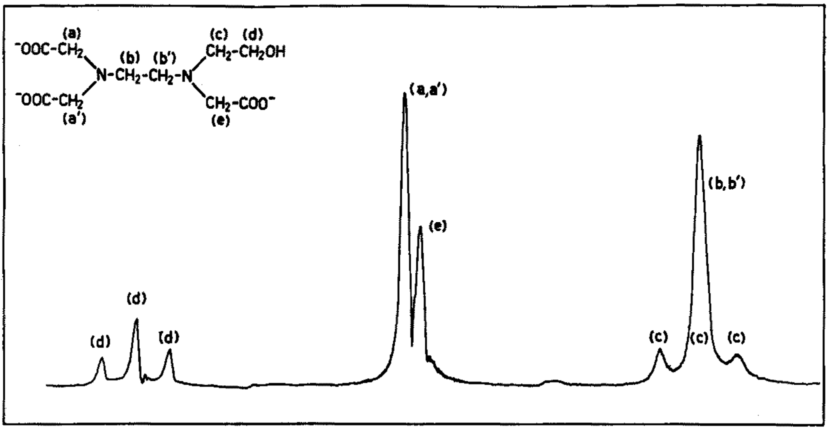


Fig. 1. Spectre de résonance magnétique nucléaire de HEDTA en solution aqueuse. Concentration 0.50 mole/litre; pH 13; t 25°.

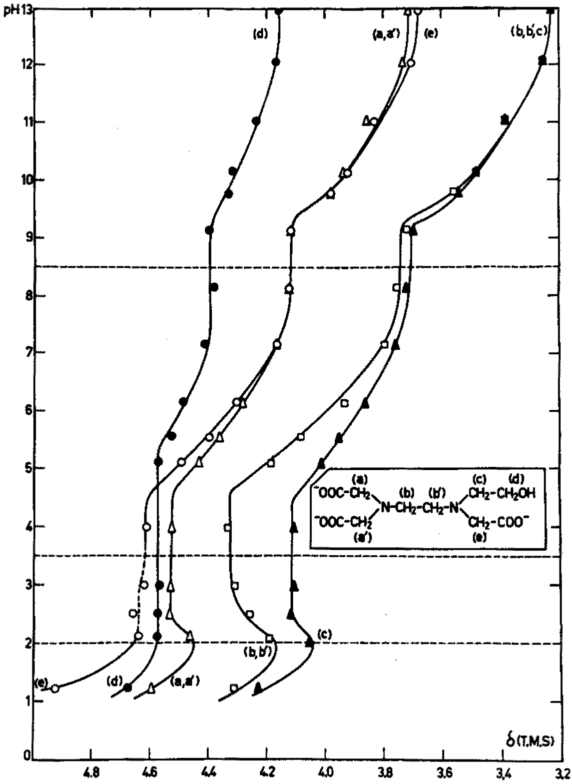


Fig. 2. Déplacement chimique des pics NMR de différents groupes de protons de HEDTA en fonction du pH.

Le graphique est divisé en quatre zônes, correspondant aux protonisations successives de HEDTA.

Première zône. Elle s'étend de pH 13 à pH 9 environ et encadre ainsi le premier pK dont il est difficile de définir la valeur exacte, étant donné la force ionique élevée du milieu dans lequel nous travaillons; on peut le situer aux environs de 9.5.

Le Tableau I résume les informations fournies par les spectres NMR dans cette région de pH.

TABLEAU I

SPECTRES NMR DANS LE RÉGION DE pH 13 À 9

Protons	*Déplacement chimique en p.p.m. par rapport au T.M.S.*[a]	*Remarques*
(b) (b′)	0.50	Les protons (b) et (b′) restent équivalents
(a) (a′)	0.40	Les protons (a) et (a′) restent équivalents
(c)	0.43	Déplacement plus important que les protons (a) (a′)
(d)	0.24	Légère déformation du triplet
(e)	0.43	Légère déformation du triplet

[a] Une valeur positive de ce déplacement représente un décalage vers les champs faibles; une valeur négative, un déplacement vers les champs élevés.

Le déplacement important que subissent les protons (b) et (b′) vers les valeurs faibles du champ, preuve d'une désélectronisation importante de l'atmosphère de ces protons, implique nécessairement la fixation du premier hydrogène sur les atomes d'azote. La question se pose de savoir si la fixation se fait préférentiellement sur l'un ou l'autre de ces azotes.

Nakamoto *et al.*[5] concluent d'études infrarouges que c'est l'azote (1) qui subit la première protonisation. Cette interprétation est en contradiction avec les résultats obtenus par NMR et pour deux raisons: tout d'abord, la fixation d'un proton sur un seul des deux azotes provoquerait une dissymétrie des protons (b) et (b′); or le pic NMR correspondant à ces deux paires de protons reste unique et résolu en un parfait singulet. Ensuite, on devrait, dans le cas de la fixation du proton sur l'azote (1), observer un déplacement plus important des protons (a) et (a′) vis à vis des protons (e); on observe exactement l'inverse.

Sudmeier et Reilley[6], sur la base de spectres NMR, admettent que c'est sur l'azote (2) que se fixe le premier proton. Si cette interprétation permet d'expliquer le comportement des protons (e), elle rencontre la même objection que la précédente en ce qui concerne les protons (b) et (b′).

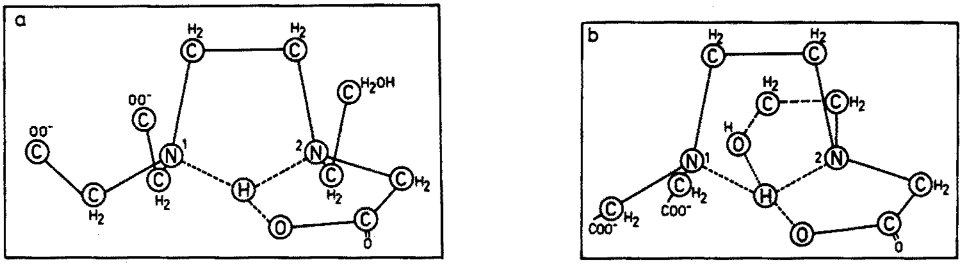


Fig. 3. Structure moléculaire du sel bipotassique de HEDTA en solution aqueuse.

La formule de structure que nous présentons sur la Fig. 3a nous paraît répondre parfaitement à toutes les exigences des spectres NMR: (b) et (b′) sont parfaitement équivalents, et les protons (e) sont plus influencés que les protons (a), (a′).

On peut pousser plus loin encore l'étude de la structure moléculaire de HEDTA dans cette région de pH en tenant compte d'une information supplémentaire fournie par les spectres NMR: la déformation des triplets (c) et (d). Au-dessus de pH 10, les triplets sont parfaitement dessinés, les trois pics sont parfaitement symétriques; en dessous de cette valeur de pH, une déformation apparaît dans la bande centrale des triplets et se répète à partir de ce moment dans tous les spectres, quelles que soient les conditions ou les techniques d'enregistrement.

Une étude plus poussée de la forme du couplage et de la distance entre les pics des triplets, montre qu'à partir de pH 10, les triplets sont en réalité la superposition de deux doublets caractéristiques d'un couplage spin–spin AA′ BB′. Cela signifie que les deux protons (c) ne sont plus équivalents, de même d'ailleurs que les deux protons (d) et que chacun d'eux se couple avec les deux protons du groupement méthyl adjacent.

Ce comportement ne peut s'interpréter qu'en donnant à la molécule la forme représentée sur la seconde formule de structure (Fig. 3b): l'oxygène du groupement alcoolique est légèrement attiré par le proton fixé entre les deux azotes et occupe une position statistiquement plus fréquente que n'importe quelle autre. La rotation du chaînon hydroxyethyl autour de la liaison N–CH_2 n'est plus totalement libre; il en découle une non-équivalence des protons méthyles des groupes (c) et (d) qui se traduit en NMR par l'apparition de deux doublets mal résolus, caractéristiques d'un couplage AA′ BB′.

Notons enfin que ce modèle structural permet d'interpréter le déplacement chimique important que subissent les protons (c) (déplacement de même valeur que celui des protons (e)).

Signalons aussi qu'une structure de ce type a été proposée par SCHWARZENBACH ET ACKERMANN pour le sel trisodique de l'EDTA en solution aqueuse[7].

Deuxième zône. Elle s'étend de pH 9 à pH 4 et encadre ainsi le second p*K* égal à 5.33 (avec les restrictions déjà énoncées pour le premier p*K* en ce qui concerne la force ionique).

Le graphique 2 et le Tableau II résument les caractéristiques des spectres NMR dans cette région de pH.

TABLEAU II

SPECTRES NMR DANS LE RÉGION DE pH 9 À 4

Protons	*Déplacement chimique en p.p.m. par rapport au T.M.S.*	*Remarques*
(b) et (b′)	0.61	Ces deux groupes de protons restent parfaitement équivalents (singulet)
(e)	0.48	Déplacement une fois encore plus important que celui des protons (a) et (a′)
(a) et (a′)	0.41	Accentuation de la déformation des deux triplets
(d)	0.18	
(c)	0.41	

Ici encore, le déplacement chimique important que subissent les protons (b) et (b′) vers les champs faibles nous permet de supposer que c'est aussi sur les azotes que se fixe le deuxième proton.

On arrive ainsi à une formule de structure semblable à celle proposée sur la Fig. 4a. Ce modèle moléculaire permet d'interpréter le déplacement chimique important des protons (b) et (b′), le déplacement plus important des protons (e) vis à vis des protons (a) et (a′) et l'intensification du couplage en deux doublets (le proton moins lié attire plus fort l'oxygène alcoolique), mais il est en contradiction avec un des aspects des spectres NMR. En effet, dans ce modèle, les protons (b) et (b′) ne sont pas équivalents: le proton fixé sur l'azote (2) répartit son influence entre cet azote et le groupe carboxyle alors que le proton fixé sur l'azote (1) n'agit que sur cet azote; les deux azotes sont donc différemment affectés par la présence des protons ainsi par conséquent que les groupes $-CH_2$ qui leur sont adjacents.

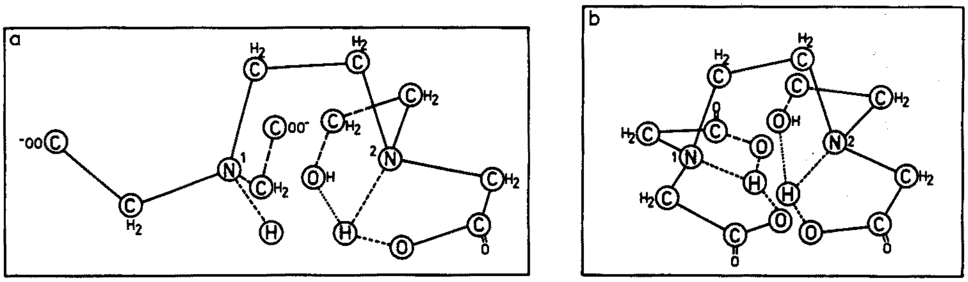


Fig. 4. Structure moléculaire du sel monopotassique de HEDTA en solution aqueuse.

Nous avons construit cinq modèles moléculaires possibles pour cette forme mononégative de l'acide: ils sont tous en contradiction avec l'un ou l'autre aspect des spectres NMR.

Seul le modèle proposé sur la Fig. 4b répond parfaitement aux diverses exigences des spectres NMR: (b) et (b′) sont influencés, mais restent équivalents; (a) et (a′) sont influencés, mais moins que (e); le couplage AA′ BB′ est renforcé par l'attraction plus forte entre l'oxygène alcoolique et le premier proton.

Troisième zône. Elle s'étend de pH 4 à pH 2 et encadre ainsi le 3ème pK égal à 2.64. Le graphique 2 et le Tableau III résument les caractéristiques des spectres dans cette région.

TABLEAU III

SPECTRES NMR DANS LE RÉGION DE pH 4 À 2

Protons	*Déplacement chimique en p.p.m. par rapport au T.M.S.*	*Remarques*
(d)	Déplacement nul	Accentuation de la déformation
(c)	−0.08	
(e)	Déplacement très faible	
(b) et (b′)	−0.16	Elargissement, puis décomposition en un triplet
(a) et (a′)	−0.03	

Deux phénomènes nouveaux et importants se manifestent dans cette région de pH:

un déplacement de certains pics vers les valeurs plus élevées du champ magnétique,

l'élargissement et la résolution en un triplet du pic correspondant aux protons (b) et (b').

La fixation du troisième proton provoque un déplacement du pic (b, b') vers les valeurs élevées du champ magnétique. On ne peut expliquer ce phénomène qu'en admettant que les protons initialement fixés sur les azotes quittent ces atomes et vont se lier aux groupements carboxyles pour donner une molécule semblable à celle présentée sur la Fig. 5. Nous allons montrer que ce modèle moléculaire permet d'interpréter tous les aspects des spectres NMR.

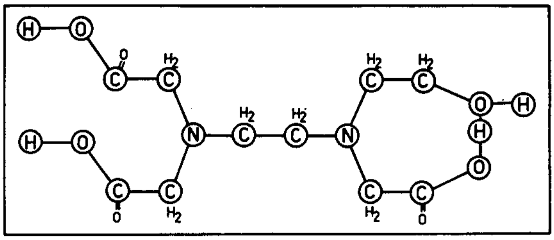


Fig. 5. Structure moléculaire de la forme triacide de HEDTA en solution aqueuse.

Le déplacement de (c) vers les champs élevés est normal puisque ces protons ne subissent plus l'influence du proton fixé sur N(2).

L'indifférence des protons (d) et (e) est aisément explicable également: leur atmosphère électronique est peu modifiée par le changement de position du proton.

Le couplage AA′ BB′ entre les protons (c) et (d) doit se manifester de façon plus marquée. Il peut à présent se former un véritable pont hydrogène entre l'oxygène alcoolique et le proton du groupe -COOH: en effet, le proton n'est plus lié qu'au seul groupement carboxyl et en plus, la distance entre l'oxygène et le proton est plus faible que dans les modèles précédents.

Enfin, en ce qui concerne la non-équivalence des protons (b) et (b'), il est aisé de voir que la partie gauche de la molécule subit l'influence de deux protons alors que la partie droite n'est affectée que par la présence d'un seul proton (dont l'influence est encore diminuée par la proximité du groupement alcoolique).

Nous allons voir que les phénomènes qui se passent au-delà de pH 2 sont une preuve supplémentaire de la validité de cette troisième formule de structure.

Quatrième zône. Elle se caractérise par un déplacement brusque et important de tous les pics NMR vers les valeurs plus faibles du champ magnétique; les plus affectés sont les protons (b) et (b').

Si l'on admet la validité du modèle moléculaire précédent, les derniers sites accessibles de cette molécule sont les atomes d'azote, capables de fixer deux nouveaux protons pour former des ammonium quaternaires. L'évolution des spectres NMR dans cette région de pH est en accord parfait avec cette hypothèse: tous les protons, mais surtout les protons (b) et (b') sont déplacés vers les valeurs faibles du champ magnétique. Le modèle de structure est présenté sur la Fig. 6.

Le spectre à pH 0.40

Les caractéristiques de ce dernier spectre ne sont pas reprises sur le graphique 2. Ce dernier enregistrement est en effet très différent de tous les autres. Les pics sont dans un ordre inhabituel, ils sont fort larges, difficiles à identifier et apparaissent pour des valeurs très élevées du champ magnétique.

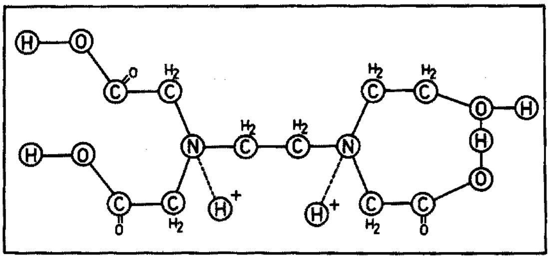


Fig. 6. Structure moléculaire de l'acide HEDTA en milieu fort acide (pH $\leqq$ 1).

Un phénomène semblable a été observé par CHAPMAN *et al.* dans une étude NMR réalisée sur l'EDTA[8]. Les auteurs interprètent ces anomalies en admettant qu'en solution sursaturée (et c'est le cas pour une solution 0.5 *M* en HEDTA en milieu très acide) la molécule se prépare à la cristallisation: elle se réarrange, en solution, pour donner une forme semblable à celle que l'on trouve dans les cristaux. Le spectre d'une solution à ce pH serait donc en fait plus proche du spectre NMR du cristal de HEDTA.

CONCLUSION

On peut se rendre compte, par ces premiers résultats, des renseignements précieux que la résonance magnétique nucléaire peut apporter dans la recherche des formules des structures des molécules en solution. Nous espérons qu'elle nous apportera d'aussi précieux renseignements sur la structure moléculaire des complexes formés entre le HEDTA et les terres rares.

Quoi qu'il en soit, il est dès à présent possible de formuler certaines hypothèses.

Nous avons conclu, d'études chromatographiques[1-3], qu'il existe au moins deux types de complexes formés entre le HEDTA et les terres rares: un complexe neutre MeY d'une part, un complexe double chargé négativement $MeY_2H_n^{(3-n)-}$ d'autre part. La formation du complexe 1:2 se manifeste pour des valeurs déterminées de pH; certaines terres rares forment des complexes mononégatifs $MeY_2H_2^-$ et binégatifs MeY_2H^{2-}, d'autres, par contre, ne présentent que la forme binégative du complexe, et de plus, il n'a pas encore été possible de mettre en évidence un complexe double, neutre ou trinégatif, du type MeY_2H_3 ou MeY_2^{3-}.

Il semble logique d'admettre que certaines formes moléculaires du complexant, par leur géométrie, par la position et le nombre de leurs sites de coordination, sont, plus que d'autres, susceptibles de se fixer sur le complex MeY pour former le complexe double $MeY_2H_n^{(3-n)-}$.

Si l'on admet que le nombre de coordination des lanthanides varie entre 8 et 9, que la première molécule de complexant occupe 5 de ces valences coordinatives, il n'en reste que 3 ou 4, occupées vraisemblablement par des molécules d'eau, disponibles pour la fixation de la seconde molécule de HEDTA.

On pourrait donc supposer que certaines formes du complexant en solution, dont certaines valences coordinatives sont auto-satisfaites par cyclisation des chaînes acétiques, sont prédisposées pour une fixation sur ces complexes (c'est le cas notamment pour les formes mono- et binégatives du complexant).

Ce qui nous semble plus important encore, c'est que si ce sont réellement ces formes cycliques qui se fixent sur le complexe 1:1 et si elles gardent cette forme une fois fixées (en partie tout au moins), il est possible d'expliquer l'augmentation de cinétique qui se manifeste dans les expériences d'élution au moment de l'apparition des complexes doubles. Cette molécule complexe aurait en effet un caractère polaire extrêmement faible ce qui favorise sa diffusion particulaire dans un échangeur d'ions.

Nous espérons pouvoir confirmer ces hypothèses ou trouver d'autres interprétations par les études entreprises par thermogravimétrie, spectrométrie Raman et NMR et analyse thermique différentielle des complexes formés entre les lanthanides et le HEDTA.

Il nous est agréable de remercier ici l'I.I.S.N. pour les subsides accordés qui nous ont permis de mener à bien ces recherches. Nous voudrions également exprimer au professeur J. DEPIREUX et à Monsieur E. DEROUANE notre gratitude pour leurs conseils judicieux et leur aide précieuse dans la manipulation de l'appareil ainsi que dans l'interprétation des résultats.

RÉSUMÉ

Les auteurs étudient, par résonance magnétique nucléaire, la structure moléculaire de HEDTA en solution aqueuse, à différents pH. Ils déterminent ainsi les différents sites occupés successivement par les protons lors de la neutralisation du triacide et proposent différents modèles de structure susceptibles d'interpérter l'aspect et l'évolution des spectres NMR en fonction du pH.

SUMMARY

The molecular structure of HEDTA in aqueous solutions at different pH values, has been studied by nuclear magnetic resonance. The different sites occupied by the protons during the successive neutralisation of the triacid have been established. Different molecular models are proposed to explain the form and the evolution of the NMR spectra as a function of pH.

ZUSAMMENFASSUNG

Die Molekularstruktur von HEDTA wurde durch kernmagnetische Resonanzmessungen in wässrigen Lösungen bei verschiedenen pH-Werten untersucht. Dadurch konnten die von den Protonen eingenommenen Stellungen während der Neutralisierung der drei Säurefunktionen bestimmt werden. Es werden Strukturmodelle vorgeschlagen, die es erlauben, die pH-Abhängigkeit der KMR-Spektren zu deuten.

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DIAZOCOPULATION DES AMINES ET DES HETEROCYCLES AZOTES A L'AIDE DU REACTIF HMBT

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La présente étude précise les modalités de la diazocopulation à l'aide du réactif HMBT (hydrazone de la 3-méthylbenzothiazoline-2-one), ainsi que les applications quantitatives à différentes structures aminées. Avec les amines aromatiques, la copulation s'effectue, comme il est classique, sur le noyau, et conduit à des colorants de coefficients d'extinction particulièrement élevés. Les amines aliphatiques et hétérocycliques copulent par l'atome d'azote d'autant plus volontiers que leur pK_{BH^+} est plus élevé; toutefois, parmi les amines hétérocycliques, la réactivité la plus élevée s'observe lorsque la formation d'une structure quasi aromatique apparaît privilégiée. Enfin, la sélectivité de certaines réactions permet d'envisager l'emploi du réactif HMBT à des fins d'analyse structurale.

Parmi les réactions de dosage des amines et plus particulièrement des arylamines, les méthodes par diazocopulation occupent une place de choix, par leur sensibilité ou leur sélectivité[1].

Les principaux réactifs utilisés sont:

1. Les sels de diazonium de la *p*-nitraniline, notamment le fluoroborate de *p*-nitrophényldiazonium qui, par condensation avec les alcoylamines primaires ou avec les arylamines, conduit à un dérivé diazoaminé coloré en milieu alcalin[2,3].
2. Le fluoroborate de 4-azobenzènediazonium pour le dosage des arylamines[4].
3. Le 3-phényl-1,2,4-thiadiazo-5-diazonium[5] qui se combine aux arylamines pour former des amino-azoïques colorées en milieu alcalin.
4. Le sel de diazonium de l'acide *p*-sulfanilique couramment utilisé pour la détermination des arylamines ou des hétérocycles azotés: imidazoles[1,6], pyrazoles, etc.
5. L'hydrazone de la 3-méthylbenzothiazoline-2-one ou réactif HMBT, qui a été appliqué par HÜNIG ET NOTHER[7] à la copulation avec la N-diméthylaniline. SAWICKI et coll.[8] ont étudié également la formation de dérivés colorés avec certaines aryl ou aralkylamines primaires substituées, des dérivés aminés polycycliques et certains hétérocycles (indoles, carbazoles, phénothiazines) dans une étude particulière sur la détection des dérivés cancérigènes. Nous avons repris l'étude de la copulation du HMBT avec différentes catégories d'amines: alcoylamines, arylamines, amines hétérocycliques, dans le but de préciser les conditions de la réaction quantitative. Nous avons ensuite appliqué la même méthode à l'étude de certains cycles ou hétérocycles d'intérêt thérapeutique.

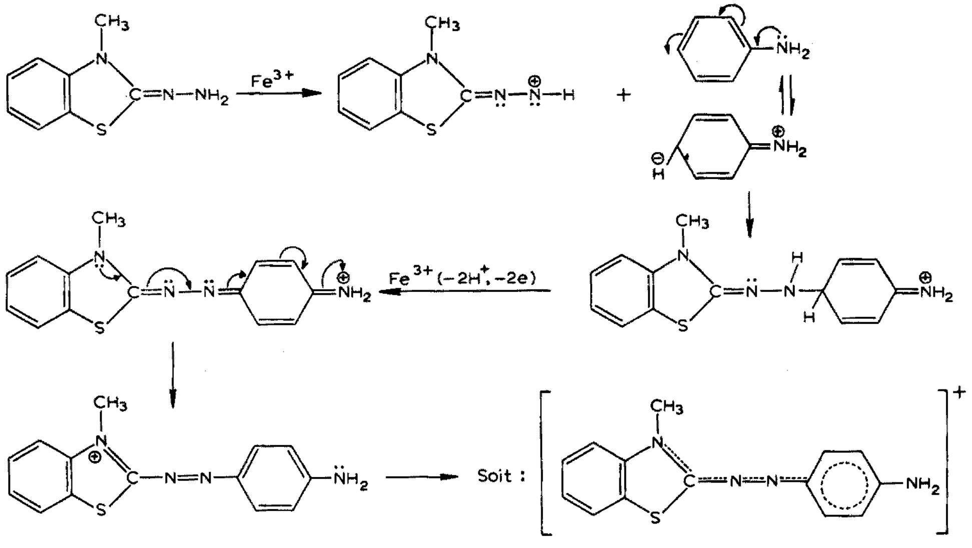
Principe général de la réaction

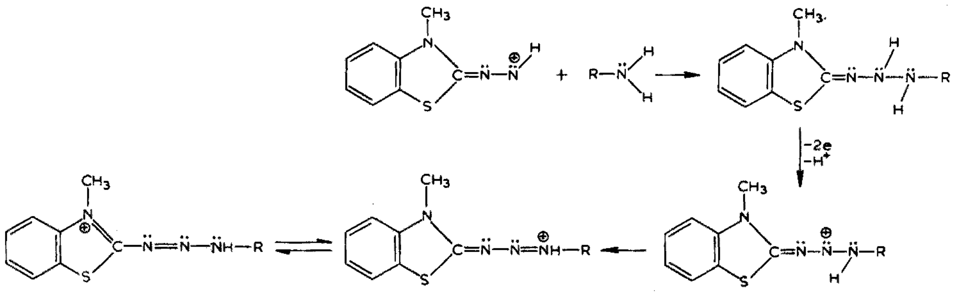
L'hydrazone de la 3-méthylbenzothiazoline-2-one (Réactif HMBT) fournit en milieu oxydant (Fe^{3+}) un sel de diazonium qui est copulé en milieu acide avec les amines.

Les amines sont utilisées en solution aqueuse sous forme de chlorhydrates, ou en solution organique (méthanol, DMSO). La réaction est développée en présence de HMBT et de chlorure ferrique en solutions aqueuses, le pH étant maintenu entre 1.5 et 2 par addition de l'acide hydrochlorique.

Selon la nature des amines, la réaction est plus ou moins sensible; les colorations obtenues sont rouge-violacé, bleu ou bleu-vert et les lectures s'effectuent au spectrophotomètre à des longueurs d'onde comprises entre 550 et 630 nm.

Les réactions les plus sensibles sont obtenues avec les amines aromatiques susceptibles d'une copulation sur le noyau aromatique (coloration rouge-violacé) en *para*. Pour les autres amines (aliphatiques ou cyclaniques), la copulation s'effectue sur le groupement amine et conduit à des réactions colorées beaucoup plus faibles (coloration bleu-vert).





PARTIE EXPÉRIMENTALE

Réactifs

Solution aqueuse de chlorure de fer(III) à 5% (on utilise un chlorure de fer(III) anhydre P.A.).

Réactif HMBT (environ 0.150 *M*). Dissoudre 270 mg d'hydrazino-3-méthylbenzothiazoline-2-one dans 10 ml d'acide chlorhydrique 0.1 *N*.

Mode opératoire

Prélever 0.01 à 0.2 ml de solution d'amine 10^{-3} *M*, 10^{-2} *M* ou *M* dans l'acide chlorhydrique 0.1 *N* (ou: dans le diméthylsulfoxyde, dans le méthanol).

Ajouter 0.2 ml d'acide chlorhydrique 0.1 *N* (ou: diméthylsulfoxyde redistillé, méthanol redistillé), 0.1 ml de réactif HMBT et 0.1 ml de solution de chlorure de fer(III).

Attendre 30 min et ajouter 10 ml d'eau distillée. Examiner les colorations obtenues au spectrophotomètre: mesurer le maximum d'extinction, en faisant varier la longueur d'onde, pour chaque cas.

Remarque. Lorsque les amines sont dissoutes dans un solvant organique (DMSO, méthanol), ajouter 0.1 ml HCl 2 *N* avant l'addition du réactif HMBT.

RÉSULTATS EXPÉRIMENTAUX

Amines aromatiques (voir Tableau I)

Les amines aromatiques, dont la position *para* est libre, copulent avec le réactif HMBT et conduisent à une coloration rouge-violacé dont la sensibilité est fonction de la structure ($10 < E^{1\%}_{1\text{cm}} < 5.5 \cdot 10^3$).

La position *ortho* est peu réactive; la *p*-bromoaniline qui ne peut copuler qu'en *ortho*, réagit faiblement; la réaction est lente, tandis que l'*o*-chloroaniline réagit de façon très sensible et la réaction est immédiate; il en est de même pour la *p*-toluidine, la *p*-anisidine et la benzidine.

La N-diméthylaniline, activée par la présence des deux méthyles est beaucoup

TABLEAU I

AMINES AROMATIQUES

Amines aromatiques	$E^{1\%}_{1\,\text{cm}}$	λ_{max} *(nm)*	*Coloration*
Aniline	1,500	560	Rouge-violacé
N-Diméthylaniline	4,700	575	Rouge-violacé
2,6-Diméthylaniline	5,000	570	Rouge-violacé
o-Chloroaniline	3,800	575	Rouge-violacé
p-Bromoaniline	250	575	Rouge-violacé
o-Toluidine	5,500	560	Rouge-violacé
m-Toluidine	4,500	560	Rouge-violacé
p-Toluidine	130	600	Vert-bleu
p-Anisidine	260	580	Gris-bleu
m-Phénylènediamine	2,200	545	Rouge-violacé
p-Phénylènediamine	1,100	545	Rouge-violacé
Diphénylamine	3,700	610	Bleue
α-Naphtylamine	2,400	550	Rouge-violacé

plus réactive que l'aniline. Il en est de même des *o*- et *m*-toluidines ou de la 2,6-diméthylaniline qui copulent toutes en *para* du groupement aminé (coloration rouge-violacé).

La 2,4,6-triméthylaniline ne réagit pas.

La réaction avec l'*o*-phénylènediamine conduit à une coloration violacée instable avec formation rapide d'un précipité noir soluble dans le DMSO (coloration brune). Par contre, la *m*-phénylènediamine réagit sensiblement en fournissant une coloration rouge-violacé. La *p*-phénylènediamine réagit également, mais plus faiblement. Cette différence de réactivité s'explique par une possibilité de copulation supérieure dans le cas de la *m*-phénylènediamine (4,6 et 2) que dans celui du dérivé *para* (2,5 et 3,6).

La diphénylamine qui est une base faible, réagit par double copulation sur les noyaux aromatiques (coloration bleue). Remarquons que l'oxydation de la diphénylamine peut conduire, elle aussi, à l'apparition d'une coloration bleue. En fait, lorsque la concentration en Fe^{3+} est élevée, il se forme en l'absence d'HMBT, un précipité bleu-vert. Par contre, en présence d'une solution diluée de fer(III) (toujours sans HMBT), on observe une coloration verte, faible et fugace; l'addition, à ce stade, de HMBT fait apparaître une coloration bleue intense et stable.

L'α-naphtylamine conduit à un mono-azoïque, vraisemblablement en position β.

Les dérivés N-acétylés de ces différentes amines ne réagissent plus.

Dérivés sulfamidés

Notre intérêt a été centré sur les principaux sulfamides thérapeutiques. Ceux-ci sont susceptibles de réagir par copulation avec le réactif HMBT soit en milieu aqueux pH 1 à 1.5, soit en solution hydro-organique en présence de DMSO.

La copulation nécessite la présence à l'état libre du groupement amine aromatique: les dérivés disubstitués en 1,4, tels le phtalylsulfathiazol et le succinylsulfathiazol, ne deviennent réactifs qu'après hydrolyse.

Les colorations obtenues sont généralement violettes ($\lambda_{max}=570$ nm). Elle est bleue dans le cas particulier de la sulfamérazine ($\lambda_{max}=600$ nm) et peu sensible, car la copulation ne peut s'effectuer qu'en position *ortho* ($E_{1cm}^{1\%}$ généralement de l'ordre de 100 à 200).

Sulfanilamide ($E_{1cm}^{1\%}=230$) et sulfaguanidine ($E_{1cm}^{1\%}=230$) sont les plus réactives.

Amines aliphatiques

Les amines aliphatiques sont très peu réactives, mais certaines conduisent à une faible coloration verte correspondant à une fixation du diazonium sur le groupement aminé. Cette réaction n'est pas susceptible d'application quantitative.

La méthylamine ne réagit pas. Les réactions sont faibles pour les autres amines de ce groupe: propylamine ($E_{1cm}^{1\%}\sim 5.7$), butylamine ($E_{1cm}^{1\%}\sim 6$) ($pK_{BH^+}=10.61$), ethylamine ($E_{1cm}^{1\%}\sim 8$) ($pK_{BH^+}=10.75$), qui donnent une coloration vert-bleu. La *tert.*-butylamine ne réagit pas. La benzylamine réagit plus sensiblement ($E_{1cm}^{1\%}\sim 65$, coloration vert-bleu).

La diméthylamine ne réagit pas, la diéthylamine réagit faiblement. Les amines tertiaires ne réagissent pas. La cyclohexylamine, amine cyclanique primaire, ne réagit pas.

Amines hétérocycliques

La réactivité est également assez faible et correspond souvent à une fixation sur l'azote aminé (coloration vert-bleu); elle est fonction du pK_{BH^+}, comme le montre le Tableau II.

TABLEAU II

AMINES HÉTÉROCYCLIQUES

Amines hétérocycliques	pK_{BH^+}	*Réaction*
Pyrrole	0.4	0
Pyrimidine	1.3	0
1,2,4-Triazole	2.3	0
3-Amino-5-phényl-1,2,4-triazole	3.5	0
3-Amino-1,2,4-triazole	4	0
Pyrazole	2.5	0
Pyridine	5.15	0
α-Picoline	6.48	0
2,6-Lutidine	6.7	0
2,4,6-Collidine	7.32	$E_{1cm}^{1\%} \sim 10$
Pipérazine	5.6	0
Morpholine	8.4	$+ E_{1cm}^{1\%} \sim 3$
Pipéridine	11.21	$+ E_{1cm}^{1\%} \sim 5$
Pyrrolidine	11.3	$+ E_{1cm}^{1\%} \sim 17$

Remarquons que la pyridine elle-même ne réagit pas, alors que la 2,4,6-collidine réagit faiblement; l'existence d'une forme tautomère du type amine secondaire permet d'interpréter ce comportement, lié, comme chez les amines secondaires, à la valeur du pK_{BH^+}.

Aminopyridines. Les 2-amino-, 2-amino-3-bromo-, et 2-amino-3,5-dibromopyridines ne réagissent pas. La 3-aminopyridine réagit faiblement (coloration gris-bleu).

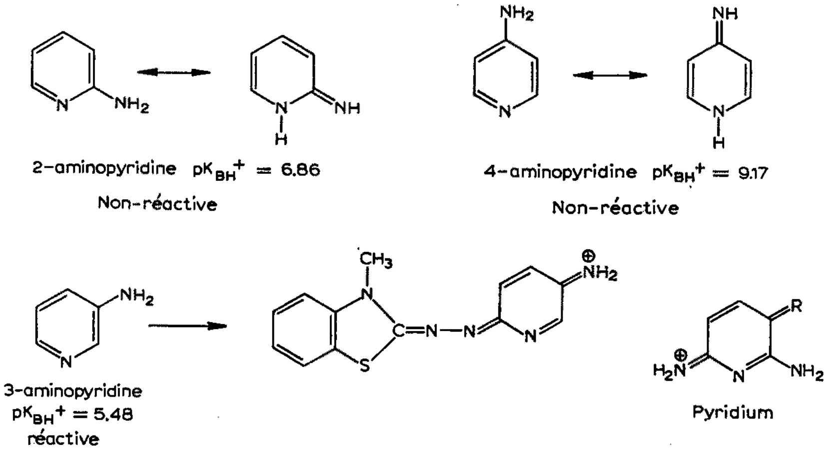


Fig. 1.

La 2,3-diaminopyridine réagit plus sensiblement et conduit à une coloration violette ($E_{1cm}^{1\%} \sim 3,250$).

La 2,3-diamino-5-bromopyridine—et surtout la 2-chloro-3-aminopyridine—sont plus réactives (coloration violette).

La 4-aminopyridine ne réagit pas.

Ces résultats sont à rapprocher de ceux obtenus en série aromatique. Le rôle majeur n'est pas joué ici par la basicité, mais par l'existence éventuelle de conformations aromatiques privilégiées (voir pK sur Tableau). La 4-aminopyridine est une base forte, par effet de résonance additionnel correspondant à l'existence d'une forme imine qui apparaît aussi, mais à un moindre degré, chez la 2-aminopyridine. La 3-aminopyridine se comporte comme une amine aromatique, ce qui facilite l'attaque électrophile en 6 (accessoirement en 4); cette structure se prête aisément à une copulation du sel de diazonium en *para* du groupement 3-amino, position la plus favorable à une délocalisation électronique, encore renforcée par un halogène en 2. Dans le cas de la 2,3-diamino-5-bromopyridine, l'effet inducteur accepteur du groupe amino-2 en milieu acide, favorise l'apparition du carbocation en 5 et l'attaque électrophile en 6.

A titre de comparaison, rappelons que le Pyridium (Mallophène* ou Bistoril*) résultant de la copulation de la 2,6-diaminopyridine avec l'aniline diazotée, ou le Néopyridium (copulation avec l'acide anthranilique diazoté) sont ainsi substitués en 3, c'est-à-dire en *ortho* et *para* des groupements aminés.

Aminoquinoléines. Le noyau quinoléique est un noyau plan et la réaction colorée décrite repose sur une importante délocalisation électronique, à la fois le long de la chaîne du HMBT et au travers du noyau quinoléique jusqu'au groupement aminé. L'attaque du HMBT est donc localisé sur un sommet d'où une chaîne résonante stable peut s'établir, reliant ainsi le groupement aminé de la quinoléine au groupement benzothiazole.

La position la plus favorable à une attaque électrophile du noyau quinoléique est la position 8. Ainsi, la 5-aminoquinoléine réagit très sensiblement ($E_{1cm}^{1\%} \sim 3,000$) en fournissant une coloration violet-bleu. De même, la 8-aminoquinoléine conduit à une coloration identique par copulation en 5, la sensibilité étant légèrement plus faible ($E_{1cm}^{1\%} \sim 2,500$). Les autres positions du noyau quinoléique sont moins favorables à la copulation envisagée; toutefois, la 3-aminoquinoléine peut engendrer une légère coloration bleu lavande ($E_{1cm}^{1\%} \sim 240$) pour laquelle ne peut être retenue qu'une copulation en 7; une copulation en 4,5 ou 8 n'assurerait pas une délocalisation électronique le long de la chaîne diazoïque.

Pour des considérations géométriques ou spatiales analogues, par suite de la présence de l'azote quinoléique, un certain nombre d'aminoquinoléines ne sont pas réactives; ce sont: la 4-aminoquinoléine, pour laquelle une copulation sur le cycle benzénique est aussi impossible que sur le cycle pyridinique; la 2-méthyl-4-aminoquinoléine (ou 4-aminoquinaldine); la 4-amino-7-chloroquinoléine; la 2-aminoquinoléine: la réactivité du groupement aminé est ici inhibée par la proximité de l'azote quinoléique, comme dans le cas de la 2-aminopyridine.

Nous avons de plus étudié quelques dérivés substitués à l'azote en 4 et en 8, en raison de leur utilisation thérapeutique. Les dérivés de la 8-aminoquinoléine (pamaquine, pentaquine, primaquine) se comportent comme la 8-aminoquinoléine elle-même; les coefficients d'extinction des colorants formés sont, toutefois, plus faibles.

Les 4-aminoquinoléines substituées (chloroquine et hydroxychloroquine) tout comme la 4-aminoquinoléine, ne peuvent être réactives et ne conduisent à aucune coloration. Notons que le diazonium de l'acide *p*-sulfanilique se condense sur ces aminoquinoléines[1]. En ce qui concerne la pamaquine, la copulation en 5 a été proposée par BRODIE *et al.*[9]; toutefois, une copulation en 1 avait été supposée par SANCHEZ[10].

Aminoacridines. Deux molécules de cette série ont été étudiées:

l'acriflavine: chlorure de 3,6-diamino-10-méthylacridinium;

l'éthacridine: lactate de 2-éthoxy-6,9-diaminoacridine.

Ces deux substances réagissent différemment: l'éthacridine conduit à une coloration violette en milieu aqueux (pH 1 à 1.5) ou en solution dans le DMSO. Coloration analogue à celle constatée pour les amines aromatiques ($\lambda_{max} = 540$ nm). L'acriflavine conduit à une coloration brune ($\lambda_{max} = 450$ nm).

Les deux réactions sont sensibles (éthacridine $E^{1\%}_{1cm}$ eau $= 10^3$, $E^{1\%}_{1cm}$ DMSO $= 10^3$; acriflavine $E^{1\%}_{1cm}$ eau $= 1{,}250$, $E^{1\%}_{1cm}$ DMSO $= 1{,}500$), mais les colorations observées montrent bien que les mécanismes sont différents. Remarquons que les amines en 3 et en 9 sont des bases faibles, tandis que le groupement 6-amino correspond[11] à une base forte de $pK_{BH^+} = 10$.

Donc, pour l'éthacridine, la basicité du groupement 6-amino et l'apparition d'une coloration violette laissent supposer que la copulation a lieu sur le cycle aromatique, vraisemblablement en 5.

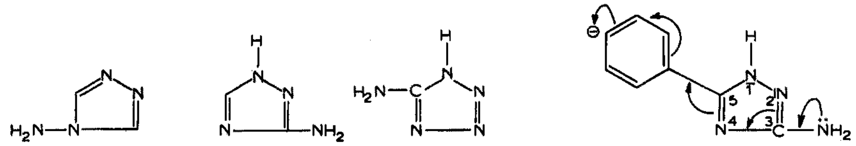
Pour l'acriflavine, le groupe chlorométhylate diminue la conjugaison entre les deux noyaux et la copulation a vraisemblablement lieu en 9.

Remarque. Les aminopyridines, les aminoquinoléines et les aminoacridines ont été classées avec les amines hétérocycliques: les résultats précédents montrent clairement que le comportement de ces composés dépend plus de la position de l'atome d'azote extranucléaire que de la réactivité de l'atome d'azote endocyclique.

Triazoles et tétrazoles substitués. Parmi les composés de cette série, quelques amino-1,2,4-triazoles et aminotétrazoles ont été étudiés.

Le 3-amino-1,2,4-triazole ($pK_{BH^+} = 4$), le 4-amino-1,2,4-triazole, le 5-amino-1,2,4-tétrazole, ne réagissent pas.

Par contre, le 3-amino-5-phényl-1,2,4-triazole est réactif ($pK_{BH^+} = 3.5$). Les pK_{BH^+} de ces dernières amines sont voisins et la réaction positive du 3-amino-5-phényl-1,2,4-triazole correspond vraisemblablement à une copulation sur le noyau aromatique favorisée par la résonance interne entre l'hétérocycle et le noyau phényle. La réaction est faible et ne se développe pas en milieu aqueux. On obtient seulement une coloration bleue en présence de méthanol; la réaction est très irrégulière dans le DMSO.



4-amino-1,2,4-triazole

3-amino-1,2,4-triazole

5-amino-1,2,3,4-tetrazole

3-amino-5-phényl-1,2,4-triazole

Fig. 2.

Deux cas particuliers

Les dérivés de la pyrazole-5-one. Deux types ont été étudiés:

Pyrazole-5-ones non substituées en 4. La réaction se développe en milieu aqueux (pH 1 à 1.5) ou en présence de DMSO ou de DMF. Seule l'antipyrine donne naissance à une réaction colorée quantitative; les autres composés forment un précipité brun-rouge.

Pyrazole-5-ones substituées en 3 et 4. Les quatre composés testés conduisent tous à une coloration bleue en milieu aqueux ou à une coloration vert-bleu en présence de DMSO ou de DMF. Il faut noter un léger effet bathochrome et hyperchrome avec le composé II en raison de la présence du groupement CHO. Le composé IV est également réactif ($E^{1\%}_{1cm}$ 230), plus que le pyramidon ($E^{1\%}_{1cm}$ 35), plus encore que le dérivé acétylaminé (III) ($E^{1\%}_{1cm}$ 6).

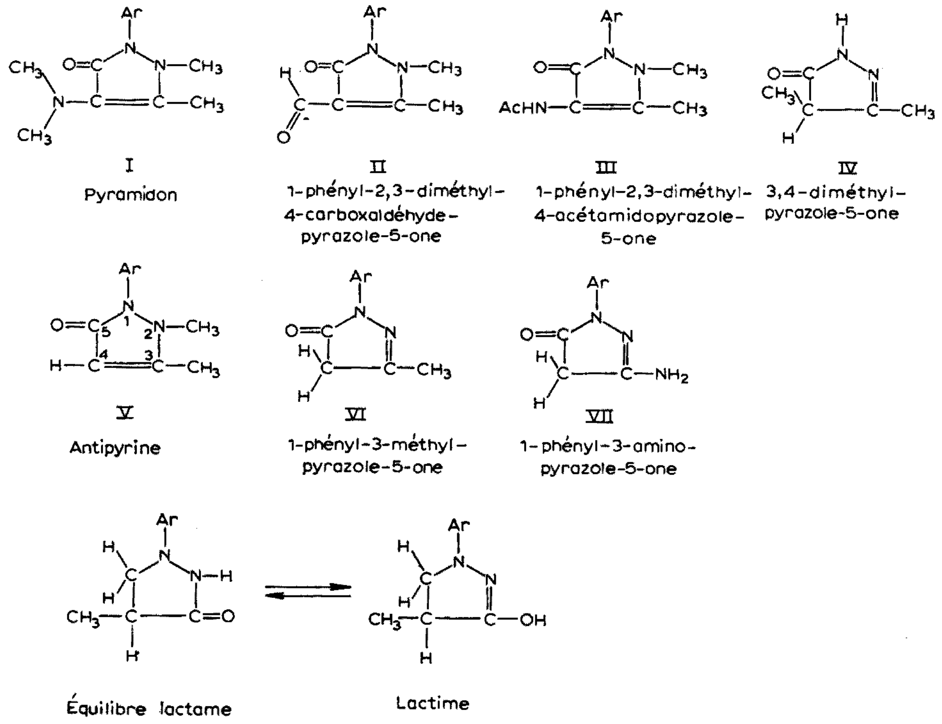
Deux types de réaction sont donc ici observés, correspondant à deux mécanismes différents que nous allons préciser.

La possibilité d'une copulation sur le noyau aromatique fixée en 1 doit être exclue, car le composé IV exempt de substitution phényle réagit comme les composés II et III en formant un dérivé coloré de même λ_{max}. De plus le 1-phényl-4-acétyl-5-méthylpyrazole ne réagit pas; la 1-phényl-4-méthylpyrazole-3-one non plus.

La réaction des pyrazolones 3,4-substituées (I à IV) se développe comme celle des dérivés carbonylés[12], c'est-à-dire à partir du groupement C=O en 5 de la forme lactame, avec apparition d'une coloration bleue. La faible sensibilité est due à la condensation d'une seule molécule de HMBT avec formation d'un dérivé stable, non ionisé dans le cas général; l'accroissement de sensibilité observé avec le composé IV est lié à la formation particulière d'un composé ionique dont la délocalisation électronique est plus élevée. Rappelons que dans le cas des dérivés carbonylés, la réaction met en jeu deux molécules de HMBT et conduit à une structure ionique. Pour leur part, les pyrazolones non substituées en 4 développent une coloration ou un précipité brun-rouge. La forte réactivité en 4 conditionne la copulation sur ce sommet, selon le mécanisme général de diazocopulation de ces hétérocycles. De fait, le sel de diazonium de l'acide *p*-sulfanilique copule aisément en 4 avec les composés V, VI et VII, conduisant ainsi à une coloration brun-rosé. Dans les mêmes conditions les composés I, II et III ne réagissent pas. Les réactivités comparées de ces deux catégories de pyrazolones permettent de conclure que chez les composés non substitués en 4, la forme lactame n'est pas mise en évidence; les pyrazole-5-ones se comportent comme des hydroxy-5-pyrazoles.

L'hexaméthylènetétramine. Considérée comme une amine tertiaire polycyclique, l'hexaméthylènetétramine ne devrait pas être, a priori, dosable par le réactif HMBT. En fait, en phase aqueuse, mieux encore en milieu acide, ce composé est rapidement décomposé en sel d'ammonium et formaldéhyde. La plupart des méthodes de dosage de l'hexaméthylènetétramine sont fondées sur cette réaction, le formol formé étant mesuré après séparation par distillation. Or, en raison de la très grande sensibilité de la réaction entre formol et HMBT[11], il est apparu possible de doser cet aldéhyde sans séparation.

L'hydrolyse d'une solution 10^{-4} *M* est conduite en milieu sulfurique ou chlorhydrique normal à l'ébullition sous reflux pendant 30 min. Après refroidissement, le dosage colorimétrique du formol est conduit à un pH compris entre 0 et 0.5. On dose alors, conformément à la théorie six molécules de formol, sans interférence des constituants secondaires, en particulier des sels ammoniacaux. Remarquons qu'une solution extemporanée 10^{-4} *M* libère avant toute hydrolyse acide, 40% de son formol



I Pyramidon

II 1-phényl-2,3-diméthyl-4-carboxaldéhyde-pyrazole-5-one

III 1-phényl-2,3-diméthyl-4-acétamidopyrazole-5-one

IV 3,4-diméthyl-pyrazole-5-one

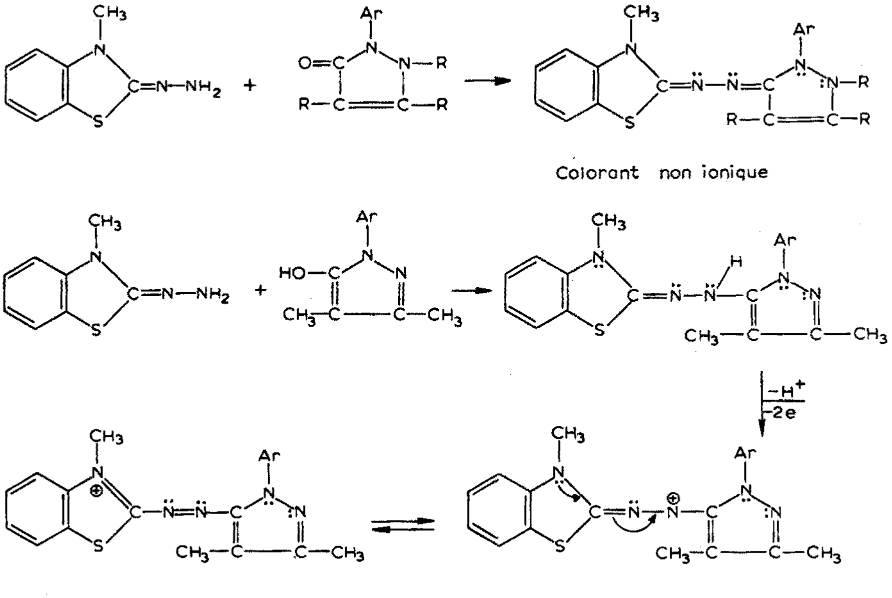
V Antipyrine

VI 1-phényl-3-méthyl-pyrazole-5-one

VII 1-phényl-3-amino-pyrazole-5-one

Équilibre lactame Lactime

Fig. 3.



Colorant non ionique

Colorant ionique

Fig. 4.

dans les conditions du dosage. Après six heures de contact à froid en milieu acide, on dose 52% du formol total.

CONCLUSIONS

La présente étude a pour but de préciser les modalités de diazocopulation à l'aide du HMBT, ainsi que les applications quantitatives à différentes structures aminées et hétérocycliques.

Les modalités de diazocopulation

Les amines aromatiques réagissent par copulation sur le noyau aromatique. La réaction est très sensible pour les arylamines dont la position 4 (en *para* du groupement aminé) est libre. La coloration est violette. La sensibilité est accrue avec les arylamines N-substituées.

Lorsque la position *para* est substituée, la réaction de copulation s'effectue comme il est classique en *ortho*; on observe alors un effet bathochrome et hypochrome.

De rares alcoylamines réagissent faiblement et conduisent à une coloration verte. Les amines tertiaires, la méthylamine ne réagissent pas.

Les hétérocycles azotés sont également assez peu réactifs Seuls les dérivés de $pK_{BH^+} > 6$ sont susceptibles de se condenser. Toutefois, mécanismes et sensibilité des réactions peuvent être différents en fonction des substituants. Parmi ces hétérocycles:

les aminopyridines réagissent si la structure permet une délocalisation électronique intense. Dans ce cas, la réactivité ne dépend plus du pK_{BH^+}; ainsi, la 2-aminopyridine et la 4-aminopyridine de pK_{BH^+} plus élevé que celui de la 3-aminopyridine, ne réagissent pas. Par contre, la 3-aminopyridine, la 2,3-diaminopyridine, les 3-amino, 2- ou 5-halogéno pyridines réagissent de façon sensible par copulation en 6.

pour les mêmes raisons, les aminoquinoléines en 8 ou en 5, sont réactives. La diazocopulation s'effectue en 5 ou en 8 respectivement. Il faut cependant remarquer que les dérivés substitués sur la fonction amine réagissent plus faiblement. Les 4-aminoquinoléines ne réagissent pas.

Les aminoacridines réagissent par copulation en 9. Dans le cas où la position 9 est substituée, la réaction peut s'effectuer sur un noyau aromatique si la basicité est suffisante.

Pour les pyrazolones dont la position 4 est libre, la copulation s'effectue en ce point. Les pyrazole-5-ones, dont la position 4 est substituée, réagissent par condensation en 5, selon un mécanisme apparenté à celui précédemment décrit pour les dérivés carbonylés[12].

L'hexaméthylène tétramine peut être dosée par libération du formaldéhyde après hydrolyse.

Les applications quantitatives

Elles sont particulièrement intéressantes pour:

le dosage de l'hexaméthylènetétramine, en raison de la grande sensibilité de la réaction de condensation du réactif HMBT avec le formaldéhyde.

le dosage des arylamines dont la position *para* est libre;

le dosage des 3-aminopyridines substituées en 2 ou en 5 en présence des autres aminopyridines non réactives;

le dosage des 5- ou 8-aminoquinoléines libres ou substituées, en présence d'autres aminoquinoléines.

le dosage des 6-aminoacridines.

Nous préciserons ultérieurement les modalités réactionnelles de certains cas particuliers, pour lesquels une étude est en cours.

Par ailleurs, pour toutes les structures envisagées ci-dessus, les réactions de diazocopulation ont également été développées à l'aide du réactif HBT (hydrazinobenzothiazole), et feront l'objet d'une communication ultérieure.

RÉSUMÉ

Les auteurs décrivent une méthode de dosage colorimétrique par diazocopulation à l'aide du réactif HMBT. Cette méthode est applicable à la détermination quantitative des amines primaires aromatiques, de quelques amines hétérocycliques, ainsi qu'à celle de l'hexaméthylènetétramine et de quelques dérivés de la pyrazole-5-one.

SUMMARY

A colorimetric determination of various compounds containing amino groups is described, with 3-methylbenzothiazoline-2-one hydrazone as reagent. Primary aromatic amines, some heterocyclic amines, hexamethylenetetramine and some derivatives of pyrazol-5-one can be determined.

ZUSAMMENFASSUNG

Die kolorimetrische Bestimmung verschiedenartiger Verbindungen, welche Aminogruppen enthalten mit 3-Methylbenzothiazolin-2-on wird beschrieben. Primäre aromatische Amine, einige heterozyklische Amine, Hexamethylentetramin und einige Derivate von Pyrazol-5-on können bestimmt werden.

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PHOTOMETRISCHE BESTIMMUNG NIEDRIGER OZONKONZENTRATIONEN IN WÄSSERN

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Kürzlich wurde von uns[1] eine neue, auf der Reaktion des Ozons mit dem Diphosphatkomplex des Mangans(II) im sauren Milieu gegründete Methode beschrieben, bei welcher der violett gefärbte Diphosphatkomplex des Mangans(III), dessen Eigenschaften für die photometrische Bestimmung geeignet sind, entsteht. Diese Methode ist für die Ozonbestimmung in wässrigen Lösungen, Trink- und Nutzwässern geeignet und ermöglicht das Ozon in Konzentrationen von mehr als 1 mg O_3/l beim Vorhandensein von Chlor und dessen sauerstoffhaltigen Verbindungen zu bestimmen.

In der vorliegenden Arbeit wurde der Steigerung der Empfindlichkeit der genannten Methode besondere Aufmerksamkeit gewidmet und ferner die Beseitigung von störenden Einflüssen durch die in verunreinigten Oberflächen- und einigen Abwässern vorkommenden Stoffe, die den Ozonzerfall fördern, berücksichtigt. Die ausgearbeitete Methode beruht auch auf der Ozonreaktion des Mn(II)-Diphosphatkomplex und auf der Steigerung der Empfindlichkeit durch die Reaktion des Mn(III)-Diphosphatkomplexes mit *o*-Tolidin. Störende Einflüsse wurden durch die Überführung des Ozons aus der Probe in die Lösung des Mn(II)-Diphosphatkomplexes beseitigt.

EXPERIMENTELLER TEIL

Geräte

Hilger Spekker Spektrophotometer (Hilger & Watts, Ltd., London) Filter Nr. 601 (Abs. Max. bei *ca.* 430 nm) und Filter Nr. 605 (Abs. Max. bei *ca.* 550 nm). Reagenzflasche mit normal. Schliff und Frittenaufsatz. Frittenwaschflasche für je 100 ml mit normal. Schliff, die mittels einer Glasrohrleitung mit kurzen Polyäthylen-Verbindungsstücken verbunden sind. Gasflasche mit Luft oder Stickstoff mit Reduzierventil oder eine geeignete Belüftungsanlage.

Reagentien

Natriumdihydrogendiphosphat, 0.75 *M* Lösung. 199 g $Na_4P_2O_7$ p.a. und 208.0 ml H_2SO_4 (1+4) auf 1000 ml.

Mangansulfat, 3 *M* Lösung.

Mn(II)-Diphosphatkomplex, 0.15 *M* $Na_4[Mn(H_2P_2O_7)_3]$ und 0.45 *M* H_2SO_4

Absorptionslösung. 60 ml 0.75 M $Na_2H_2P_2O_7$ Lösung, 12.5 ml H_2SO_4 (1+4) und 5 ml 3 M $MnSO_4$ Lösung werden mit Wasser bis zu 100 ml ergänzt.

Mn(II)-Diphosphatkomplex, 0.15 M $Na_4[Mn(H_2P_2O_7)_3]$ und 6 M H_2SO_4 Reaktionslösung. 60 ml 0.75 M $Na_2H_2P_2O_7$ Lösung, 35 ml H_2SO_4 konz. und 5 ml 3 M $MnSO_4$ Lösung gemischt und die Mischung gekühlt.

Mn(III)-Diphosphatkomplex, 0.0005 N Eichlösung. Zu 10 ml der Lösung in einer Konzentration von 0.15 M $Na_4[Mn(H_2P_2O_7)_3]$ und 0.45 M H_2SO_4 wird genau 1 ml 0.05 N $K_2Cr_2O_7$ Lösung abpipettiert und nach fünf Minuten Stehen bis zu 100 ml ergänzt.

o-Tolidin, 0.135% Lösung. 1.35 g *o*-Tolidin wird in 500 ml siedenden destillierten Wasser gelöst und mit 350 ml Wasser und 150 ml HCl konz. nachgefüllt.

Zur Verdünnung wurde redestilliertes Wasser verwendet.

Die Reaktion vom Mn(III)-Diphosphatkomplex mit o*-Tolidin*

Zunächst wurde die Reaktion des durch die Oxydation von Mn(II)-Diphosphatkomplex mit Ozon entstandenen Mn(III)-Diphosphatkomplexes mit *o*-Tolidin verfolgt. Bei dieser Reaktion entsteht ein gelbes Reaktionsprodukt, dessen Färbung die gleiche ist, wie die des Reaktionsproduktes von *o*-Tolidins mit Ozon allein und mit Mangan(IV). Das Absorptionsmaximum liegt bei *ca.* 440 nm. Der Mn(III)-Diphosphatkomplex ist weniger intensiv gefärbt, als sein Reaktionsprodukt mit *o*-Tolidin, was deren molare Extinktionskoeffizienten beweisen ($1.5 \cdot 10^2$ l/Mol cm und $3.5 \cdot 10^4$ l/Mol cm).

Die optimalen aziditiven Bedingungen der oben angeführten Reaktion wurden in der Ozonlösung in der jodometrisch ermittelten Konzentration von 0.39 mg O_3/l festgestellt. Von der Vorratslösung mit 3.90 mg O_3/l wurden gleichzeitig 10 ml auf 100 ml verdünnt. Die Beständigkeit der Färbung wurde in Lösungen mit 0.15, 0.30 und 0.45 M H_2SO_4 festgestellt. Die Ergebnisse in der Abb. 1 zeigen, dass bei 0.3 M Schwefelsäure sich die Extinktion der Lösung während 25 Minuten nicht ändert, was der üblichen analytischen Praxis entspricht.

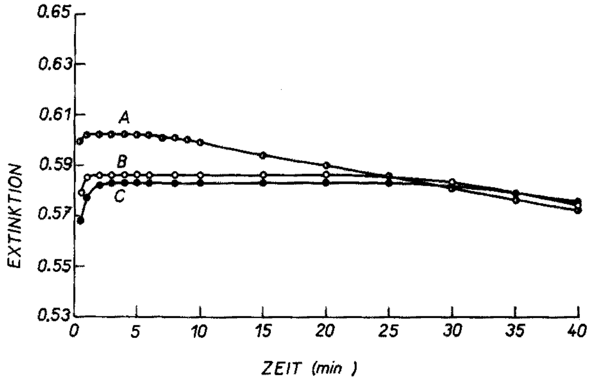

Abb. 1. Abhängigkeit der Extinktion von der Zeit für die Reaktionsprodukte des Mn(III)-Diphosphatkomplex mit *o*-Tolidin bei verschiedenen Schwefelsäurekonzentrationen. Ozonlösung 0.39 mg O_3/l. (A) 0.15; (B) 0.30; (C) 0.45 M H_2SO_4. Schichtdicke l = 2.00 cm.

Weiter wurde die Farbbeständigkeit des Reaktionsproduktes vom Mn(III)-

Diphosphatkomplex und *o*-Tolidin mit der Farbbeständigkeit bei der, nach der *o*-Tolidin[2] und der Mn-*o*-Tolidin[3,4]-Methode durchgeführten Ozonbestimmung verglichen. Es wurde mit Lösungen, die 0.24 mg O_3/l enthielten, die durch Verdünnung der Vorratslösung angesetzt wurden, gearbeitet. Der Wert der Ozonlösung wurde jodometrisch festgestellt. Die in der Abb. 2 angeführten Ergebnisse zeigen, dass die bei der Reaktion des *o*-Tolidins mit dem Mn(III)-Diphosphatkomplex entstandene Färbung am beständigsten ist.

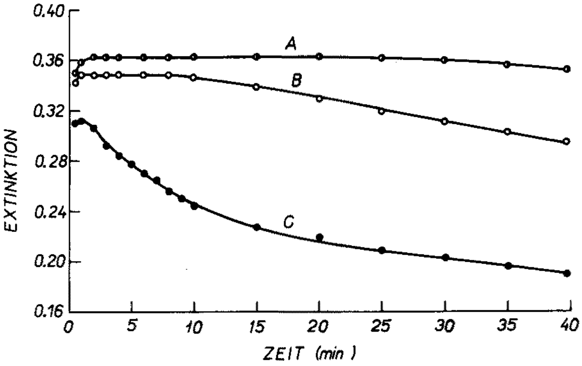

Abb. 2. Abhängigkeit der Extinktion von der Zeit für verschiedene Methoden von Ozonbestimmung. Ozonlösung 0.24 mg O_3/l. (A) Mn-Diphosphatkomplex-*o*-Tolidin-Methode; (B) Mn-*o*-Tolidin-Methode; (C) *o*-Tolidin-Methode. Schichtdicke l = 2.00 cm.

Zur Aufstellung der Eichkurve wurden verschiedene Präparate des *o*-Tolidins verwendet. Dabei wurde festgestellt, dass die Farbintensität des Reaktionsproduktes von der Art und dem Alter des verwendeten *o*-Tolidin Präparates abhängt.

Die Ozonabsorption in der Mn(II)-Diphosphatkomplex Lösung

Mit Rücksicht auf die Geschwindigkeit der Analyse und den Eigenschaften einzelner störender Einflüsse ist es erforderlich, das Ozon aus der Probe in kürzester Zeit zu verdrängen. In einer Reihe von Versuchen, bei denen der Durchfluss des Trägergases, das Volumen der Probe und die Art des Ausblasens geändert wurden, ergab sich dass es zur quantitativen Austreibung des Ozons aus einem Volumen von 1000 ml notwendig ist, das Trägergas mittels eines Frittenzuführungsrohrs mit einer Durchflussgeschwindigkeit von 15–20 ml/sek 5 Min lang einzuführen.

Die Intensität des Durchblasens muss jedoch auf der anderen Seite mit der Ozonabsorption in der Lösung des Mn(II)-Diphosphatkomplexes im Einklang stehen. Diese Bedingungen werden durch die Reaktionsgeschwindigkeit, die Ozonkonzentration im Trägergas, das Volumen der Absorptionslösungen und durch die Anordnung der Absorber beeinflusst. Der geforderte Durchfluss des Trägergases schloss die Verwendung von Mikroabsorbern aus, auch die Empfindlichkeit der Reaktion in Bezug auf die von der Praxis geforderten Bestimmung machte deren Verwendung nicht erforderlich.

In den 100-ml Frittenwaschflaschen mit 50 ml Mn(II)-Diphosphatkomplex-Absorptionslösung (s. *Reagentien*), bei der aktiven Höhe von 52 mm der durchblasenen Flüssigkeit war die Absorption, selbst bei der Verwendung von vier hintereinander geschalteten Absorbern, nicht quantitativ. Es wurde deshalb die Möglichkeit einer Steigerung der Reaktionsgeschwindigkeit des Ozons mit dem Mn(II)-Diphosphatkomplex verfolgt. In einer Reihe von vorhergehenden Versuchen mit verschiedenen Schwermetallsalzen wurde festgestellt, dass die Verbindungen des dreiwertigen Chroms[5] sehr gute katalytische Eigenschaften für die verfolgte Reaktion haben.

Der Einfluss des Katalysators auf die Geschwindigkeit der Reaktion vom Mn(II)-Diphosphatkomplex mit Ozon wurde in den oben beschriebenen Absorbern verfolgt; diese werden mit 50 ml der Absorptionslösung in der Konzentration von 0.15 M $Na_4[Mn(H_2P_2O_7)_3]$ und 0.45 M H_2SO_4 und 0 bis 0.002 M Cr^{3+} gefüllt. Durch die Absorber wurde das Gas mit konstanter Ozonkonzentration durchgeblasen. Die Extinktion wurde in den Durchflussküvetten mit Schichtdicke $l = 3.46$ cm gegen destilliertes Wasser gemessen. Die in der Tabelle I angeführten Ergebnisse zeigen, dass der Färbung der das Chrom(III)-salz enthaltenden Absorptionslösung etwa zweimal schneller geschieht als die Färbung der bloss den Mn(II)-Diphosphatkomplex enthaltenden Lösung.

TABELLE I

OZONABSORPTION IN EINER LÖSUNG MIT DEM Mn(II)-DIPHOSPHATKOMPLEX ALLEIN UND IN DER GEGENWART VON DREIWERTIGEN CHROM

Zeit (min)	*Extinktion ($l = 3.46$ cm)*	
	0.15 M $Na_4[Mn(H_2P_2O_7)_3]$ *und 0.45 M* H_2SO_4	*0.15 M* $Na_4[Mn(H_2P_2O_7)_3]$ *und 0.45 M* H_2SO_4; *0.002 M* Cr^{3+}
0.5	0.02	0.06
1.0	0.05	0.11
2.0	0.09	0.22
3.0	0.14	0.33
4.0	0.19	0.43
5.0	0.25	0.55
7.0	0.xx	0.xx

Arbeitsvorschrift

Verfahren A. Zu 100.0 ml einer Probe im geschliffenen Kolben werden 5.0 ml Reaktionslösung (s. *Reagentien*) pipettiert und nach 5 Min werden 5.0 ml Lösung des *o*-Tolidins zugegeben. Nach weiteren 5 Min wird die Extinktion der Lösung photometrisch (bei 518–525 nm[1]) gemessen. Als Vergleichslösung wird die mit 5.0 ml 6 M H_2SO_4 auf 100 ml angesäurte Wasserprobe verwendet.

Für die Aufstellung der Eichkurve wird eine künstliche Standardlösung verwendet. Es werden 0.0–5.0 ml 0.0005 N der Eichlösung vom Mn(III)-Diphosphatkomplex abgemessen (s. *Reagentien*) und bis zu je 100 ml mit destilliertem Wasser aufgefüllt. Zu jeder Lösung werden je 5.0 ml *o*-Tolidinlösung und je 5.0 ml destilliertes Wasser zugegeben. Nach 5 Min Stehen wird die Extinktion der Lösungen photometrisch gemessen und im Diagramm im Vergleich mit den entsprechenden Ozon-Konzentrationen 0.00, 0.06, 0.12, 0.24, 0.36, 0.48 und 0.60 mg O_3/l aufgezeichnet.

Die Bestimmung wird durch die oxydierenden Stoffe, die mit *o*-Tolidin reagieren, gestört. Gase, wie Chlor oder Chlordioxyd, lassen sich nach der Zugabe des Mn(II)-Diphosphatkomplexes und vor der Zugabe des *o*-Tolidins und zwar durch Durchlüftung beseitigen. Den Einfluss von anderen Stoffen muss durch einen

Blindversuch eliminiert werden; dazu verwendet man die betreffende Probe nach vorheriger Beseitigung des Ozons.

Verfahren B. Es werden maximal 1000.0 ml der Probe in die Reagenzflasche mit normalem Schliff abgemessen. Die Flasche wird mit einer Gasflasche mit Luft, oder mit einer Belüftungsanlage, und mit drei Frittenwaschflaschen verbunden, die je 49.0 ml Absorptionslösung (s. *Reagentien*) und 1.0 ml 0.1 *M* $KCr(SO_4)_2$ enthielten. Sofort nach dem Anschliessen der Probe-Flasche wird Luft mit einer Durchflussgeschwindigkeit von 15–20 ml/sek 5 Min lang durchgeblasen.

Im Falle, dass die Probe auch andere, mit dem Mn(II)-Diphosphatkomplex reagierende Gase, z.B. Chlor oder Chlordioxyd, enthält, muss man die Absorptionslösungen bis zu deren vollkommener Beseitigung belüften. Dann werden die Inhalte der ersten zwei Waschflaschen zusammen gegossen, 5.0 ml *o*-Tolidin-Lösung zugegeben und die Lösung photometrisch gemessen. Zum Vergleich wird die Absorptionslösung vom Mn(II)-Diphosphatkomplex verwendet.

Die Aufstellung der Eichkurve stimmt mit dem Verfahren A überein; bei der Berechnung ist es notwendig, das Verhältnis der Probevolumina und der Absorptionslösungen in Betracht zu ziehen.

BESTIMMUNG DER STANDARDABWEICHUNG

Die Methoden wurden an einer Probe, zehnmal unter Einhaltung des Verfahrens A und dreimal bei Anwendung des Verfahrens B untersucht. Die Probe wurde durch Verdünnung der Ozonlösung mit redestilliertem Wasser angesetzt. Der Wert der Lösung wurde massanalytisch jodometrisch bestimmt.

Die Berechnung der Standardabweichung wurde für 10 parallele Experimente mit der Ozonlösung in einer Konzentration von 0.52 mg O_3/l bei Einhaltung des Verfahrens A durchgeführt. Die Standardabweichung beträgt $\pm 3.1\%$ (0.016 mg O_3/l).

In der Tabelle II sind die Ergebnisse für drei parallele Ozonbestimmungen bei Einhaltung des Verfahrens B im Vergleich mit der jodometrischen Bestimmung angeführt. Von der jodometrisch festgestellten Vorratslösung in einer Konzentration von 5.2 mg O_3/l wurden dazu je 10 ml pipettiert und mit redestilliertem Wasser bis zu 1000 ml nachgefüllt. Die Extinktion wurde gegen destilliertes Wasser bestimmt.

TABELLE II

ÜBERPRÜFUNG VON VERFAHREN B

Nr.	*Jodometrische Ozonbestimmung mg O_3/l*	*Verfahren B*	
		Extinktion ($l = 2.0$ cm)	*mg O_3/l*
1	0.520	0.761	0.515
2		0.756	0.512
3		0.735	0.497

DISKUSSION

Die Verwendung des *o*-Tolidins bei der kolorimetrischen Bestimmung ist bekannt. Es werden zwei Modifikationen angewendet, von denen die erste eine direkte

Ozonreaktion mit *o*-Tolidin[2,4] vorstellt, während die zweite auf der Ozonreaktion mit Mangan(II) bei Entstehung des weiter mit dem *o*-Tolidin[3,4] reagierenden Mangandioxyds begründet ist. Die in dieser Arbeit vorgeschlagene Methode verwendet in der ersten Phase die Ozonreaktion mit Mn(II)-Diphosphatkomplex und in der zweiten Phase die Reaktion vom Mn(III)-Diphosphatkomplex mit *o*-Tolidin.

Diese Methode hat ungefähr die gleiche Empfindlichkeit wie die zwei vorhergehenden Methoden, sie hat jedoch einige Vorteile. Das Ozon lässt sich in der Gegenwart von Chlor und Chlordioxyd bestimmen. Nach der Ozonreaktion mit Mn(II)-Diphosphatkomplex werden beide genannten Gase mittels Belüftung aus der Probe beseitigt, was bei den beiden anderen angeführten Methoden nicht angewendet werden kann. Bei der ersten Methode reagieren beide Gase gleichzeitig mit dem Ozon, bei der zweiten Methode kommt es mit Rücksicht auf die niedrige Azidität des Reaktionsmilieus (etwa 0.01 M H_2SO_4) zur Reaktion des Chlors mit Mangan(II)[5].

Der weitere Vorteil ist die höhere Farbstabilität des Reaktionsproduktes vom Mn(III)-Diphosphatkomplex mit *o*-Tolidin, als Folge der durch Ozon oder Mangan von höherer Valenz hervorgerufene Färbung des *o*-Tolidins. Die unterschiedliche Stabilität wird dadurch erklärt, dass das normale Redoxpotential des Systems $[Mn(H_2P_2O_7)_3]^{3-} \rightleftharpoons [Mn(H_2P_2O_7)_3]^{4-}$ ($E_0 = 1.15$ V)[6] niedriger ist, als das des Ozons ($E_0 = 2.07$ V). Im zweiten Falle (Mn-*o*-Tolidin-Methode) wirkt der heterogene Charakter der Reaktion des Mangandioxydhydrats mit *o*-Tolidin auf die Stabilität des Reaktionsproduktes ein. Bei reinen Lösungen ist es möglich, das Ozon sofort nach der Probeentnahme durch seine Überführung auf den sehr beständigen Mn(III)-Diphosphatkomplex zu fixieren. Sein Wert ändert sich bei der Einhaltung normaler Bedingungen nicht einmal nach einigen Tagen. Die Beendigung der Bestimmung, d.h. die Zugabe des *o*-Tolidins und die photometrische Messung muss daher nicht sofort nach der Probeentnahme durchgeführt werden.

Die Einführung des *o*-Tolidins erhöhte zwar stark die Empfindlichkeit der, in der vorhergehenden Arbeit[1] beschriebenen Mangan-Diphosphatkomplex-Methode, auf der anderen Seite wird jedoch die Zahl der störenden Einflüsse erweitert. Das Verfahren B nützt die Zweckmässigkeit des Mangan-Diphosphatkomplex-Systems aus, insbesondere des Umstandes, dass Chlor und Chlordioxyd die Reaktion nicht beeinflussen und dass mit Hilfe der Ozonverdrängung aus der Probe und durch dessen Überführung in die Absorptionslösung alle übrigen störenden, mit Mn(II)-Diphosphatkomplex oder *o*-Tolidin reagierenden Stoffe, wie z.B. Dichromat, Bromat und Manganverbindungen von höherer Valenz, einschliesslich der Trübung eliminiert werden.

Ein bedeutsamer Faktor in verunreinigten Wasser bleiben die mit Ozon reagierenden Stoffe. Intensive Ozonaustreibung mittels des Treibgases ist hier für die Ausschliessung dieses störenden Einflusses unerlässlich. Die gefundene geeignete Art der Katalyse der Ozonreaktion mit dem Mn(II)-Diphosphatkomplex machte es möglich, die nötige Zeit zur quantitativen Überführung des Ozons in die Absorptionslösung, in der laboratoriumsmässigen Anordnung, auf das Minimum zu beschränken.

Das Prinzip der Methode ermöglicht die Wahl der Empfindlichkeit durch ein geeignetes Verhältnis des Probevolumens und des Volumens von Absorptionslösung. Bei dem empfohlenen maximalen Probevolumen von 1000 ml und maximalen Volumen der Absorptionslösung von 100 ml dauert die Ozonüberführung 5 Min. Hier kommt es zur zehnfachen Empfindlichkeitssteigerung, was eine direkte photometrische Messung des violetten Mn(III)-Diphosphatkomplexes[1] ermöglicht. Unter diesen Bedingungen kann man das Ozon in höheren Konzentrationen als 0.1 mg O_3/l bestimmen. In diesem Falle wird die Bestimmung nicht einmal durch das vorhandene Chlor und Chlordioxyd gestört.

Bei Proben, bei denen die Zeit der Ozonüberführung, über Einhaltung der Empfindlichkeit, noch verkürzt werden soll, nimmt man eine kleinere Menge der Probe in Arbeit, und gibt zu der Absorptionslösung vor der photometrischen Messung *o*-Tolidin.

Bei beiden Verfahren kann man mit Vorteil die von uns vorgeschlagene einfache Art der Aufstellung einer Eichkurve mittels der Standardlösung von Kaliumdichromat[1] verwenden oder eventuell eine Standardlösung vom Mn(III)-Diphosphatkomplex modifizierte Art.

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ZUSAMMENFASSUNG

Es wurde eine photometrische Methode der Ozonbestimmung in wässrigen Lösungen für Konzentrationen von mehr als 0.01 mg O_3/l ausgearbeitet. Diese Methode beruht auf der Ozonreaktion mit dem Mn(II)-Diphosphatkomplex und der nachfolgenden Reaktion des entstandenen Mn(III)-Diphosphatkomplexes mit *o*-Tolidin. Das Verfahren, das sich sowohl der Ozonverdrängung aus der Probe als auch der nachfolgenden Ozonabsorption in der Mn(II)-Diphosphatkomplexes Lösung in Gegenwart von Chrom(III) als Katalysators bedient, ist für die Analyse von stark verunreinigten Wässern geeignet. Für 0.52 mg O_3/l beträgt die Standardabweichung 3.1%. Die Methode kann auch zur Ozonbestimmung in Gasen verwendet werden.

SUMMARY

A photometric method for the determination of ozone in waters down to a 0.01 mg O_3/l level is described. Ozone reacts with the manganese(II) diphosphate complex to form the manganese(III) diphosphate complex which is then reacted with *o*-tolidine. If ozone is swept out of the sample by a stream of gas and absorbed in manganese(II) diphosphate solution in the presence of chromium(III) as catalyst, the method can be applied to heavily polluted waters; at the 0.52 mg O_3/l level, the standard deviation was 3.1%. The method can be easily applied for the determination of ozone in gases.

RÉSUMÉ

On décrit une méthode photométrique pour le dosage de l'ozone dans des eaux, jusqu'à une concentration de 0.01 mg O_3/litre. L'ozone réagit avec le complexe manganèse(II)-diphosphate pour donner le complexe manganèse(III)-diphosphate; ce dernier réagit avec l'*o*-toluidine. En chassant l'ozone de l'échantillon par un courant de gaz et en l'absorbant dans une solution du complexe manganèse(II)-diphosphate, en présence de chrome(III) comme catalyseur, la méthode peut s'appliquer à des eaux fortement polluées. Pour une concentration de 0.52 mg O_3/l, la déviation standard est de 3.1%. Ce procédé peut être utilisé pour le dosage de l'ozone dans les gaz.

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ATOMIC ABSORPTION SPECTROPHOTOMETRY OF ANTIMONY

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Few papers have described the atomic absorption of antimony. MOSTYN AND CUNNINGHAM[1] studied the determination of antimony in metallurgical materials and reported few interferences from acids and the major metals present. They also mentioned preliminary work involving extraction of the pyrollidine dithiocarbamate complex, but details were not given. SLAVIN AND SATTUR[2] demonstrated that spectral interferences occurred from absorption of the 2176 Å antimony line by lead.

The use of solvent extraction in conjunction with atomic absorption appears to be effective for elimination of interferences, and results in the greater sensitivity. The present paper describes some aspects of the atomic absorption of antimony in the presence of immiscible organic solvents.

EXPERIMENTAL

Apparatus

A Hitachi 207 atomic absorption spectrophotometer was fitted with a double-pass system, a 10-cm (or 5-cm) premix burner, HTV R136 photomultiplier tube, and Hitachi QPD54 recorder. A modulated antimony hollow-cathode lamp was used as light source. An air–acetylene flame was generally used but nitrous oxide–acetylene flames were also used for comparison.

Extractions were done with an electric shaking device.

Reagents

Standard antimony solution. Dissolve 0.274 g of potassium antimonyl tartrate hemihydrate in 100 ml of water. Dilute the stock solution just before use for standard solutions.

Methyl isobutyl ketone. Purify by distillation.

All reagents used were of analytical-reagent grade.

Extraction procedure

Transfer the sample solution to a separatory funnel and add enough hydrochloric acid to make the acid concentration 6 *M* when diluted to 20 ml. Add 0.5 ml of sodium nitrite solution (5%) and dilute to 20 ml. Shake the solution for 1 min to oxidize antimony(III) to $SbCl_6^-$. Extract for 2 min with 5 ml of methyl isobutyl ketone. Measure the atomic absorption of the antimony by spraying the organic phase into the flame.

RESULTS AND DISCUSSION

Analytical lines

Three lines, 2068.3, 2175.9 and 2311.5 Å, were absorbed by antimony; the highest absorption was measured at 2175.9 Å and this line was adequate for traces of antimony. The 2068.3 Å line showed higher flame absorption. The ratio of absorption signals was 0.6:1:0.5 for the 2068.3, 2175.9 and 2311.5 Å lines.

Flame conditions

Atomic absorption of antimony was compared in three flames, air–propane, air–acetylene and nitrous oxide–acetylene. The 2175.9 Å line was strongly absorbed by the gases of air–propane flame and signals in this flame were much noisier. The ratio of the absorption signals obtained in air–acetylene and nitrous oxide–acetylene flames was 1.0:0.7. Absorption was measured under the conditions which gave maximum absorption. Accordingly, air–acetylene flames were preferred to nitrous oxide–acetylene flames.

The absorption of antimony was dependent on flame conditions and the height of the absorption light path in the flame. Figure 1 shows the variation in absorption measured in various flame conditions and in various areas of the flame. The results indicated that a fuel-rich flame provided higher absorption when organic solutions were sprayed. Measurements could not be made in highly fuel-rich conditions because of fluctuations of the flame.

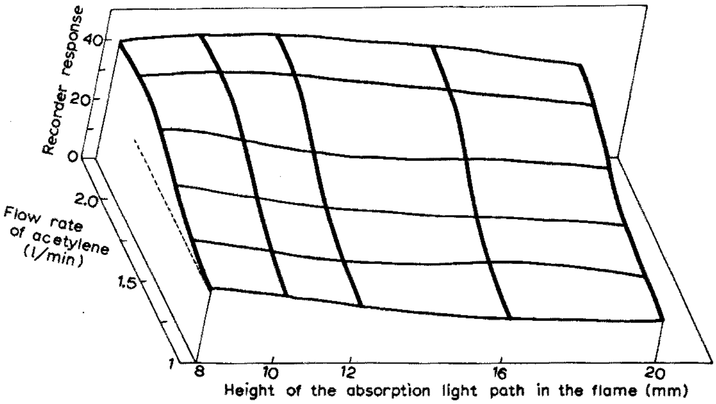

Fig. 1. Antimony absorption as a function of the flow rate of acetylene (flow rate of air, 9.0 l/min) and as a function of the height of the absorption light path in the flame. Antimony extracted with 5 ml of methyl isobutyl ketone from 20 ml of 6 *M* hydrochloric acid solution.

Extraction of antimony

Antimony can be extracted into organic solvents as a chelate or ion-association complex. Three extraction systems were tested for atomic absorption spectrophotometry. The chloride complex of antimony(V) could be effectively extracted from hydrochloric acid solutions. Increasing the hydrochloric acid concentration led to higher extractability of antimony. Figure 2 shows the extractability of antimony(V) as a function of the hydrochloric acid concentration. Higher hydrochloric acid concentrations resulted in increased extraction of acid into the organic phase, which caused some absorption of the antimony line when the organic phase was sprayed, while higher solubility of methyl isobutyl ketone in the aqueous phase was observed. Because the apparent higher extraction of antimony from strongly acid solutions might be due to a reduction in the volume of solvent, 6 *M* hydrochloric acid solution was chosen as a suitable compromise.

Oxidizing agents were compared for the conversion of antimony(III) to the pentavalent state. Sodium nitrite[3,4] was preferred because of its convenience in use for atomic absorption. However, some effect of nitrite was observed in measuring the absorption of antimony. Figure 3 shows the effect of nitrite which was added to the aqueous phase to oxidize antimony. The absorption of antimony was lowered with increase in the amount of nitrite added to the aqueous phase. The organic phase became brownish yellow and the infrared spectrum showed the presence of nitrogen dioxide. To confirm the cause of the reduction in the absorption of antimony, antimony(V) and nitrite were separately extracted from hydrochloric acid solutions followed by mixing both organic phases just before spraying. The reduction in the absorption was also observed in this instance. However, the absorption of antimony was increased when the extractions were made from solutions which were treated with hydroxylamine after the oxidation with nitrite; the extract had no color. The reduction in the absorption of antimony appeared to be due to the effect of nitrogen compounds against antimony in the flame. Therefore, a fixed amount of nitrite was preferred for the oxidation of antimony. Other oxidizing agents, dichromate and bromine, gave slightly lower results compared with nitrite. No improved extractability was observed when tartrate was added.

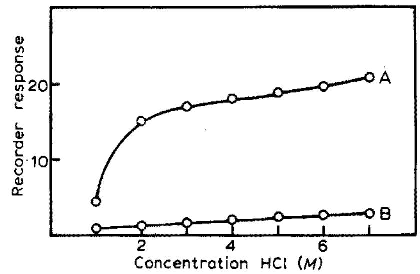

Fig. 2. Extractability of chloroantimonate by methyl isobutyl ketone as a function of the hydrochloric acid concentration in the aqueous phase. Aq. phase, 20 ml; methyl isobutyl ketone phase, 5 ml: (A) 10 μg Sb; (B) no antimony.

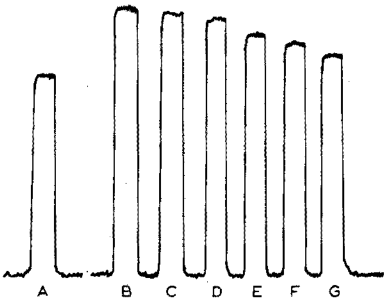

Fig. 3. Effect of nitrite added in the aqueous phase. Aq. phase: 20 μg Sb(III), 20 ml 6 *M* HCl, 5 ml methyl isobutyl ketone. Volume of nitrite solution (5%) used: (A) none, (B) 0.2 ml, (C) 0.5 ml, (D) 1.0 ml, (E) 2.0 ml, (F) 3.0 ml, (G) 4.0 ml. Antimony absorption measured at 2175.9 Å.

The extractability of antimony(III) was about 72% of that of antimony(V). The extraction method showed approximately a five-fold absorption enhancement over that obtained in spraying the aqueous solution.

The antimony(III) diethyldithiocarbamate (or pyrollidine dithiocarbamate) chelate was extracted into methyl isobutyl ketone at a pH value of 3.7. Some absorption also occurred in spraying an organic extract from solutions containing no antimony; this absorption may be derived from dithiocarbamic acid extracted into organic phase. The formation of dithiocarbamate chelates with many other metals limited the application to extraction of traces of antimony from a matrix. Oxine was also tested for chelate formation but was found to be ineffective.

Interferences

Arsenic(III and V), germanium(IV), gold(III), iron(III) and tin(II and IV) were extracted completely or partially into methyl isobutyl ketone with antimony(V) from hydrochloric acid solution. No interferences were encountered from these metals (100 µg) which were extracted into organic phase. Antimony was quantitatively extracted from solutions containing matrix metals, copper (100 mg), aluminum (50 mg) or tin (50 mg).

APPLICATIONS

Determination of antimony in metallurgical products

Small amounts of antimony in metallurgical products can be conveniently determined by atomic absorption combined with extraction.

Procedure for copper and its alloys or for aluminum alloys. Dissolve 1 g of sample in aqua regia and evaporate to a small volume to remove nitric acid. Cool and add enough hydrochloric acid to make the acid concentration 6 *M* when diluted to 100 ml. Transfer to a 100-ml volumetric flask, and dilute to volume. Transfer an aliquot (2–45 µg Sb) to a separatory funnel and proceed as in the extraction procedure. Prepare a calibration curve by extracting antimony from standard solutions.

TABLE I

DETERMINATION OF ANTIMONY IN METALLURGICAL PRODUCTS

Sample	*Sb added (%)*	*Sb found (%)*	
		Atomic absorption	*Another method*
Crude copper A[a]	—	0.064, 0.064	0.064[g]
Crude copper A[a]	0.005	0.069	
Crude copper B[b]	—	0.078, 0.076	0.078[g]
Crude copper B[b]	0.005	0.084	
Copper alloy (BCS 183/1)[c]	—	0.24, 0.24	0.24[h]
Copper alloy (BCS 183/1)[c]	0.10	0.33	
Copper alloy (NBS 124C)[d]	—	0.17, 0.18	0.20[h]
Copper alloy (NBS 124C)[d]	0.04	0.21	
Tin metal[e]	—	0.003_0, 0.002_6	0.0024[g]
Tin metal[e]	0.004	0.007	
Aluminum alloy (BCS 216/1)[f]	—	0.047, 0.048	0.05[h]
Aluminum alloy (BCS 216/1)[f]	0.02	0.069	

[a] 0.005% Fe, 0.047% As, 0.007% Au.
[b] 0.012% Fe, 0.044% As, 0.01% Au.
[c] 5.01% Sn, 0.14% As.
[d] 5.13% Sn, 0.107% Fe.
[e] 0.002% Fe, 0.001% As.
[f] 0.40% Fe, 0.055% Sn.
[g] Polarographic.
[h] Certificate value.

Tin. Dissolve 1 g of sample in 10 ml of hydrochloric acid (6 *M*). Cool and dilute to 100 ml with 6 *M* hydrochloric acid. Proceed as for copper.

Some results for metallurgical samples are presented in Table I. Addition of hydroxylamine was not necessary, provided that the fixed volume of nitrite was used for both standard and sample solutions. The accuracy of the procedure can be judged from these results. One sample (0.13% Sb) was analyzed eight times to evaluate the reproducibility of the method; the coefficient of variation was 1.2%.

Determination of antimony in synthetic fibers

Some synthetic fibers contain antimony derived from the catalyst for polymerisation. Atomic absorption spectrophotometry could conveniently be applied for this determination of antimony. Synthetic fibers also contain titanium dioxide.

Procedure. Place 0.5 g of sample in a platinum crucible and add 0.5 g of sodium carbonate as solution. Dry the contents of the crucible and then ash the sample. After ashing, heat the residue until the sodium carbonate melts and maintain at dull redness for few minutes. Cool and treat the melt with hydrochloric acid (6 *M*). Transfer the solution to a separatory funnel, and make the acid concentration 6 *M* and the total volume of the solution 20 ml. Proceed with the extraction. Prepare a calibration curve by extracting antimony from standard solutions.

Typical results are given in Table II for some synthetic fibers; a recovery test of antimony is also presented.

TABLE II

DETERMINATION OF ANTIMONY IN SYNTHETIC FIBERS

Sample[a]	*Sb added (%)*	*Sb found (%)*
T-255	—	0.013, 0.013
T-255	0.006	0.019
T-300	—	0.009, 0.008
T-300	0.010	0.018
T-B	—	0.001, 0.001
T-B	0.004	0.005

[a] Polyethylene terephthalate.

SUMMARY

The atomic absorption of antimony in combination with extraction of the chloride complex provides a suitable determination of antimony in various materials. The effect of variables on antimony absorption and the extraction of antimony were studied. Procedures for small amounts of antimony in metallurgical products and synthetic fibers are given.

RÉSUMÉ

L'absorption atomique de l'antimoine combinée avec une extraction du chlorure complexe permet un dosage de cet élément dans divers produits. On a examiné l'influence de divers facteurs sur l'absorption et l'extraction de l'antimoine. On décrit des procédés pour le dosage de faibles quantités d'antimoine dans des produits métallurgiques et dans des fibres synthétiques.

ZUSAMMENFASSUNG

Die Bestimmung des Antimons mit der Flammenabsorptionsanalyse in Kombination mit einer Extraktion des Chloridkomplexes ist für verschiedene Materialien geeignet. Die Einflüsse der Variablen auf die Antimonabsorption und die Extraktion des Antimons wurden untersucht. Verfahren für kleine Gehalte Antimon in metallurgischen Produkten und synthetischen Fibern werden angegeben.

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SPECTROPHOTOMETRIC DETERMINATION OF ANIONS BY SOLVENT EXTRACTION WITH CUPROIN- OR NEOCUPROIN-COPPER(I) CHELATE CATIONS

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Cuproin and neocuproin are specific reagents which have been studied by HOSTE *et al.*[1] and SMITH AND MCCURDY[2] for the colorimetric determination of copper, and are both widely used in practical analyses. However, they are not soluble in water and therefore a solvent extraction technique with amyl or hexyl alcohol solution of the reagents should be used for colorimetry of copper. In these extractions, it has not been clear which anion is transferred with the reagent–copper cations into alcohol. The authors were interested in this point and studied a series of extraction systems, where combinations of various anions in the aqueous phase and different organic solvents were examined .In the course of this series, it was found that when a small amount of certain anions such as perchlorate, nitrate[3], phthalate[4] or tetraphenylborate[5] were present in the aqueous phase, copper(I) ions could be extracted into a specific organic solvent, which contained cuproin or neocuproin, as cuproin– or neocuproin–copper(I)–anion ion pairs. The color intensity of the organic phase was proportional to the amounts of these anions initially present in the aqueous phase.

Tetraphenylborate has been used as a precipitation reagent for potassium[6]. By combining the precipitation and extraction methods which were proposed in a previous paper[5], potassium could be determined with a very high degree of sensitivity.

The main discussion of this paper deals with the determination of perchlorate with cuproin–chloroform; the results of the determinations of the anions or potassium mentioned above are then summarized. The proposed method for the determination of perchlorate has a very good reproducibility and a high sensitivity, and there are few interferences except from anions such as cyanide, thiocyanate, iodide and bromide. However, these ions could be masked by addition of mercury(II) sulfate solution.

In 1959, NABAR AND RAMACHANDRAN[7] reviewed the literature on the determination of perchlorate ion. The methods fall into one of three main categories: reduction to chloride by wet reactions with subsequent determination of the chloride so formed; reduction to chloride by dry ignition, again followed by the determination of the chloride produced; and the formation of insoluble compounds with substances such as methylene blue or the copper–pyridine complex, with colorimetric estimation of the loss of soluble reagent. In the first two, any chloride originally present gives high results. The colorimetric methods are affected by other ions such as sulfate and, further, quantitative work is difficult. In 1962, JOHANNESSON[8] reported an isotopic dilution method for perchlorate in which volatile anions were removed by evaporation. TRAUTWEIN AND GUYON[9] presented a colorimetric method with α-furildioxime, which is apparently simple but yet its accuracy is doubtful. Recently, spectrophotometric methods based on the extraction of ion pairs of perchlorate with strong colored cations such as metal chelates[10-12] or dyestuffs[13,14] have been developed.

EXPERIMENTAL

Standard solution of anions

Potassium perchlorate solution. A stock solution was prepared by dissolving 1.393 g of potassium perchlorate (dried at 110°) and diluting to 1 l with water. The resulting solution was $1.0 \cdot 10^{-2}$ *M*.

Potassium nitrate solution. A stock solution was prepared by dissolving 1.011 g of potassium nitrate (dried at 110°) and diluting with water to make the solution $1.0 \cdot 10^{-2}$ *M*.

Sodium tetraphenylborate solution. To prepare the solution, 0.342 g of sodium tetraphenylborate (Kalibor: Dotite reagent) was dissolved in a small amount of sodium hydroxide solution. This was diluted to 100 ml with water and filtered. The solution was $1.0 \cdot 10^{-2}$ *M*. It should be stored in the refrigerator to prevent decomposition.

Phthalic acid solution. A $1.0 \cdot 10^{-2}$ *M* solution was prepared by dissolving 1.661 g of phthalic acid and diluting to 1 l with water.

These stock solutions may be used to prepare the standard solutions with desired concentrations.

Reagents

Cuproin solution. Weighed amounts of cuproin (mol. wt. 256.3) were dissolved in distilled chloroform, chlorobenzene, *o*-dichlorobenzene or dichloroethane.

Neocuproin solution. Weighed amounts of neocuproin (mol. wt. 208.3) were dissolved in distilled methyl isobutyl ketone (MIBK).

Copper sulfate solution. Solutions with various concentrations were prepared by dissolving recrystallized copper(II) sulfate pentahydrate in water.

Hydroxylamine sulfate solution. Solutions with various concentrations were prepared by dissolving hydroxylamine sulfate in water.

Buffer solutions. The acetate buffer was prepared by mixing $2 \cdot 10^{-1}$ *M* sodium acetate and $2 \cdot 10^{-1}$ *M* acetic acid.

The phosphate buffer was prepared by mixing $2.5 \cdot 10^{-1}$ *M* potassium dihydrogen phosphate and $2.5 \cdot 10^{-1}$ *M* disodium hydrogen phosphate in a suitable ratio.

All the chemicals were of reagent grade and the water used was passed through a monobed ion-exchange resin.

Apparatus

The spectrophotometric measurements were made with a Hitachi Model

EPU-2A, Hitachi Model 139 and Shimazu Model QR-50 spectrophotometer, with 10-mm cuvettes. An Iwaki Model KM shaker with a time switch was used for the extraction. The pH measurements were made with a Hitachi-Horiba M-3 pH meter.

Recommended procedures for the determination of anions

Perchlorate. Pipette 2 ml of copper sulfate solution ($2 \cdot 10^{-3}$ *M*), 2 ml of hydroxylamine sulfate solution ($1 \cdot 10^{-1}$ *M*), 5 ml of acetate buffer solution and 2–10 ml of perchlorate solution ($1.0 \cdot 10^{-4}$ *M*) into a separating funnel. Adjust the pH of the solution to 3.8–6.7 and dilute with water to 25 ml. Finally add 10 ml of cuproin–chloroform or –chlorobenzene solution ($1 \cdot 10^{-3}$ *M*) and shake for 5 min. After separation of the two layers, run off the extract into a small glass tube. Add 0.5 g of anhydrous sodium sulfate and shake vigorously to remove the trace amount of water. Measure the absorbance of the transparent extract at 550 nm in a 10-mm cuvette using a reagent blank as a reference.

Nitrate. Pipette 2 ml of copper sulfate solution ($1 \cdot 10^{-2}$ *M*), 2 ml of hydroxylamine sulfate solution ($3 \cdot 10^{-1}$ *M*), 5 ml of phosphate buffer solution and 2–10 ml of nitrate solution ($2.0 \cdot 10^{-4}$ *M*) into a separating funnel and adjust the pH of the solution to 5.5–6.5. Add water to make the volume to 25 ml and shake for 1 min with 10 ml of neocuproin–MIBK solution ($2 \cdot 10^{-3}$ *M*). Treat the extract in the same manner as the perchlorate extract was treated and measure the absorbance at 456 nm.

Tetraphenylborate. Pipette 2 ml of copper sulfate solution ($5 \cdot 10^{-3}$ *M*), 2 ml of hydroxylamine sulfate solution ($1 \cdot 10^{-1}$ *M*), 5 ml of acetate buffer solution and 2–10 ml of standard tetraphenylborate solution ($1.0 \cdot 10^{-4}$ *M*) in a separating funnel. Adjust the pH of the solution to 3.8–5.0 and dilute with water to 25 ml. Add 10 ml of cuproin–chloroform or –chlorobenzene solution ($1 \cdot 10^{-3}$ *M*) and treat the mixture in the same manner as described for the determination of perchlorate.

Phthalate. (1) Determination with cuproin. Pipette 2 ml of copper sulfate solution ($5 \cdot 10^{-3}$ *M*), 2 ml of hydroxylamine solution ($1 \cdot 10^{-1}$ *M*), 5 ml of acetate buffer solution and 2–10 ml of standard phthalate solution ($1 \cdot 10^{-4}$ *M*) into a separating funnel. Adjust the pH to 4.1 and dilute with water to 25 ml. Add 10 ml of cuproin–chloroform or –chlorobenzene solution ($1 \cdot 10^{-3}$ *M*) and treat the mixture in the same way as for the determination of perchlorate.

(2) Determination with neocuproin. Pipette 1 ml of copper sulfate solution ($1 \cdot 10^{-2}$ *M*), 2 ml of hydroxylamine solution ($3 \cdot 10^{-1}$ *M*), 5 ml of phosphate buffer solution and varying amounts of standard phthalate solution ($1.0 \cdot 10^{-4}$ *M*, 2–10 ml) into separating funnel. Adjust the pH of the solution to 5.0–7.0. Dilute the mixture with water to 25 ml and shake for 2 min with 10 ml of neocuproin–MIBK solution ($2 \cdot 10^{-3}$ *M*). Treat the extract as detailed in the nitrate determination.

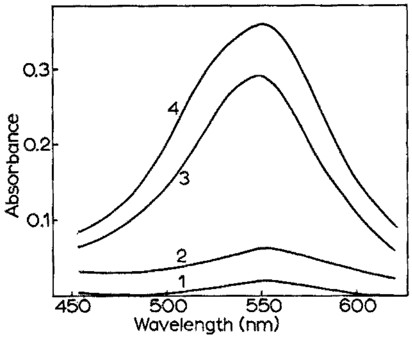
Recommended procedure for the determination of potassium

Place the sample solution containing 20–200 μg of potassium in a centrifuge tube and adjust the pH to 4.0–5.0 with an acetate buffer solution. Add 1.0 ml of tetraphenylborate solution ($1.0 \cdot 10^{-2}$ *M*). Dilute the mixture to 10.0 ml with water. After ageing for about 30 min, separate the precipitate by centrifuge. Pipette 1 ml of the supernate into a separating funnel. Determine the resulting tetraphenylborate equivalent to a specific amount of potassium by the procedure described for the determination of tetraphenylborate.

RESULTS AND DISCUSSION

Absorption spectra

Figure 1 shows the visible absorption spectra of perchlorate extracts with chloroform–cuproin or chlorobenzene–cuproin, treated as described above. It can be seen that the presence of perchlorate in aqueous solution leads to a considerable increase in the extraction. The absorbance maximum of the extracts is at 550 nm. The absorption spectra of nitrate extracts with MIBK–neocuproin are shown in Fig. 2; the absorbance maximum of the spectra is found at 456 nm. The same absorption spectra as Fig. 1 were obtained for phthalate or tetraphenylborate with cuproin, and the same as Fig. 2 for phthalate with neocuproin.



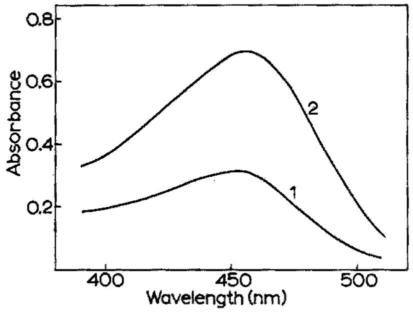
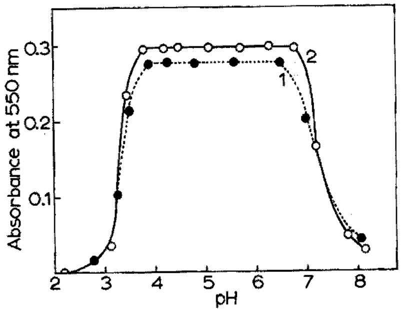


Fig. 1. Absorption spectra for perchlorate. (1) Extract with cuproin–chlorobenzene solution without perchlorate. (2) Extract with cuproin–chloroform solution without perchlorate. (3) Extract with cuproin–chlorobenzene solution with $2 \cdot 10^{-5}$ *M* perchlorate. (4) Extract with cuproin–chloroform solution with $2 \cdot 10^{-5}$ *M* perchlorate. Reference: chlorobenzene or chloroform. Temperature: 28°.

Fig. 2. Absorption spectra for nitrate. (1) Extract with neocuproin–MIBK solution without nitrate. (2) Extract with neocuproin–MIBK solution with $4 \cdot 10^{-5}$ *M* nitrate. Reference: MIBK. Temperature: 25°.



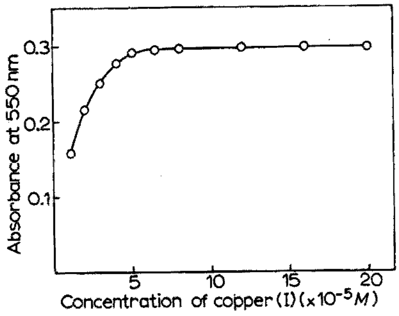


Fig. 3. Effect of pH. Perchlorate: $2 \cdot 10^{-5}$ *M*. Solvent: curve 1, chlorobenzene; curve 2, chloroform. Copper(I): $1.6 \cdot 10^{-4}$ *M*. Hydroxylamine sulfate: $8 \cdot 10^{-3}$ *M*. Reference: reagent blank. Temperature: 28°.

Fig. 4. Effect of concentration of copper(I). Perchlorate: $2 \cdot 10^{-5}$ *M*. Hydroxylamine sulfate: $8 \cdot 10^{-3}$ *M*. Solvent: chloroform. Reference: reagent blank. Temperature: 28°.

Effect of pH

The degree of extraction of perchlorate as cuproin–copper(I)–perchlorate is constant in the pH range 3.8–6.7, when chloroform or chlorobenzene is used as solvent (Fig. 3). In more acidic or more alkaline solutions, the extraction decreased presumably because of the decomposition of cuproin–copper(I) chelate.

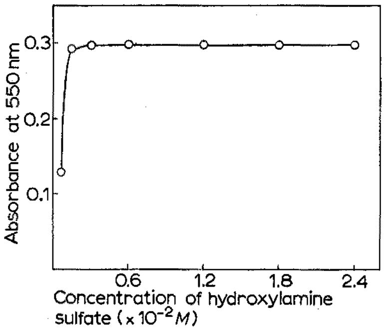
Studies of pH effect on extraction of the other anions led to the recommended procedures described above.

Effect of reagent concentration

The influence of copper(I) concentration on the extraction is illustrated in Fig. 4, where the absorbance of the extract from a $2 \cdot 10^{-5}$ *M* perchlorate (2 p.p.m.) solution is plotted against copper(I) concentrations ranging from 1 to $20 \cdot 10^{-5}$ *M*. It is apparent that the concentration of copper(I) should be maintained at more than 2.5-fold molar excess over perchlorate to obtain a constant extraction.

As a reducing agent, hydroxylamine sulfate was found to be effective. Hydroxylamine chloride was not favorable for this extraction, because the presence of chloride led to a considerable decrease in the recovery of perchlorate. Figure 5 shows the effect of hydroxylamine sulfate concentration. When the concentration of hydroxylamine sulfate is maintained at more than $1.5 \cdot 10^{-3}$ *M*, a constant extraction from $2 \cdot 10^{-5}$ *M* perchlorate solution is obtained.

Excess amounts of acetate buffer solution are without deleterious effect.



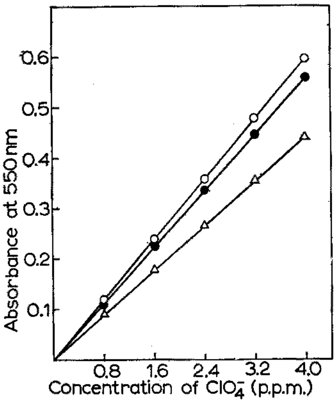


Fig. 5. Effect of concentration of hydroxylamine sulfate. Perchlorate: $2 \cdot 10^{-5}$ *M*. Copper(I): $1.6 \cdot 10^{-4}$ *M*. Solvent: chloroform. Reference: reagent blank. Temperature: 28°.

Fig. 6. Calibration curves for perchlorate. Solvent: (○) chloroform or *o*-dichlorobenzene, (●) chlorobenzene, (△) dichloroethane. Reference: reagent blank. Temperature: 28°.

Solvent

The behavior of various solvents in the extraction was studied. Solvents were found to be classified into the following three categories.

1. Those with which the presence of perchlorate leads to a considerable increase in the extraction of cuproin–copper(I) or neocuproin–copper(I) cation: *e.g.* chloroform, chlorobenzene, *o*-dichlorobenzene, dichloroethane, MIBK. (For the neocuproin–copper(I) system, chloroform and dichloroethane should be included in the third category.)

2. Those which do not extract the cuproin- or neocuproin-copper(I) cation even in the presence of perchlorate: *e.g.* carbon tetrachloride, benzene, cyclohexane.

3. Those with which the cuproin- or neocuproin-copper(I) cation is extractable even without perchlorate: *e.g.* amyl alcohol, hexyl alcohol, *n*-butyl acetate, isoamyl acetate.

MIBK was found to be most suitable for the extraction of a neocuproin-copper(I)-nitrate or -phthalate system.

Effect of shaking time

The shaking time for the extraction was varied from 0.5 to 10 min, while the other variables were kept constant. Quantitative extraction of perchlorate was found with 5 min of shaking.

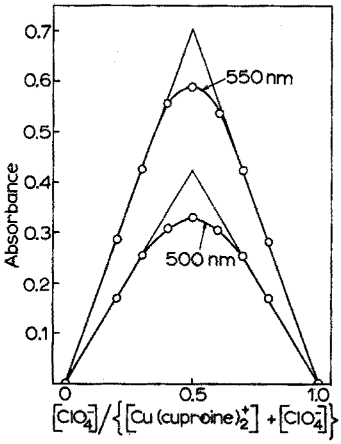
The effects of reagent concentration, solvent or shaking time were studied also for other anions. The recommended procedures described above were established on the bases of these results.

Calibration curves

For example, Fig. 6 shows the calibration curves for perchlorate ion by the recommended procedure described above, with four solvents for extraction. Higher sensitivity was obtained with chloroform or *o*-dichlorobenzene. Under the optimum conditions thus established, a linear relationship was observed between the absorbance of the extract and the concentration of perchlorate (10^{-6}–10^{-5} M) in the aqueous solution.

Composition of the extracted species

The composition of the extracted species was determined to be 1:1 by the continuous variation method for each anion. Figure 7 shows the continuous variation



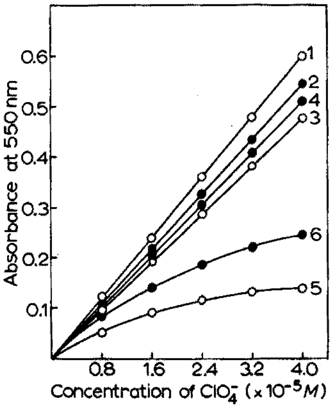


Fig. 7. Continuous variation curves. $[Cu(cuproine)_2^+] + [ClO_4^-] = 1.2 \cdot 10^{-4}$ M. Solvent: chloroform. Temperature: 25°.

Fig. 8. Effect of temperature. Temperature at the extraction: curves 1, 2, 28°; curves 3, 4, 20°; curves 5, 6, 10°; Solvent: curves 1, 3, 5, chloroform; curves 2, 4, 6, chlorobenzene. Reference: reagent blank.

curve for perchlorate. The extracted species, therefore, may be formulated as $[Cu(cup)_2]^+ A^-$, where cup represents cuproin or neocuproin and A represents perchlorate, nitrate, tetraphenylborate or phthalate.

Effect of temperature

The extraction of perchlorate was carried out at various temperatures, with chloroform or chlorobenzene. The temperature coefficients for extraction with chloroform or chlorobenzene from solutions containing 2 p.p.m. of perchlorate ($2 \cdot 10^{-5}$ *M*) were, respectively, 0.007 or 0.002 absorbance unit per degree over the range 18–28° (Fig. 8). Under 10°, a remarkable decrease in extraction was observed.

For the neocuproin–MIBK system, the extraction was not affected so strongly by temperature as the cuproin–chloroform or cuproin–chlorobenzene system. The temperature coefficient for the MIBK extract from solutions containing phthalate ($2 \cdot 10^{-5}$ *M*) was −0.002 absorbance unit per degree over the range 5–25°.

Color stability and precision

The color intensity of chlorobenzene extracts remains constant for several hours. In the case of chloroform or *o*-dichlorobenzene, a slight fading was observed within hours.

The reproducibility of the proposed method was estimated from the results of seven sample solutions, each $2 \cdot 10^{-5}$ *M* (2 p.p.m.) in perchlorate. The standard deviation for chloroform extractions was calculated to be 0.005 absorbance unit from a mean value of 0.297, *i.e.* a relative error of 1.7%, and for chlorobenzene extractions 0.002 from a mean value of 0.278, *i.e.* a relative error of 0.7%.

The standard deviation for MIBK extractions (neocuproin–phthalate) was 0.005 absorbance unit from a mean value of 0.288, *i.e.* a relative error of 1.7%.

Effect of foreign substances

Tables I and II show the effect of cations and anions on the determination of

TABLE I

EFFECT OF CATIONS ON THE DETERMINATION OF PERCHLORATE

Cation	*Added as*	*Mole ratio*	*Recovery of ClO_4^- (%)*[a]	
			Solvent $CHCl_3$	*Solvent C_6H_5Cl*
Fe^{3+}	$Fe_2(SO_4)_3$	100	99.0	101.4
Al^{3+}	$Al_2(SO_4)_3$	100	101.7	100.4
Co^{2+}	$CoSO_4$	100	99.0	101.1
Ni^{2+}	$NiSO_4$	100	100.3	98.2
Mn^{2+}	$MnSO_4$	100	101.4	99.5
Zn^{2+}	$ZnSO_4$	100	98.6	100.0
Cd^{2+}	$CdSO_4$	100	101.4	101.1
Pb^{2+}	$Pb(Ac)_2$	100	98.3	100.4
Mg^{2+}	$MgSO_4$	500	100.7	101.4
Ca^{2+}	$CaSO_4$	100	102.3	102.0
Hg^{2+}	$HgSO_4$	20	98.5	99.0
Ag^+	Ag_2SO_4	5	98.1	98.0
NH_4^+	$(NH_4)_2SO_4$	500	100.0	101.1

[a] ClO_4^- taken: $2 \cdot 10^{-5}$ *M* as $KClO_4$.

TABLE II

EFFECT OF ANIONS ON THE DETERMINATION OF PERCHLORATE

Anion	*Added as*	*Mole ratio*	*Recovery of ClO_4^- (%)*[a]	
			Solvent $CHCl_3$	*Solvent C_6H_5Cl*
PO_4^{3-}	KH_2PO_4	1000	101.2	101.8
SO_4^{2-}	Na_2SO_4	1000	100.8	100.5
SiO_3^{2-}	Na_2SiO_3	50	101.7	101.5
Cl^-	KCl	10	100.0	100.2
		100	86.6	90.3
Br^-	KBr	10	89.2	92.4
		10		102.4[b]
I^-	KI	10	13.1	15.0
		10		100.3[b]
CN^-	KCN	10	10.2	10.6
		10		102.4[b]
SCN^-	KSCN	10	5.0	4.5
		10		97.6[b]
BrO_3^-	$KBrO_3$	10	96.2	95.8
ClO_3^-	$KClO_3$	1	128.4	139.9
IO_3^-	KIO_3	1	97.6	98.1

[a] ClO_4^- taken: $2 \cdot 10^{-5}$ *M* as $KClO_4$.

[b] $HgSO_4$ added: 2 or 3 fold molar excess over the interfering anion.

TABLE III

EFFECT OF CATIONS ON THE DETERMINATION OF NITRATE

Cation	*Added as*	*Mole ratio*	*Recovery of NO_3^- (%)*[a]
Na^+	Na_2SO_4	1000	102.0
K^+	K_2SO_4	1000	103.1
Ca^{2+}	$CaSO_4$	10	98.5
Mg^{2+}	$MgSO_4$	10	97.4
Fe^{3+}	$Fe_2(SO_4)_3$	20	67.8
		20	96.0[b]
		10	68.3
		10	98.0[b]
		5	70.0
		5	98.6[b]
		1	89.5
Al^{3+}	$Al_2(SO_4)_3$	20	56.9
		20	95.8[b]
		10	65.7
		10	96.5[b]
		5	79.5
		5	99.1[b]
		1	91.3

[a] NO_3^- taken: $4 \cdot 10^{-5}$ *M* as KNO_3.

[b] Tartaric acid added: $2 \cdot 10^{-3}$ *M*.

perchlorate. Considerable amounts of sulfate, phosphate or various metallic ions do not interfere. Cyanide, thiocyanate, iodide and bromide decrease the recovery of perchlorate by forming insoluble copper(I) salts. However, if a mercury(II) sulfate solution is added, these interferences are eliminated presumably because of the formation of undissociated mercury(II) complexes. Large amounts of chloride, bromide or iodide should be precipitated by adding a slight excess of silver sulfate.

In the case of nitrate determination, the effects of diverse cations and anions, which are apt to exist in various concentrations with nitrate in fresh water, were investigated. The results are shown in Tables III and IV. In this case, because the pH value of the aqueous phase is moderately higher, iron(III) or aluminum(III) interfere with the extraction because of precipitation of hydroxide; however, they could be masked by adding tartaric acid. Large amounts of chloride should be precipitated by adding silver sulfate and nitrite should be decomposed by boiling with sulfamic acid solution.

TABLE IV

EFFECT OF ANIONS ON THE DETERMINATION OF NITRATE

Anion	*Added as*	*Mole ratio*	*Recovery of NO_3^- (%)*[a]
SO_4^{2-}	Na_2SO_4	1000	103.1
CO_3^{2-}	Na_2CO_3	100	102.0
SO_3^{2-}	Na_2SO_3	10	105.0
Cl^-	KCl	10	132.3
		10	100.9[b]
		1	102.1
NO_2^-	$NaNO_2$	20	130.4
		20	103.0[c]
		2	102.0
SCN^-	KSCN	1	118.7
CN^-	KCN	1	74.3
Br^-	KBr	1	129.0
I^-	KI	1	129.5
SiO_3^{2-}	Na_2SiO_3	1	100.0

[a] NO_3^- taken: $4 \cdot 10^{-5}$ *M* as KNO_3.
[b] Cl^- precipitated as AgCl.
[c] NO_2^- decomposed by boiling with 0.04% sulfamic acid.

TABLE V

EFFECT OF HOMOLOGUES ON THE DETERMINATION OF PHTHALATE

Homologue	*Mole ratio*	*Recovery of phthalate (%)*[a]
Isophthalic acid	10	107.0
	1	100.0
Terephthalic acid	10	110.4
	1	100.8
Benzoic acid	1	107.6

[a] Phthalic acid taken: $2 \cdot 10^{-5}$ *M*.

The effects caused by the presence of two isomers and benzoic acid on the determination of phthalic acid are shown in Table V. It may be seen that equal amounts of isomers do not interfere.

Analyses of practical samples

Tables VI and VII show analyses in which nitrate in fresh water or potassium in sea water and cigarettes were determined by the proposed method. For the determination of nitrate, the proposed method has about a five-fold higher sensitivity than the phenoldisulfonic acid method[15]. The indirect method with cuproin for potassium required only one-fiftieth of the sample volume necessitated by gravimetry with tetraphenylborate.

TABLE VI

ANALYSES FOR NITRATE IN FRESH WATER

Sample	*NO_2^- found (p.p.m.)*	*Cl^- found (p.p.m.)*	*NO_3^- found (p.p.m.)*	
			Neo. m.	*Ph. acid m.*
			(Sample taken	
			10 ml	*100 ml)*
Otagawa (Ota-river)	0.01	2.5	1.49	1.09
			1.50	1.05
			1.52	1.12
			7.70[a]	6.95[a]
Pool	0.01	7.1	2.71	1.33
			1.92[b]	1.69[b]
			1.92[b]	1.61[b]
			8.10[a,b]	7.81[a,b]

[a] NO_3^- added: 6.20 p.p.m.

[b] Cl^- precipitated as AgCl.

TABLE VII

ANALYSES FOR POTASSIUM IN SEA WATER OR CIGARETTES

Sample	*Potassium found (mg)*	
	Gravimetry	*Colorimetry*
Sea water A	3.57/10 ml	3.70/10 ml
Sea water B	3.41/10 ml	3.50/10 ml
Cigarette A (in 1 piece)	26.9/ash 0.10 g	27.6/ash 0.10 g
Cigarette B (in 1 piece)	19.7/ash 0.08 g	19.8/ash 0.08 g

The proposed method for perchlorate, though novel and relatively accurate, has not yet applied to any practical samples because suitable materials were not available.

SUMMARY

Spectrophotometric methods are proposed for the determination of anions such as perchlorate, nitrate, phthalate and tetraphenylborate. The methods are based on solvent extraction of the ion pairs formed between colored copper(I) chelate cations and the anions, into organic solvents. Perchlorate or tetraphenylborate is easily extracted with the cuproin–copper(I) chelate into chloroform or chlorobenzene, and nitrate with the neocuproin–copper(I) chelate into methyl isobutyl ketone. Either system can be used for the determination of phthalate. Potassium can be determined in the range 20–200 μg by means of the tetraphenylborate procedure. Calibration graphs were linear in the range 10^{-6}–10^{-5} M for each anion in aqueous solution. The effects of diverse ions are described; anionic interferences can be largely eliminated by addition of silver(I) or mercury(II) salts.

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NEW STUDIES ON METALLOFLUORESCENT INDICATORS*

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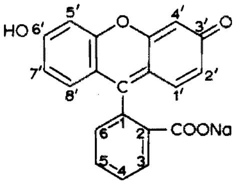
Various studies of new metallofluorescent indicators have been made in this laboratory[1-3]. In recent work, bis-N,N-glycinemethylenefluorescein, a new analog of "calcein" prepared from glycine instead of iminodiacetic acid, was synthesized. Difficulties were later encountered owing to the different products which are available commercially under the name "dichlorofluorescein".

The problems encountered were caused not only by different methods of manufacture, but also by confusion in nomenclature owing to different systems of numbering the rings. In *Beilstein*'s system for fluoresceins, primed numbers refer to substituents in the phthalic ring whereas in *Ring Index*, *Chemical Abstracts*, and in *IUPAC*'s system, primed numbers refer to the positions in the major constituent of the molecule. According to the IUPAC system, which will be used in this paper, the numbering is as follows:



The first attempts to prepare bis-N,N-glycinemethylenedichlorofluorescein were made with 4',5'-dichlorofluorescein (di-Na salt) from E. Gurr, Ltd, London. However, further batches from this firm were said to be the disodium salt of 4,5-dichlorofluorescein (Michrome No. 327). British Drug Houses, Ltd, provided the monosodium salt of 2',7'-dichlorofluorescein, with the name dichloro(R)fluorescein, whereas T. Schuchardt (Munich) provided 3,6-dichlorofluorescein, under the name *p*-dichlorofluorescein. The different types of commercial dichlorofluorescein are due to different methods of preparation. Thus, 4',5'-dichlorofluorescein (Gurr) is the product of chlorination of fluorescein, whereas 2',7'-dichlorofluorescein (B.D.H., Eastman Kodak, etc.) is produced by condensation of 4-chlororesorcinol and phthalic anhydride.

All the dichlorofluoresceins mentioned were intended as adsorption indicators for argentimetric titrations. However, other dichlorofluoresceins are also available, mainly as dyes, and these are usually crude mixtures prepared from dichlorophthalic anhydride which contains several isomers, as well as monochlorinated derivatives.

Since three kinds of dichlorofluorescein, were available, the synthesis of bis-

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* Part XLIX in the series "Analytical Applications of Chelons".

N,N-glycinemethylenedichlorofluorescein was repeated with each of the commercial products, and the properties of the indicators were compared.

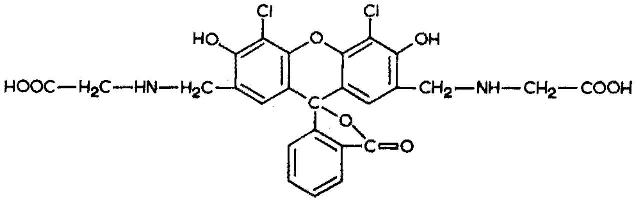
PREPARATION AND PROPERTIES OF THE INDICATORS

Initially, the glycine analogue of calcein was synthesized by Mannich condensation of glycine with fluorescein and formaldehyde. The product was an orange powder which decomposed at 350° and was soluble in sodium hydroxide solution or pyridine but insoluble in ether, chloroform or acetone.

For comparison purposes, bis-N,N-glycinemethylenedichlorofluorescein was prepared from the three available dichlorofluoresceins mentioned above; 4',5'-dichlorofluorescein was used by MARGALET *et al.*[1] for the first synthesis of this indicator. In all cases, the compounds were synthesized by Mannich condensation of glycine with the dichlorofluorescein and formaldehyde. The product obtained with *3,6-dichlorofluorescein* was an orange powder which decomposed at 350° and was soluble in sodium hydroxide solution or pyridine. When *2',7'-dichlorofluorescein* was used the product was a red powder which decomposed at 350° and was soluble in sodium hydroxide solution or pyridine (yield 60%). With *4,5-dichlorofluorescein*, the product was a red powder (m.p. 69.5°) which was soluble in pyridine, sodium hydroxide solution or ammonia (yield 70%).

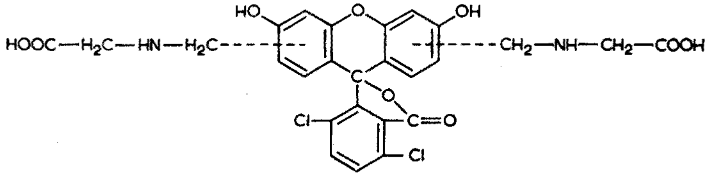
Possible structures of bis-N,N-glycinemethylenedichlorofluorescein

When 4',5'-dichlorofluorescein, obtained by chlorination of fluorescein is used in the synthesis[1], the position of the hydroxyl groups is such that the glycine groups appear in the 2' and 7' positions and the compound formed is 2',7'-bis(carboxymethylaminomethyl)-4',5'-dichlorofluorescein (I).



(I)

When 2',7'-dichlorofluorescein is used in the synthesis, the glycine groups appear in the 4' and 5' positions and the product is 4',5'-bis(carboxymethylaminomethyl)-2',7'-dichlorofluorescein. However, when 3,6-dichlorofluorescein is used, there is no tendency for the glycine groups to substitute in one position rather than another, and a mixture of two products is obtained (II), although the 2',7'-derivative is probably predominant.



(II)

Likewise, when 4,5-dichlorofluorescein is used in the synthesis, a mixture of two products is obtained.

Chromatography

In order to study the homogeneity of the synthesized indicators, their chromatographic behavior was examined by thin-layer chromatography. Kieselgel 6 (Merck) was used as adsorbent, in a Desaga DS 200/0; 3 apparatus with 20 × 20 cm glass plates, the layers being 0.5 mm thick. A mixture of ethanol–butanol–water

TABLE I

R_F VALUES OBTAINED FOR THE VARIOUS STARTING MATERIALS AND PRODUCTS

Indicator	*R_F values*	*Colour in ordinary light*	*Fluorescence under UV light*
Bis-N,N-glycinemethylenefluorescein (Fluka)	0.65	Yellow	Green
	0.60	Yellow	Green
	0.3	Yellow	Green
	0.25	Yellow	Green
Fluorescein (Fluka)	0.65	Yellow	Green
Bis-N,N-glycinemethylenefluorescein (Geigy)	0.65	Yellow	Green
	0.45	Yellow	Green
	0.25	Yellow (tailing)	Green
	0.2	Yellow (tailing)	Green
Fluorescein (Geigy)	0.65	Yellow	Green
	0.25	Yellow	Green
Bis-?-N,N-glycinemethylene-3,6-dichlorofluorescein	0.65	Yellow	Yellow
	0.60	Yellow	Yellow
	0.45	Orange	Yellow
	0.3	Pink	Yellow
3,6-Dichlorofluorescein	0.65	Yellow	Green
	0.6	Yellow	Green
Bis-4′,5′-N,N-glycinemethylene-2′,7′-dichlorofluorescein	0.65	Yellow	Green
	0.6	Yellow	Green
	0.4	Orange	Green
	0.3	Pink	Green
2′,7′-Dichlorofluorescein	0.65	Yellow	Green
Bis-?-N,N-glycinemethylene-4,5-dichlorofluorescein	0.65	Yellow	Green
	0.6	Orange	Yellow
	0.4	Orange	Yellow
	0.3	Pink	Yellow
4,5-Dichlorofluorescein	0.65	Yellow	Green
Bis-2′,7′-N,N-glycinemethylene-4′,5′-dichlorofluorescein[a]	0.45	Yellow	Green
	0.4	Yellow	Blue[b]
	0.3	Pink	Pink[b]
	0.1	Pink	Green

[a] The parent compound could not be analyzed since it was no longer available.
[b] No fluorescence was shown in these cases.

(1:1:0.5) adjusted to pH 11.7 with concentrated ammonia was used as eluant. The compounds were applied about 2 cm from the lower edge of the plate, as solutions in 1% (w/v) sodium hydroxide.

The thin-layer chromatogram of bis-N,N-glycinemethylenefluorescein showed four fluorescent spots under ultraviolet light, two of which fluoresced more intensely than the others. A comparison chromatogram of the fluorescein starting material indicated that these two spots corresponded to spots formed by the fluorescein itself. The acetylated derivative of this bis-N,N-glycinemethylenefluorescein showed similar spots but with less tailing.

With the bis-2′,7′-N,N-glycinemethylene-4′,5′-dichlorofluorescein chromatogram under ultraviolet light (prepared by MARGALET[1]), a blue spot appeared which did not appear in any of the chromatograms prepared with the other dichlorofluorescein indicators.

The R_F values obtained from the chromatograms of the fluoresceins, dichlorofluoresceins, and the synthesized indicators are shown in Table I. From these values, it can be concluded that in all the preparations, two or three new products were obtained and residual starting materials remained. It is of interest to note that some of the commercial fluoresceins did not show chromatographic homogeneity.

EXAMINATION OF THE COMPOUNDS AS INDICATORS IN EDTA TITRATIONS

In order to study the applicability of the synthesized products as metallofluorescent indicators, the compleximetric titration of copper was examined. In preliminary tests, the green fluorescence of the indicator solution, adjusted in the pH range 3.7–10, was found to be quenched by the addition of copper solution, the fluorescence being restored by an excess of EDTA solution. The fluorescence was most intense at pH 5.5–6.5.

Reagents

Standard copper solution. Solutions of copper sulphate pentahydrate (A.R.) were standardized electrogravimetrically.

Standard EDTA solutions. These were prepared from the disodium salt of ethylenediaminetetraacetic acid and were standardized against zinc solution with eriochrome black T as indicator.

Indicator solutions. 0.1% (w/v) solutions were prepared in 0.001 *F* potassium hydroxide solution.

Buffer solutions. These were prepared as described by WALPOLE, SCHWARZENBACH, and BRITTON AND WELFORD[4].

Procedure

The copper solution (0.0520 *F*) was diluted with distilled water and 5 ml of buffer pH 5.5 (1 ml of 0.2 *F* acetic acid and 9 ml of 0.2 *F* sodium acetate diluted to 250 ml) were added. After addition of a drop of indicator solution, the mixture was titrated with EDTA solution of appropriate strength, under ultraviolet light to a change from yellow to a green fluorescence in the case of the dichlorofluorescein derivative indicators, or from a dark color to a green fluorescence in the case of the fluorescein derivatives.

Results and discussion

The results obtained for the EDTA titration of copper with the different indicators are shown in Table II; for comparison results obtained with 2′,7′-N,N-glycinemethylene-4′,5′-dichlorofluorescein[1] are also given. In these titrations, the change in fluorescence appears a little before the equivalence point, but a localized fluorescence persists around each drop of standard solution until the true equivalence point is reached.

TABLE II

TITRATIONS OF COPPER WITH FLUORESCEIN DERIVATIVES AS INDICATOR AT pH 5.5–6.5

Cu added (mg)	*Cu found (mg)*	*% Error*	*Cu added (mg)*	*Cu found (mg)*	*% Error*
Bis-N,N-glycinemethylene-3,6-dichlorofluorescein as indicator			*Bis-4′,5′-N,N-glycinemethylene-2′,7′-dichlorofluorescein as indicator*		
6.34	6.32	0.3[a]	6.34	6.32	0.3[a]
9.52	9.42	0.6[a]	9.52	9.49	0.3[a]
11.10	11.05	0.4[a]	15.86	15.81	0.3[a]
14.27	14.19	0.6[a]	27.81	27.78	0.1[c]
97.59	97.85	0.2[b]	69.52	69.37	0.2[c]
130.12	130.89	0.5[b]	128.09	128.35	0.2[b]
	Average error = 0.4%			Average error = 0.2%	
Bis-N,N-glycinemethylene-4,5-dichlorofluorescein as indicator			*Bis-N,N-glycinemethylenefluorescein as indicator*		
7.93	7.97	0.4[a]	7.93	7.97	0.5[a]
9.52	9.46	0.5[a]	9.52	9.46	0.6[a]
11.10	11.05	0.6[a]	22.21	22.16	0.2[a]
12.69	12.63	0.4[a]	65.06	64.81	0.4[b]
97.59	97.21	0.3[b]	97.59	97.21	0.3[b]
113.85	113.73	0.1[b]	130.12	129.98	0.1[b]
	Average error = 0.4%			Average error = 0.4%	
Bis-2′,7′-N,N-glycinemethylene-4′,5′-dichlorofluorescein as indicator					
16.13	16.10	0.1[d]			
32.26	32.30	0.1[d]			
40.32	40.35	0.1[d]			
56.45	56.49	0.02[d]			
72.58	72.60	0.04[d]			
129.0	129.1	0.07[e]			
	Average error = 0.1%				

[a] 0.0098 *F* EDTA.
[b] 0.1000 *F* EDTA.
[c] 0.0437 *F* EDTA.
[d] 0.0264 *F* EDTA.
[e] 0.1292 *F* EDTA.

The best results were obtained with the bis-2′,7′-N,N-glycinemethylene-4′,5′-dichlorofluorescein. However, since 4′,5′-dichlorofluorescein does not seem to be commercially available now, bis-4′,5′-N,N-glycinemethylene-2′,7′-dichlorofluorescein is the best remaining indicator of those described here. The procedure can be applied successfully to a wide range of copper concentrations with a mean error of 0.2%.

We are grateful to Dr. A. J. BARNARD, JR., J. T. Baker Chemical Co., Phillipsburgh, N.J., for his advice with the nomenclature problem.

SUMMARY

Four new metallofluorescent indicators, analogous to calcein but prepared from glycine instead of iminodiacetic acid, have been synthesized and studied by thin-layer chromatography. In addition to fluorescein itself, three isomers of dichlorofluorescein were used in the syntheses. The product obtained with 2′,7′-dichlorofluorescein, bis-4′,5′-N,N-glycinemethylene-2′,7′-dichlorofluorescein, is recommended as a fluorescent indicator for the titration of copper(II) with EDTA solutions.

RÉSUMÉ

Quatre nouveaux indicateurs métallofluorescents, analogues à la calcéine, mais préparés à partir de glycine et non d'acide iminodiacétique ont été synthétisés et examinés par chomatographie sur couche mince. En plus de la fluorescéine elle-même, trois isomères de la dichlorofluorescéine ont été utilisés pour ces synthèses. Le produit obtenu avec la dichloro-2′,7′-fluorescéine, la bis-4′,5′-N,N-glycine-méthylène-dichloro-2′,7′-fluorescéine, est recommandé comme indicateur fluorescent pour le titrage du cuivre(II) avec l'EDTA.

ZUSAMMENFASSUNG

Vier neue Metallfluoreszenz-Indikatoren, analog dem Calcein aber aus Glycine anstelle von Iminodiessigsäure hergestellt, wurden synthetisiert und mit der Dünnschichtchromatographie untersucht. Zusätzlich zum Fluorescein wurden 3 Isomere des Dichlorofluoresceins bei der Synthese verwendet. Das mit 2′,7′-Dichlorofluorescein erhaltene Produkt Bis-4′,5′-N,N-glycinemethylene-2′,7′-dichlorofluorescein empfiehlt sich als Fluoreszenzindikator für die Titration von Kupfer(II) mit AeDTE-Lösungen.

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SHORT COMMUNICATIONS

Kriterien für die Eignung einer chemischen Verbindung als Indikatorelektrodenmaterial bei potentiometrischen Verfahren auf der Grundlage von einfachen Redoxsystemen

Früher berichteten wir über die Eignung von Carbiden, Boriden und Nitriden[1], Wolframbronzen[2] und Sulfiden[3] als unangreifbare Indikatorelektroden in Redoxsystemen*. In der vorliegenden Arbeit fassen wir die gewonnenen Ergebnisse unter Berücksichtigung weiterer Elektrodenmaterialien zusammen und leiten daraus einige Zusammenhänge zwischen der Eignung als Redoxindikatorelektrodenmaterial und allgemeinen Stoffeigenschaften ab.

In den Tabellen I und II führen wir die untersuchten Materialien geordnet nach ihrer Eignung als Redoxindikatorelektroden an. In den Tabellen geben wir weiterhin die Kristallstruktur, Sprungtemperatur der Supraleitfähigkeit und in einigen Fällen auch die Valenzelektronenkonzentration der jeweiligen Verbindung und ihre Eignung in verschiedenen Redoxsystemen an. Das Verhalten der Elektrode kennzeichnen wir mit den Symbolen + +, +, – entsprechend guter, bedingt geeigneter und ungeeigneter Indikatorelektrode unter Berücksichtigung der Nernst'schen Potentialfunktion in der untersuchten Lösung und des Charakters der Überspannungskurven. Die Messungen, die sowohl mit den in diesen beiden Tabellen angegebenen als auch mit weiteren Verbindungen ausgeführt wurden, zeigten die Einflüsse der folgenden Parametern auf das Verhalten des Redoxindikatorelektrodenmaterials.

Chemische Beständigkeit

Es ist eine allgemein bekannte Bedingung für ein Redoxindikatorelektrodenmaterial, dass es in dem untersuchten System chemisch stabil sein muss und nicht mit der Lösung reagieren darf. Einige chemische Verbindungen wie zum Beispiel Zementit und verschiedene Hexaboride der Erdalkalimetalle und Lanthaniden eignen sich nur im Bereich ihrer chemischen Beständigkeit entsprechend dem pH-Wert und der Redoxkraft des Systems als Indikatorelektrodenmaterial.

Kristallstruktur

Das Verhalten einiger sehr korrosionsbeständiger Verbindungen wie Borcarbid, Siliciumcarbid, Übergangsmetallphosphide und -silicide ist auffallend, da sie sich nicht als Redoxindikatorelektrodenmaterial eignen.

Betrachten wir die Tabellen I und II, so stellen wir fest, dass die gut geeigneten Indikatorelektroden allgemein einfache kubische Strukturen, besonders häufig die Steinsalzstruktur besitzen. Auch von dieser Struktur ableitbare Typen wie Pyrit und das Gitter der Erdalkalihexaboride ergeben gute Indikatorelektrodenmaterialien. Besonders interessant ist das Paar Pyrit (FeS_2) mit einer Struktur hoher Symmetrie und Markasit (FeS_2) mit einer Struktur niederer Symmetrie, von denen sich nur Pyrit als Redoxindikatorelektrodenmaterial eignet.

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* Siehe die Literaturangaben und die Versuchsmethoden in den erwähnten Arbeiten[1–3].

TABELLE I

GUT GEEIGNETE REDOXINDIKATORELEKTRODENMATERIALIEN

Nr.	*Phase*	*Kristall-struktur*	*Sprung-temperatur (°K)*	*Valenz elektronen Konzentration*	*Kaliumhexacyanoferrat*			*J_3^-/J^-*	*Fe^{2+}/Fe^{3+}*	*Chin-hydron*
					Sauer	*Neutral*	*Alkalisch*			
1	TiC	NaCl	< 1.2	8	++	++	−	+	−	+
2	TiC + C				++	++	−	+	−	+
3	ZrC	NaCl	2–4	8	++	+	−	+	−	+
4	VC	NaCl		9	++	++	−	−	−	−
5	$WTiC_2$	NaCl			++	++	+	+	+	+
6	Cr_7C_3 + C				++	++	+	+	−	++
7	Cr_3C_2 + C				++	++	+	+	++	++
8	Cr–W–Carbide				++	++	++	+		
9	Fe_3C	Fe_3C			+	+	++	+	−	+
10	W_2C	Mo_2C	2–3.5		++	++	−	+	−	+
11	Pd_3B[a]	Fe_3C			++	++	−	++	−	+
12	VN	NaCl	7.5	10	++	++	−	+	−	+
13	CrN	NaCl			++	++	+	+	−	−
14	Pd_3Si[a]	Fe_3C			++	+	+	++	−	+
15	Cr_3Si	β-W			++	++	+	+	−	+
16	FeS_2	Pyrit			++	++	−	++	++	++
17	1/2 Ti_2BN	NaCl		8	++	++	+	+	−	+
18	Wolframbr. kubisch.				++	++	+	+	+	+
19	ReO_3	Kubisch			++	++			++	
20	BaB_6[b]	CaB_6	< 1.2							

[a] Von diesen Verbindungen wurde keine Phasenanalyse ausgeführt.

[b] Entsprechend der chemischen Beständigkeit nur in $TiCl_3$–$TiCl_4{}^4$-Lösungen geprüft.

TABELLE II

BEDINGT UND NICHT GEEIGNETE REDOXINDIKATORELEKTRODENMATERIALIEN

Nr.	*Phase*	*Kristall-struktur*	*Sprungtem-peratur (°K)*	*Kaliumhexacyanoferrat*			*J_3^-/J^-*	*Fe^{2+}/Fe^{3+}*	*Chin-hydron*
				Sauer	*Neutral*	*Alkalisch*			
1	$Cr_{23}C_6$, Cr_7C_3, Cr						+	−	+
2	Cr_7C_3	Cr_7C_3		+	−	−	+	−	−
3	Cr_3C_2	Cr_3C_2		+	−	−	−	−	−
4	Mo_2C	Mo_2C	2–3	+	−	−	−	−	+

5	MoC	NiAs	7–8	+	+	—	—	—	+
6	WC	NiAs	3–4	—	—	—	—	—	—
7	B_4C	B_4C		+	+	+	—	—	—
8	SiC			+	+	+	+	+	+
9	NbC[a]	NaCl	6–10	+	+	—	+	—	+
10	TaC[a]	NaCl	9–11	+	+	—	—	—	+
11	Be_5B, BeB_6			—	—	—	—	—	—
12	BeB_6, BeB_2, Be_2B			—	—	—	—	—	—
13	TiB_2[b]	AlB_2		+	+	—	+	+	—
14	V_3B_4, VB_2						—	—	—
15	Cr-Boride			—	—	—	+	—	+
16	Mo-Boride		5	—	—	—			
17	Mn-Boride				—	—	—	—	+
18	Si_3N_4, SiO_2			—	—	—	+	—	+
19	TiN[a]	NaCl	5	+	+	—	+	—	+
20	ZrN[a]	NaCl	8–10	+	+	+	+	—	—
21	Nb–O–N	Hexagonal	10–15	—	—	—	—		
22	TaN	Hexagonal	10	—	—	—	—		
23	Ti_5Si_3	Mn_5Si_3		+	++	—	+	—	—
24	Zr-Silicid			—	—		—	—	+
25	V-Silicid		14–17	—	—		—	—	—
26	Cr-Silicid			—	—		+	—	+
27	Mo_5Si_3, Mo_3Si			—	—		—	—	—
28	$MoSi_2$	$MoSi_2$		+	—		—	—	—
29	WSi_2	$MoSi_2$		—			—	—	—
30	Mn_3Si	Mn_3Si		—	—	—	—	—	—
31	PbS	NaCl		—	—	—	—	—	+
32	Sb_2S_3	Sb_2S_3		—	—	—	—	—	—
33	FeS	NiAs		+	+	—	—	—	—
34	FeS_2	Markasit		—	—	—	—	—	—
35	FeAsS			+	+	—	—	+	
36	Cu_5FeS_4			—	—	—	—	—	—
37	$CuFeS_2$			—	—	—	—	—	—
38	Ag_2S	Monoklin		—	—	—	—	—	—
39	TiS	NiAs		—	—	—	—	—	—
40	TiS_2	CdJ_2		—	—	—	—	—	—
41	TiS_3			—	—	—	—	—	—
42	$TiPbS_3$	Tetragonal		—	+	—	+	—	+
43	MoS_2	MoS_2		—	—	—	+	—	—
44	Wolframbrom.	Tetragonal		—	—	—	—	—	—
45	Ti-Phosphide			—	—	—	—		—
46	V-Phosphide			—	—	—	—		—
47	Mo-Phosphide			—	—	—	—	—	—
48	Ti_2BeO			—	—	—	—		—

---

[a] Valenzelektronenkonzentration 9.

[b] Valenzelektronenkonzentration 10.

Weitere gute Indikatorelektroden ergeben die mit Perowskit-Struktur kristallisierenden kubischen Wolframbronzen und Rheniumtrioxid; Wolframbronzen niederer Symmetrie eignen sich nicht zu diesen Zweck.

Valenzelektronenkonzentration pro Mol

Valenzelektronen bedeuten die Anzahl von Elektronen ausserhalb abgeschlossener Edelgasschalen, also bei Titan und Zirkon 4, bei Bor 3, bei Kohlenstoff 4 und bei Stickstoff 5[4].

Die chemisch und vielfach auch kristallographisch sehr ähnlichen Verbindungen Titancarbid, Titannitrid, Titandiborid, Zirkoncarbid, Zirkonnitrid und Ti_2BN zeigen unterschiedliche Eignung als Indikatorelektrodenmaterial. Das Verhalten der Verbindungen TiC, TiN, TiB_2 und Ti_2BN, die alle ausser TiB_2 mit Steinsalzstruktur kristallisieren, ist besonders auffällig. Titandiborid mit hexagonaler AlB_2-Struktur stellt ein wenig geeignetes Material für Indikatorelektroden dar. Der Mischkristall aus Titan, Titandiborid und Titannitrid mit der Summenformel Ti_2BN besitzt Steinsalzstruktur, und die gleiche Valenzelektronenkonzentration wie Titancarbid und eignet sich ebenfalls gut zur Herstellung von Indikatorelektroden. Titannitrid ist nicht als Elektrodenmaterial geeignet.

Supraleitfähigkeit

Betrachten wir die Sprungtemperaturen der von uns untersuchten Verbindungen, soweit sie bekannt sind, so können wir feststellen, dass Stoffe mit hoher Sprungtemperaturen wie Niob- und Tantalverbindungen, Titannitrid und Zirkonnitrid sich nicht als Redoxindikatorelektrodenmaterialien eignen. Andererseits weisen die Verbindungen Titancarbid, Zirkoncarbid und die Erdalkalihexaboride recht niedere Sprungtemperaturen auf.

Die gleiche Beobachtungen können wir bei den Elementen anstellen. Platin, Gold, Palladium und auch Graphit, die als gute Redoxindikatorelektrodenmaterialien bekannt sind, zeigen keine Supraleitfähigkeit. Bei den Metallen der Platingruppe nimmt mit steigender Sprungtemperatur von Iridium zu Ruthenium auch die Eignung als Redoxindikatorelektrodenmaterial ab[5].

Bei unseren Messungen beobachteten wir, dass die Verhaltensweise einer Indikatorelektrode ausser den angeführten Beziehungen noch vom Lösungsmittel und von der Art der Redoxpartner beeinflusst werden kann, so dass die geeigneten Elektrodenmaterialien in verschiedenen Redoxsystemen verschiedene Elektrodenkinetik aufweisen.

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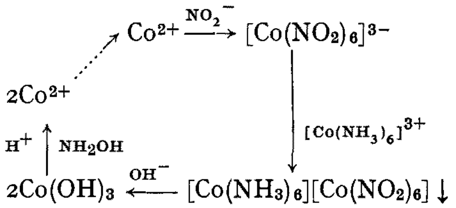
Amplification of cobalt by precipitation as hexamminocobalt(III) hexanitritocobaltate(III)

Amplification reactions have recently attracted much attention as a means of increasing the sensitivity of analytical procedures. The subject has been reviewed by BELCHER[1]. In most amplification methods for metals, the final analytical procedure does not involve the measurement of the metal. For example, bismuth can be precipitated as $Bi[Cr(SCN)_6]$; the thiocyanate in the precipitate is titrated with permanganate so that 48 equivalents of permanganate are required for each mole of bismuth precipitated[2,3]. The present paper describes the development of a direct amplification of cobalt. Cobalt has been determined gravimetrically[4] after conversion to hexanitritocobaltate(III) and precipitation with hexamminocobalt(III) chloride as the yellow, crystalline $[Co(NH_3)_6][Co(NO_2)_6]$.

In the present work, it proved possible to modify this method to give an amplification procedure by suitably dissolving the precipitate to a solution of cobalt(II), and repeating the precipitation process; each cycle gives a two-fold amplification of cobalt. The original method[4] was used for the determination of 8–40 mg of cobalt, although as little as 0.05 mg could be precipitated quantitatively; many metals, including Ni, Cu, Mn, Zn, Pb and Cd, did not interfere. The precipitate was weighed after an elaborate washing and vacuum-drying procedure.

In the present work, the original procedure[4] has been modified so that 0.1–2 mg of cobalt are precipitated quantitatively in 2 ml of solution in a small test tube. The precipitate, after centrifugation and washing, is converted to cobalt(III) hydroxide by heating with sodium hydroxide solution. The hydroxide is dissolved in an acetic acid solution of hydroxylamine to give cobalt(II). After the excess hydroxylamine has been destroyed with hydrogen peroxide, the cobalt is again converted to hexanitritocobaltate(III) by addition of sodium nitrite, and the precipitation process is repeated. The cycle is shown below:



Results and discussion

Two-fold amplification of cobalt was achieved quantitatively for 0.5–2 mg of cobalt by a single amplification cycle. Two consecutive cycles gave a quantitative, four-fold amplification of as little as 125 μg of cobalt. The results are summarized in Table I. Indeed, there is no reason why further cycles should not be carried out to give even greater amplification, provided that the precipitate does not become too bulky to handle. When the small test tubes described below are used, this limit is reached when the yellow precipitate contains 4 mg of cobalt.

As found by PIRTEA *et al.*[4], precipitation of cobalt by this procedure is quantitative. Moreover, the presence of excess of nitrite in the solution does not affect the recovery of cobalt. It is best to add the precipitant slowly, so as to form a layer above

TABLE I

AMPLIFICATION OF COBALT BY PRECIPITATION AS $[Co(NH_3)_6][Co(NO_2)_6]$

Co taken (μg)	500	2000	125	250	500
Amplification cycles	1	1	2	2	2
Co found (μg)	1010 ± 10[a]	4020 ± 50	497 ± 10	988 ± 23	2060 ± 30
No. of determinations	3	18	8	8	8

[a] Standard deviation.

the test solution. The slow mixing of the solutions produces larger particles than if stirring is employed, so that creeping is minimised. Even when the precipitate has been formed, vigorous agitation should be avoided, as this also promotes creeping.

The investigation has established that direct amplification of a metal can readily be accomplished by a process such as is described above. By the use of other complex ions as precipitants it is possible that greater amplification factors can be achieved. For example, conversion of cobalt to $[Co(NH_3)_6]^{3+}$ followed by precipitation as $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$ would give a four-fold amplification. This precipitate has a solubility[5] of only $2.25 \cdot 10^{-4}$ *M* at 20°.

The recoveries of cobalt were measured by EDTA titration of the cobalt obtained by dissolving the cobalt(III) hydroxide in acetic acid–hydroxylamine. Titration of standard cobalt solutions with xylenol orange as indicator in hexamine-buffered media gave unsatisfactory colour changes and an inaccurate end-point. Similar titrations carried out in acetate-buffered solutions[6] showed that the end-point was accurate and sharpest at pH 5.4–5.6 at room temperature. Heating, recommended by PŘIBIL[7], was not beneficial. Hydroxylamine had no deleterious effect, so that cobalt could be accurately titrated in the acetic acid–hydroxylamine solution at pH 5.4–5.6.

Experimental

Amplification cycle. To the approximately neutral cobalt solution (1 ml, containing 0.125–2 mg of cobalt) add an excess of sodium nitrite (0.2 g) and glacial acetic acid (3–4 drops). Shake occasionally for 5 min, and then agitate to remove most of the oxides of nitrogen. Slowly add a saturated hexamminocobalt(III) chloride solution (B.D.H. Ltd., Poole, England, 1 ml), and shake gently after allowing to stand for 5 min. Centrifuge after another 5 min. Wash the precipitate by gently agitating with 0.1% hexamminocobalt(III) chloride solution (2 ml), and then with water (2 ml). Add 2 *M* sodium hydroxide solution (1 ml) and heat in boiling water for 5 min, or until all the yellow material has been converted to black cobalt(III) hydroxide. Centrifuge, and wash the precipitate in cold 0.2 *M* acetic acid (2 ml). Dissolve the precipitate by adding 0.2 *M* acetic acid (1 ml) and 2% hydroxylammonium chloride solution (0.2 ml) and heating in boiling water, to give a clear, pink solution. Add a few drops of 100-vol. hydrogen peroxide and boil to destroy the excess of hydroxylamine. The final solution contains two cobalt ions for each cobalt ion present in the initial solution. The cycle can be repeated by adding sodium nitrite, etc. and repeating the above procedure.

Determination of cobalt. Titrate cobalt (0.5–8 mg) with $5 \cdot 10^{-3}$ *M* disodium EDTA solution in an acetate buffer pH 5.4–5.6 with xylenol orange as indicator (see discussion).

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A solvent extraction procedure for the spectrophotometric determination of iron(III) with bithionol

Bithionol, bis-(2-hydroxy-3,5-dichlorophenyl)sulphide, is a useful reagent for the spectrophotometric determination of iron(III)[1]. The present communication describes a solvent extraction procedure which limits some of the interferences experienced with the previous method.

Several solvents, *viz.* chloroform, carbon tetrachloride, diethyl ether, *n*-butanol, ethylacetate, cyclohexane and *n*-hexane extract the iron(III)–bithionol complex from aqueous or water–ethanol solutions of apparent pH 5.6. Chloroform seemed to be the most suitable solvent and extractions with chloroform were studied further.

Because the reagent is only sparingly soluble in chloroform and water, ethanol must be included in the aqueous phase to prevent precipitation of bithionol. A proportion of the ethanol enters the chloroform phase. The absorption spectrum of the complex in chloroform–ethanol is identical to that of the 1:2 iron(III)–bithionol complex formed in ethanol–water, and is independent of the chloroform to ethanol ratio. A single broad absorption band occurs in the visible region with maximum absorption at 484 nm and the molar absorptivity at this wavelength is 5,600. The method of continuous variations was used to confirm that the iron(III) is extracted as the 1:2 iron(III)–bithionol complex.

Distribution determinations

The effect of pH on the extraction of iron(III) and of several other metals with bithionol was examined. The sample solutions contained 0.25 mg of the metal ion in each case, and the procedure recommended below was followed. In the case of metals other than iron(III), the unextracted metal ion was determined in the aqueous layer after extraction. Copper(II) and nickel were determined colorimetrically with sodium diethyldithiocarbamate, cobalt(II) with nitroso-R-salt and chromium(III) (after oxidation with sodium peroxide) as chromate[2]. The results of the investigation are shown in Fig. 1. Iron(III) is extracted quantitatively from solutions of apparent pH 5.1–6.0. Complete extraction of copper, nickel and cobalt, on the other hand, is only possible from solutions of apparent pH 8–10. At an apparent pH of 5.6, which is suitable for the quantitative extraction of iron(III), about 50% of the copper and much smaller amounts of nickel and cobalt are extracted. Small amounts of chromium(III) are extracted at apparent pH 1–12.

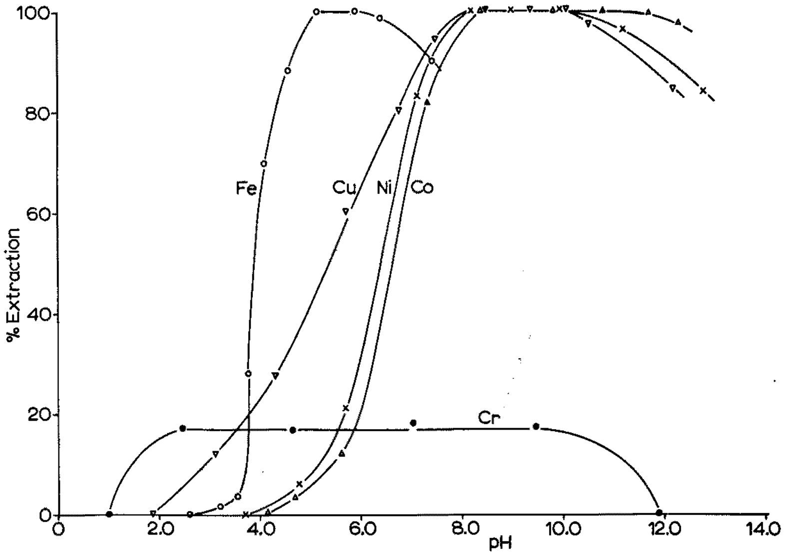

Fig. 1. Extraction of 0.25 mg of Fe(III), Cu(II), Ni(II), Co(II) and Cr(III) with 20.0 mg bithionol.

Extractive determination of iron(III)

Standard iron solution (0.1 mg of iron(III)/ml). Dissolve analytical reagent-grade iron(III) ammonium sulphate (0.864 g) in water, add concentrated hydrochloric acid (10 ml) and dilute to 1 l[3].

Procedure. Pipette an aliquot of the standard iron(III) solution (or of a weakly acid sample solution) containing up to 0.4 mg of iron(III) into a 100-ml separating funnel. Add 5 ml of 1 *M* sodium acetate–1 *M* acetic acid buffer solution, 20 ml of ethanol and 5 ml of 0.4% (w/v) bithionol solution in ethanol. Dilute to 50 ml with water and extract successively with 8-, 4- and 3-ml quantities of chloroform. Combine the chloroform extracts in a 50-ml volumetric flask, dilute to volume with ethanol and mix thoroughly. Measure the absorbance of the solution against ethanol at 484 nm in 1-cm glass cells. Deduct the absorbance of a blank solution, containing the reagent but no iron(III), also measured against ethanol.

The calibration curve obtained with the above procedure was linear, and the mean absorbance of twelve solutions containing 0.23 mg of iron(III) was 0.466 with a standard deviation of 0.002.

Interferences

No interference (*i.e.* an effect less than 1%) was observed at the 0.23-mg level of iron(III) in the presence of 80 mg of sulphate, nitrate, chloride, iodide, bromide, acetate, perchlorate and borate; 20 mg of zinc, nickel, magnesium, cobalt(II), manganese(II), cadmium, aluminium, calcium, potassium, sodium and ammonium; 2.3 mg of dichromate; 1.4 mg of fluoride ion; 0.9 mg of copper(II); 0.23 mg of chromium(III) and 0.15 mg of tartrate. Mercury(II) forms a precipitate with the reagent but 2.5 mg could be tolerated. Oxalate, phosphate and citrate at the 0.08-mg level reduced the absorbance by 3%, 5% and 10% respectively.

Discussion

With the extraction procedure described, there is a significant increase in the amounts of interfering elements that can be tolerated compared to the previous bithionol method[1]. In particular, three times the amount of copper(II), or ten times the amount of dichromate, over iron(III), can be tolerated. The increase in tolerance to Cu(II), Ni(II), Co(II) and Cr(III) is predictable from the distribution curves shown in Fig. 1.

The procedure given does not concentrate the complex, but a two-fold concentration can be effected by extracting with 7-, 2- and 1-ml aliquots of chloroform and diluting to 25 ml. The complex is soluble and stable to decomposition in both water and chloroform solutions.

Bithionol is a relatively inexpensive reagent, and its use in removing a large excess of iron might be advantageous in some applications. With 12.5 ml of a 4.0% (w/v) solution of bithionol in ethanol, 7.5 mg of iron(III) can be removed with the extraction procedure as described. Larger amounts of iron can be removed if the amounts of chloroform are increased.

Many reagents have been suggested for the extraction and spectrophotometric determination of iron. The proposed reagent, bithionol, has several limitations, but its use should be advantageous in various applications, particularly as it is readily available and inexpensive.

We would like to thank Cyclo Chemicals Ltd. for supplying us with a sample of bithionol, and Hopkin and Williams Ltd. for agreeing to make the compound available to analysts.

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Improvement in the sensitivity of the spectrophotometric determination of copper with 6,7-dimethyl-2,3-di(2-pyridyl) quinoxaline

The recent review article by BABKO[1] points out that the use of ternary complexes in analytical chemistry is a comparatively recent innovation. Only within the last five years have ternary complexes involving a chelated metal ion and a dye been used to enhance the sensitivity of spectrophotometric analyses[2–6]. This combination should prove particularly useful, as one might expect to retain most, if not all, of the selectivity of the chelating ligand while dramatically increasing the sensitivity of the analysis by the introduction of a highly colored dye molecule. This communication demonstrates this effect on the previously reported determination of copper with 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline (DMDPQ)[7].

Reagents

DMDPQ (Aldrich Chemical Company) was used without further purification. A stock solution was prepared by dissolving 1.25 g of DMDPQ in 100 ml of ethylene dichloride.

Methyl orange (J. T. Baker reagent-grade) was used without purification. A 0.001 M solution was prepared by dissolving 0.327 g of dye in distilled water and diluting to 1 l.

Procedure

Dissolve the sample containing 10–100 μg of copper in any convenient acid. If nitric or perchloric acid is used, add 3 ml of sulfuric acid after the sample has dissolved and distil off the lower boiling acid. Dilute to 40 ml with water and adjust the pH to about 3 with 10 M sodium hydroxide. Cool the solution to room temperature before proceeding. Add 20 ml of aqueous 10% hydroxylammonium chloride and 5 ml of 15% tartaric acid. Add 5 ml of the methyl orange solution by volumetric pipet, and adjust the pH to 5. The solution is well buffered, and concentrated base can be used. Transfer the resulting solution to a separatory funnel, add 2 ml of DMDPQ solution, and extract with two 15-ml portions of ethylene dichloride. Combine the organic phase in a 50-ml volumetric flask and dilute to the mark with ethanol. Measure the absorbance at 418 nm against a reagent blank.

Properties of the ternary complex

The ternary complex has a yellow-green color in ethylene dichloride, and exhibits a broad absorption peak with the maximum at 418 nm. The complex conforms to Beer's law in concentrations up to $3 \cdot 10^{-5}$ M (based on copper) with a molar absorptivity of 29,300. The optimum pH range for extraction from aqueous solution is 5–7. Below pH 5, methyl orange is extracted in appreciable quantities and the blank becomes excessive, while the copper–DMDPQ complex is unstable above pH 7. The method of continuous variation showed the composition of the ternary complex to be Cu(DMDPQ)$_2$ (methyl orange).

Interferences

The effect of foreign ions was studied by adding 100 mg of the ion to a solution containing 40 μg of copper and treating the solution as described in the procedure.

Less than 2% interference was caused by iron, cobalt, manganese(II), phosphate, molybdate, acetate, fluoride, sulfate, and chloride. The following ions were tolerated in the indicated amounts: nickel, 50 mg; vanadate, 50 mg; bromide, 50 mg; aluminum, 40 mg; lead, 35 mg; zirconium, 5 mg; iodide, 2 mg. Perchlorate interferes to such an extent that it must be completely excluded from the analysis.

TABLE I

ANALYSIS FOR COPPER IN NBS STANDARD SAMPLES

Sample	*% Cu found*	*% Cu certified*
82a (Fe)	0.075, 0.074	0.76
73b (Fe–Cr)	0.125, 0.122	0.126

Results

Two NBS samples were analyzed by the recommended procedure. Both were dissolved in hydrochloric acid. The results are summarized in Table I.

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The determination of europium(III) in borate glasses

The advent of the laser has brought renewed interest in the luminescence of rare earths in glasses. While excitation and emission of rare earths is similar in glasses and crystals, much higher concentrations of rare earths can be introduced in glasses. The purpose of this work was to study the fluorescence of europium-activated sodium borate glasses as a function of europium concentration, and to establish the value of fluorescence measurement of these glasses as a tool for their analysis.

The technique was developed for sodium borate glasses, but could be used, with possible modification, for other glasses also.

Apparatus

The spectrofluorimeter used for the measurement of excitation and fluorescence emission spectra was constructed in this laboratory and will be described in detail elsewhere. Briefly, it consists of a 500-W xenon arc (Mazda) lamp, interchangeable with a mercury medium-pressure 100-W lamp, an excitation nomochromator (Bausch & Lomb, 250-mm focal length), a sample compartment, an analysing monochromator (Bausch & Lomb, 500-mm focal length), an EMI 9558 Q/B photomultiplier connected through a 16MΩ resistor to an EIL Vibron electrometer, and a Kipp & Zonen recorder. Slow drifts in intensity were corrected by frequent measurement of a reference glass. Fast fluctuations were filtered out. The fluorescence was viewed from the front (illuminated) side of the glass at an angle of 35°. The photomultiplier was cooled to −20° for all measurements.

Reagents

Sodium tetraborate and boric acid, 99.5% purity (Baker Analyzed Reagents) and europium chloride (Research Chemical Nuclear Corporation of America, 99.9% purity) were used.

Preparation of glasses

Dry europium chloride, borax and boric acid (123 g: 62 g) were mixed in an electric vibrator in plastic vials with glass balls. Homogeneous mixtures were obtained after 10 min. These mixtures melted at temperatures lower than 1000°, but clear transparent solutions resulted only after heating at 1100° for at least 15 min. The melts were made in platinum crucibles. Drops of the hot melt were allowed to fall directly on to a clean white glazed ceramic surface. The drop was placed inside the circumference of a 1-mm thick ring and pressed with a second ceramic tile so as to obtain glasses of constant 1-mm thickness. The glasses were inserted into a glass holder with a circular opening of 12-mm diameter and their excitation and fluorescence spectra were measured at room temperature.

Excitation spectra

The excitation spectrum at 617 nm fluorescence (Fig. 1) consists of sharp lines at 320, 365, 380, 395, 465, 535 and 585 nm, and a broad band at 230–290 nm with a maximum at *ca.* 260–280 nm. The strongest line peaked at 395 nm. Table I shows the

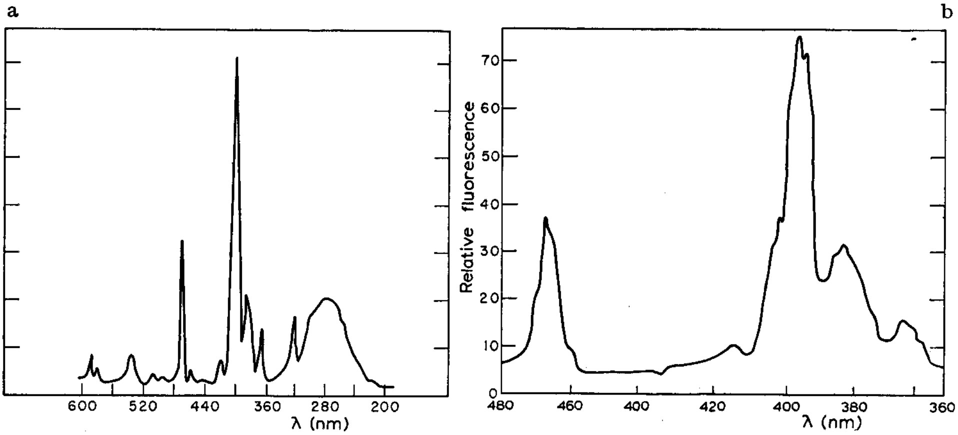


Fig. 1. (a) Excitation spectrum at 617-nm fluorescence with xenon excitation. (b) Enlarged portion between 360 and 480 nm.

TABLE I

ENERGY LEVELS OF Eu^{3+}

Levels	*Wave nos. calc. (cm^{-1})*	*Wave nos. exp. (cm^{-1})*	*Wavelength (nm)*
$^5H_6$	31248	31250	320
$^5L_{10}$	27386	27397	365
$^5L_8$	26220	26316	380
$^5L_7$	25340	25316	395
$^5D_2$	21508	21505	465
$^5D_1$	18945	18692	535
$^5D_0$	17374	17094	585

experimental lines compared to the centres of gravity of the Eu^{3+} energy levels[1]. The broad band can be attributed to the charge transfer from surrounding oxygen to europium as proposed by JØRGENSEN[2] in solutions, and $NaCdO_2$: Eu crystals as proposed by BLASSE AND BRIL[3].

Emission spectra

Figures 2 and 3 show emission spectra measured at 395-nm and 255-nm excitation, respectively; excitation at 365 nm gave a similar but less intense spectrum. The most intense line observed appeared at 617 nm; the 545-nm line obtained with 255-nm excitation is due to impurity in the borax.

Comparing these results with those of KURKJIAN *et al.*[4], who measured the luminescence of europium in silicate glasses, we assign the 580-nm band to $^5D_0 \rightarrow {}^7F_0$ transition, the 595 and 600 nm bands to $^5D_0 \rightarrow {}^7F_1$ transition and the 617-nm band to $^5D_0 \rightarrow {}^7F_2$ transition. The 655-nm band could probably be assigned to $^5D_0 \rightarrow {}^7F_3$ transition, which corresponds to 15986 cm^{-1} as presented by SINHA[1].

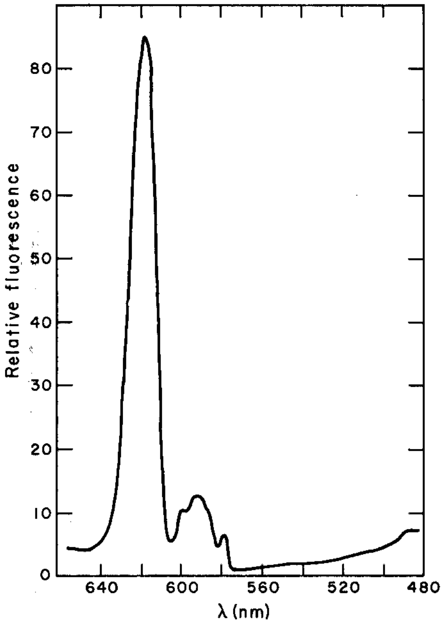
Fluorescence measurements as a function of europium concentration were performed at the following excitations: 395 nm (xenon source), 255 nm (mercury source) and 365 nm (mercury source) with emission measurements at all bands. The best linear dependence was observed for the most intense 617-nm line. The results obtained with excitation at 255 nm and 395 nm are presented in Table II; the emission at 365 nm was lower by a factor of three than that at 255 nm. A linear concentration dependence was observed in the concentration range 0.001–2%. The scattering of the experimental

TABLE II

CONCENTRATION AND RELATIVE FLUORESCENCE MEASURED AT 617 nm (1250 V)[a]

Excitation at 255 nm		*Excitation at 395 nm*			
Concn.	*RF*	*Concn.*	*RF*	*Concn.*	*RF*
0.01	310,250	0.001	9	0.75	2220
0.2	1140	0.005	50	1.0	2640
0.4	1920	0.01	24	1.3	4125
0.8	2470	0.05	84	1.7	5625
1.0	2670,3400	0.1	261	2.0	6800
1.3	3600	0.4	1150		

[a] Monochromator slits. For measurements at 255-nm excitation, the entrance/exit slits were 0.5 and 1.0 mm for excitation and 1.0 and 1.0 mm for emission. For measurements at 395-nm excitation, the respective values were 0.5 and 0.9 mm, and 1.0 and 0.5 mm.



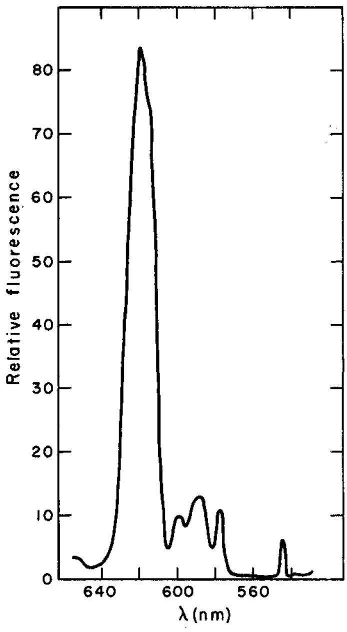


Fig. 2. Fluorescence spectrum at 395-nm excitation (xenon source).

Fig. 3. Fluorescence spectrum at 255-nm excitation (mercury source).

points with xenon excitation was much lower than that found with mercury excitation, because of excitation of impurities present in borax at 255 nm.

It is therefore concluded that the best procedure for the determination of europium(III) in borate glasses is the measurement of the emission at 617 nm with excitation at 395 nm.

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Die Zusammensetzung des Diphosphatkomplexes des dreiwertigen Mangans

Das Redoxsystem des Diphosphatkomplexes des zwei- und dreiwertigen Mangans, das in saurem Milieu angewandt wird, findet in der analytischen Chemie verhältnismässig häufig Anwendung. Einige Autoren nehmen die Zusammensetzung $[Mn(H_2P_2O_7)_3]^{3-}$ an[1,2], andere sprechen von einer Zusammensetzung des Komplexes mit einem[3] oder mit zwei Diphosphatmolekülen[4]. Bei der Untersuchung von Methoden zur Ozonbestimmung unter Anwendung des oben genannten Redoxsystems[5] versuchten die Verfasser, diese Diskrepanz aufzuklären.

Ergebnisse

Zur Aufklärung der Zusammensetzung des Diphosphatkomplexes des Mangans(III) konnte die Jobsche Methode in klassischer Anordnung nicht angewandt werden. Die Mn(III)-Verbindungen sind im benutzten Schwefelsäuremilieu ziemlich intensiv gefärbt. Die Differenzen zwischen den molaren Extinktionskoeffizienten und den Absorptionsmaxima des Mn(III)-sulfats und des Mn(III)-Diphosphatkomplexes sind nicht gross genug, um die typische Form einer Jobschen Kurve zu erhalten. Es wurde deshalb die Oxydation von Diphosphat und Mangan(II) in verschiedenen Molverhältnissen untersucht.

Kaliumbromat[3] erwies sich als nicht geeignet, da zugleich mit dem violetten Mn(III)-Diphosphatkomplex elementares Brom entsteht, welches die kolorimetrische Auswertung erschwert.

Dichromat[5] erwies sich ebenfalls als ungeeignet, da die Oxydation des Mn(II)-Diphosphatkomplexes zum dreiwertigen Mangan nur in Lösungen, die einen Überschuss an Diphosphat enthalten, gelingt.

Ozon bewährte sich ebenfalls nicht, da in einer Lösung, die keinen Überschuss an Diphosphat enthält, die Oxydation des Mangans bis zum Permanganat erfolgt.

Deshalb wurden zur Konstruktion der Jobschen Kurve Lösungen mit bestimmten Verhältnis von Diphosphat zu Mangan aus saurem Natriumdiphosphat und eine Suspension von Mangandioxydhydrat in einer Lösung von Mangan(II)-sulfat hergestellt. In Lösungen, die einen Überschuss an Diphosphat enthielten, löste sich das suspendierte $MnO(OH)_2$ vollständig. Bei einem Überschuss an Mn(II)-Ionen und Mangandioxyd reagierte nur die Menge, die dem Anteil an Mangan(III) im Diphosphatkomplex entsprach. Nicht reagiertes Mangandioxydhydrat blieb suspendiert. Unter Berücksichtigung der Reaktionsgeschwindigkeit, der Konzentration der Schwefelsäure, der Adsorption des Mn(III)-Diphosphatkomplexes an das zurückgebliebene Mangandioxydhydrat und der Darstellungsweise des MnO_2, das keinen Überschuss an Permanganat enthalten sollte, ergab sich für eine quantitative Reaktion des Diphosphats mit den Mn(II)-Ionen und dem Mangandioxydhydrat folgende Arbeitsvorschrift:

In 100-ml-Messkolben wurden 0.00, 1.00, 2.00, 3.00, 4.00, 4.50, 5.00, 5.50 und 6.00 ml einer 0.5 M Lösung von $Na_2H_2P_2O_7 \cdot 10\ H_2O$ 10 ml 1 M H_2SO_4 und 6.00, 5.50, 5.00, 4.50, 4.00, 3.00, 2.00, 1.00 und 0.00 ml 0.25 M $MnO(OH)_2$-Suspension in 0.25 M $MnSO_4$-Lösung pipettiert. Nach 10 Minuten wurden die Messkolben mit destilliertem Wasser aufgefüllt, gemischt und die klaren Lösungen gegen destilliertes Wasser in einer 2 cm-Küvette photometriert. Trübe Lösungen wurden vorher zentrifugiert.

Als Geräte wurden verwendet:

Spektrophotometer Hilger Spekker (Hilger and Watts, Ltd., London) Filter Nr. 605, Abs. Max. bei *ca.* 550 nm.

Spektrophotometer Unicam S.P. 800 (Unicam Instruments Ltd., Cambridge).

Die Ergebnisse enthält die Kurve A der Abb. 1.

Auf ähnliche Weise wurden die Kurven B und C der Abb. 1 ermittelt, nur wurden bei der Kurve B konstant 20 ml der $MnO(OH)_2$-Suspension zugegeben und bei der Kurve C konstant 20 ml der $Na_2H_2P_2O_7$-Lösung.

Abb. 2 zeigt die Diagramme des registrierenden Spektralphotometers der Lösungen aus dem rechten und linken Teil der Jobschen Kurve, d.h. die des Mn(III)-Diphosphatkomplexes, mit einem Überschuss an Diphosphat und die mit einem

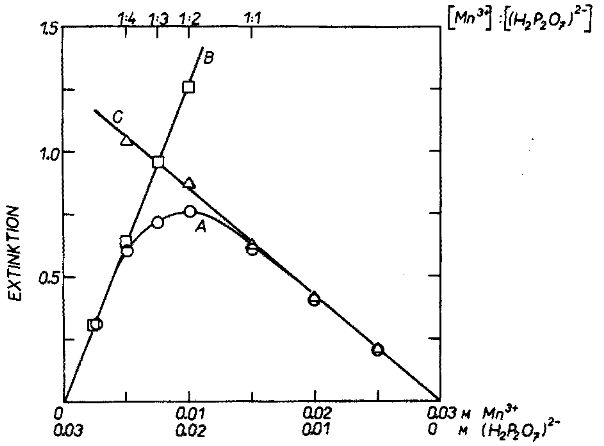

Abb. 1. Jobsche Kurve des Mn(III)-Diphosphatkomplexes. (A) Messpunkte der Jobschen Kurve; (B) Abhängigkeit der Extinktion des Mn(III)-Diphosphatkomplexes von der Diphosphatkonzentration; (C) Abhängigkeit der Extinktion des Mn(III)-Diphosphatkomplexes von der Mangankonzentration. Schichtdicke $l = 2.00$ cm.

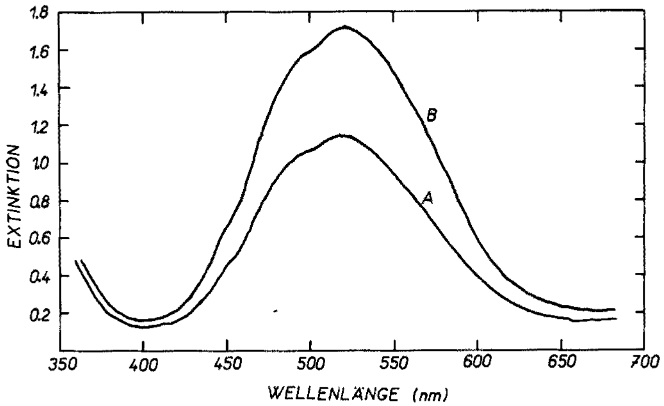

Abb. 2. Absorptionskurven des Mn(III)-Diphosphatkomplexes. (A) 0.02 M Mn^{3+}, 0.25 M $(H_2P_2O_7)^{2-}$, 0.1 M H_2SO_4; (B) 0.25 M Mn^{3+}, 0.08 M $(H_2P_2O_7)^{2-}$, 0.1 M H_2SO_4. Schichtdicke $l = 1.00$ cm.

Überschuss an Manganionen. Die Messungen wurden gegen destilliertes Wasser ausgeführt.

Diskussion

Aus der Abb. 2 ergibt sich, dass in beiden Fällen die gleiche Verbindung entsteht. Auf Grund dessen kann der Ablauf der Jobschen Kurve als Ausdruck derselben Reaktion über das gesamte untersuchte Gebiet hin angesehen werden. Das berechtigt zu folgender Auswertungsweise:

Dadurch, dass bei einem Überschuss von Mangan(II)-Ionen und Mangandioxyd enthaltendem Milieu nicht durchreagiertes Mangandioxyd zurückbleibt, wird die Gipfelpartie der Jobschen Kurve entstellt. Das Maximum dieser Kurve liegt bei dem Konzentrationsverhältnis $Mn^{3+}:(H_2P_2O_7)^{2-}=1:2$. Für die Auswertung des Verhältnisses beider Komponenten wurden die ersten Punkte in beiden Teilen der Jobschen Kurve verwendet, die sehr gut mit der Abhängigkeit der Extinktion von der Konzentration des Mangans und des Diphosphats übereinstimmen. Dabei ergibt sich für das Verhältnis von Mangan zu Diphosphat die Beziehung 1:3, was einem Komplex von der Zusammensetzung $[Mn(H_2P_2O_7)_3]^{3-}$ entspricht. Die Reaktion des Mangandioxydhydrats mit Mn(II)-Ionen und saurem Diphosphat kann durch die in der Literatur bereits angeführte Gleichung[6] ausgedrückt werden:

$$MnO(OH)_2+Mn^{2+}+6\ (H_2P_2O_7)^{2-}=2\ [Mn(H_2P_2O_7)_3]^{3-}+3\ H_2O$$

Die Ergebnisse von Gottschalk[3] werden wahrscheinlich infolge der Vernachlässigung des Einflusses des bei der Reaktion entstehenden elementaren Broms entstellt.

Ein Vergleich der Absorptionskurven einer Lösung des Mn(III)-Diphosphatkomplexes, der durch die Reaktion des zweiwertigen Mangans, von Mangandioxydhydrat und Diphosphat, und weiter durch die Oxydierung des Mn(II)-Diphosphatkomplexes in saurem Milieu durch Ozon[7], Dichromat, Permanganat und Bromat entstand, hat gezeigt, dass in allen oben genannten Reaktionen derselbe Komplex entsteht, dessen Absorptionsmaximum im Gebiete von 518–524 nm liegt.

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Separation of rare earths from other elements by selective cation exchange

Many ion-exchange methods for the separation of individual rare earths have been described but the separation of rare earths from other elements has received less attention. GORDON *et al.*[1] separated microgram amounts of rare earths from thorium by cation exchange of solutions containing EDTA at pH 2; the anionic thorium complex passes through and the rare earths are retained. Anionic sulphato complexes have also been utilized for the separation of rare earths from thorium[2,3], zirconium[4], and uranium[4,5], the rare earths being retained by the ion exchanger. Traces of rare earths can also be separated from zirconium in hydrofluoric acid solutions by cation exchange[6]. In acetate-buffered solutions, scandium forms an acetate complex so that separation from rare earths is possible[7]. FRITZ AND PALMER[8] studied the separations of several metal ions, including some rare earths, by cation exchange of solutions containing sulphosalicylate; some bivalent metal ions and trivalent rare earths were retained.

Detailed studies of the conditions for the separation of rare earths from other elements in sulphosalicylate solutions by cation exchange are described in this communication. The separation of microgram amounts of rare earths from large quantities of thorium or uranium and their spectrographic determination are also discussed; the procedure may be useful in the analysis of nuclear fuels.

Reagents and chemicals

Ion-exchange resin. Dowex 50W-X8 resin (100 mesh, Baker's Analyzed Reagent) was washed by decantation with 6 *N* hydrochloric acid and thoroughly rinsed with redistilled water. The resin slurry was poured into a conventional column (1 cm i.d.) to give an 8-cm bed. The resin was then converted to the ammonium form by passing a strong solution of ammonium chloride till no more acid was liberated, and washed with ammoniacal EDTA (ammonium salt) solution to remove traces of heavy metals, followed by thorough washing with redistilled water.

Rare earths. Lanthanum and cerium(III) nitrate solutions were prepared from G.R. grade salts (E. Merck). Yttrium, neodymium, gadolinium, terbium, ytterbium, and scandium solutions (1 mg/ml) were prepared from the spectrographically pure oxides (Johnson-Matthey), by fuming with a minimum amount of perchloric acid and diluting with redistilled water. The rare earths mentioned were considered to be representative of the whole group.

All other reagents were of Analar grade (B.D.H.) or of G.R. grade (E. Merck). Redistilled water from an all-glass still was used throughout. For interference studies, titanium sulphate, ammonium vanadate, ammonium molybdate, and sodium tungstate were used; all other elements were added as the nitrates.

Effect of pH on adsorption of rare earths

Solutions containing known amounts of rare earth (about 5 mg) were mixed with 5 ml of 1 *M* sulphosalicylic acid, diluted to 200 ml, adjusted to the desired pH with ammonium hydroxide, and passed through the resin (ammonium form); the effluent was rejected. The column was then washed with 50 ml of 0.02 *M* sulphosalicylic acid adjusted to the same pH, and finally the sulphosalicylic acid was washed out with water. Rare earths were eluted with 25 ml of saturated ammonium chloride solution, and the column was washed with 25 ml of water. Saturated ammonium chloride solution removes the rare earths quantitatively from the column, and has the advantage that the column is left ready for further use. The rare earth (or scandium) content of the eluate was determined by titration with 0.01 *M* EDTA, with xylenol orange as indicator, at the optimum pH for the particular rare earth[9].

Occasionally, it may be necessary to wash the column with ammoniacal EDTA (ammonium salt) solution to remove accumulated traces of metallic ions; EDTA must be completely removed before the column is used.

It was found that the trivalent rare earths from lanthanum to gadolinium were completely exchanged in the pH range 1.0–7.0. Yttrium and rare earths heavier than gadolinium were exchanged completely between pH 1.0 and 6.7, while scandium was exchanged between pH 1.0 and 3.0. Above pH 3.0, the exchange of scandium was incomplete and became insignificant at pH 6.0. Above pH 7.0, the exchange of rare earths was incomplete and became insignificant at pH 10.0. Nitrates, chlorides, and perchlorates did not interfere; the sulphate and sulphosalicylate concentration should not exceed 0.05 *M*.

Effect of pH on the masking of different ions

The effect of pH on the exchange of foreign ions in presence of sulphosalicylate was studied in order to assess the possibilities of selective exchange of rare earths. Solutions containing 0.05–0.1 mmole of the foreign ion were mixed with 10 ml of 1 *M* sulphosalicylic acid, diluted to 500 ml, adjusted to the required pH with ammonium hydroxide, boiled for 1 min and cooled to room temperature; the pH was then checked and readjusted. Boiling the solution ensured complexation of ions like beryllium(II) and aluminium(III), which react slowly with sulphosalicylate at room temperature. The solution was passed through the resin column (ammonium form), which was then

TABLE I

EFFECT OF pH ON MASKING OF FOREIGN IONS BY 0.05 *M* SULPHOSALICYLIC ACID

Foreign ion	*Minimum pH for complete masking*	*Remarks*
Be(II)	4.7	Partial retention below pH 4.7
Al(III)	5.4	Partial retention below pH 5.4
Fe(III)	< 2.0	Completely masked at pH 2.0–10.0
Ti(IV)	< 2.0	Completely masked at pH 2.0–10.0. Above pH 4.0, Ti interferes with R.E. exchange
Zr(IV)	< 2.0	Completely masked at pH 2.0–10.0. Above pH 4.5, Zr interferes with R.E. exchange
Th(IV)	5.8	Partial retention below pH 5.8
V(V)	2.5	Partial retention below pH 2.5. Above pH 4.0, rare earth vanadates may precipitate
Mo(VI)	2.5	Partial retention below pH 2.5
W(VI)	< 2.5	Below pH 2.5, W interferes with R.E. exchange
U(VI)	4.7	Partial retention below 4.7

washed with a solution of sulphosalicylic acid of the same pH and concentration followed by thorough washing with water. Foreign ions retained by the resin were eluted with 10 *N* hydrochloric acid and determined by standard analytical procedures. The pH limits for complete masking are given in Table I.

Separation of rare earths from different elements

Solutions containing a known amount of the particular rare earth and the element to be separated, were treated as described above for the masking study. The column was washed with a few ml of 0.02 *M* sulphosalicylic acid solution adjusted to the required pH, and then with water. The rare earth was eluted as described above, and determined by titration with EDTA. The results are given in Table II.

TABLE II

SEPARATION OF SINGLE RARE EARTHS FROM OTHER ELEMENTS

Diverse ion (mg)	*pH*	*Rare earth found (mg)*						
		La	*Ce*	*Nd*	*Gd*	*Tb*	*Yb*	*Y*
—	—	4.52	4.06	4.97	5.03	5.01	5.02	5.00[a]
Fe(III) (50)	6.5	4.48	4.06	4.94	5.07	5.01	5.02	4.98[b]
Al(III) (50)	6.5	4.48	4.06	4.97	5.03	4.97	5.06	5.02
Be(II) (25)	6.5	4.52	4.06	4.94	5.03	4.97	5.02	4.98
Ti(IV) (10)	4.0	4.52	3.99	4.94	5.03	5.01	5.06	5.02
Zr(IV) (25)	4.0	4.52	3.99	4.90	4.99	4.97	5.02	5.00
Th(IV) (500)	6.5	4.55	4.06	5.01	5.07	5.01	4.98	4.98
V(V) (10)	3.5	4.52	4.02	4.90	4.99	5.01	5.02	5.00
Mo(VI) (50)	4.0	4.45	4.06	4.93	4.99	5.01	5.02	5.00
W(VI) (25)	4.0	4.45	4.06	4.93	4.99	5.01	5.02	5.02
U(VI) (500)	6.5	4.52	4.06	4.97	4.99	5.01	5.02	4.98

[a] These are the amounts of the rare earths taken for each separation.

[b] Scandium was also examined; at pH 2.5, the recovery of 1.25 mg Sc mixed with 25 mg Fe(III) was 1.26 mg.

After the EDTA titration, the solution was evaporated with nitric acid and perchloric acid, and qualitative tests were made for the element from which separation was required; such tests were invariably negative.

Separation and spectrographic determination of microgram quantities of rare earths in presence of large amounts of thorium or uranium

A solution containing 1 g of thorium or uranium as the nitrate salt was mixed with solutions of yttrium, lanthanum, gadolinium, and ytterbium containing 16 μg of each of the rare earths, and treated with 12–15 g of sulphosalicylic acid, diluted to 500 ml, and adjusted to pH 6.5 with ammonium hydroxide. The solution was boiled, cooled, the pH readjusted, diluted to 1500 ml and passed through the resin (ammonium form), which was then washed with 50 ml of 0.02 *M* sulphosalicylic acid adjusted to pH 6.5, and then thoroughly with water. Rare earths were eluted with 25 ml of saturated ammonium chloride solution only. To the eluate were added 5 ml of beryllium nitrate solution (1.8 mg Be/ml), 10 ml of 6% cupferron solution, and a few drops of methyl red indicator, followed by ammonium hydroxide to neutralize the solution. Beryllium is quantitatively precipitated as the cupferronate from neutral solution[10], and acts as a carrier for traces of rare earths, thorium, and scandium, if the precipitation is carried out in presence of large quantities of ammonium salt[11]. After 3–4 h (with occasional stirring), the precipitate was filtered through paper, being transferred with the mother-liquor, before being washed with a few ml of 30% ammonium nitrate solution. It was then ignited at 1000°, weighed, and measured spectrographically. Blank experiments with the same amount of thorium or uranium but without rare earths, showed that the uranyl nitrate used was sufficiently pure, but that the thorium nitrate contained detectable amounts of rare earths. Thorium nitrate purified by cation exchange in presence of sulphosalicylate at pH 6.5, was therefore used for further work; no rare earth was then detectable in the blanks.

For spectrography, the precipitate was diluted with an equal weight of spectrographically pure carbon powder containing 75 p.p.m. palladium as ammonium chloropalladate and 33% silver chloride. A Hilger E-1 large quartz spectrograph with Hilger non-recording microphotometer was used with anode excitation at 220 V d. c. under the following conditions. Slit—0.01 mm; arc gap—4 mm; current—4 A for 5 sec and burnt to completion at 8.5 A; Ilford ordinary plate.

Internal standard line—Pd 3421.2 Å. Measurement lines—Y 3195.6, Y 3242.3, La 3245.1, Gd 3422.5, Gd 3032.9, Yb 2891.4, and Yb 3289.4 Å.

Standards were prepared by diluting 'specpure' rare earth oxides with beryllium oxide.

The results of the recovery of rare earths by this method are given in Table III.

TABLE III

SEPARATION AND SPECTROGRAPHIC DETERMINATION OF RARE EARTHS FROM LARGE QUANTITIES OF Th OR U

(16 μg of each rare earth was added in all cases)

Sample (1 g)	*Amount of rare earth found (μg)*			
	La	Gd	Yb	Y
Th	18	16	15	18
U	14	18	16	14

DISCUSSION

Ion exchange on Dowex 50W-X8 resin in the ammonium form in the presence of sulphosalicylate at pH 6.5 gives a clear separation of trivalent rare earths from beryllium, aluminium, iron(III), thorium, molybdenum(VI), and uranium(VI); separation from titanium(IV) and zirconium must be carried out below pH 4.0. Separation from vanadium (V) and tungsten(VI) must also be done below pH 4.0 to avoid formation of the rare earth vanadate or tungstate.

Scandium is incompletely exchanged above pH 3.0, hence separation from beryllium, aluminium, thorium, and uranium(VI) is impossible, because the latter are partially or completely exchanged below pH 3.0. Separation of rare earths from scandium may be possible at pH 6.5.

The proposed ion-exchange procedure was applied successfully for separation of microgram quantities of rare earths from large amounts of thorium or uranium. Beryllium cupferronate is an effective carrier for rare earths, and the beryllium oxide matrix ultimately obtained burns smoothly in a carbon arc. Yttrium, lanthanum, gadolinium, and ytterbium were chosen for these experiments because they easily can be determined spectrographically with quartz optics. AgCl helps in smooth volatilization of rare earths in the arc. The spectrograms obtained after separation from thorium showed only faint Th 2837.3 and Th 2870.4 lines, and uranium was not detectable after the separation from uranium. Separations were complete for all practical purposes.

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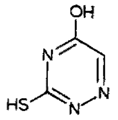
New colour reactions with asymmetric triazine derivatives for the determination of osmium

The presence of the thiocarbonyl and sulfhydryl groups in the molecule of many reagents used for the spectrophotometric determination of osmium[1–4] makes it necessary to consider the $\rangle C=S$ group as one of the functional analytical groups for this element[5].

More recent investigations[6–8] have confirmed this class of organic reagents, which also includes a series of asymmetric triazine derivatives[7,9,10].

In the present paper, further work on the elucidation of the effects of different substituents in the 1,2,4-triazine molecule on the colour reactions with osmium is described. The reagents studied are 3-mercapto-5-hydroxy-1,2,4-triazine (I) and 3-mercapto-5-hydroxy-6[(benzylmercapto)-methyl]-1,2,4-triazine (II).



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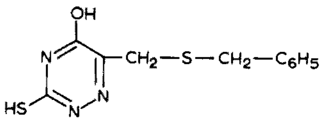


II

Experimental

Absorbances were measured with a Beckman DB recording spectrophotometer and a V.S.U.-1 Zeiss Jena spectrophotometer, in 1-cm matched cells against distilled water as reference (the reagents do not absorb in the ranges used).

The osmium solution was prepared by dissolving 1 g of osmium tetroxide (B.D.H.) in 0.2 *M* sodium hydroxide and then standardizing[6,11].

The reagent solutions (0.1% w/v) were also prepared in 0.2 *M* sodium hydroxide. Sulphuric, hydrochloric, nitric, perchloric and aminoacetic acid solutions of different concentrations, as well as chloroplatinic acid (B.D.H.), palladium(II) chloride and ruthenium(III) chloride (Fluka) were used.

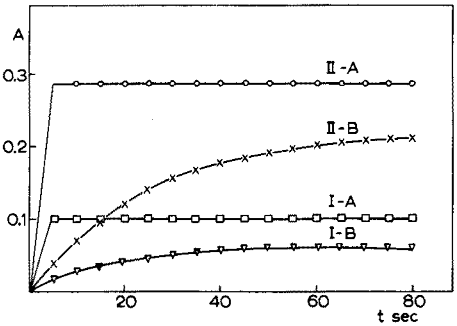
Results and discussion

The samples were prepared in 10-ml volumetric flasks, the solutions being mixed in the following order: osmium solution, reagent solution, acid solution and water for dilution.

Studies of the effect of acids showed that essentially the same absorbances were obtained when the complex was formed in solutions containing 0.5–3.0 *M* sulfuric, hydrochloric, nitric or perchloric acid; in up to 0.1 *M* acids the absorbances increased gradually. However, when aminoacetic acid was used, the absorbances increased gradually as acidity was increased from 0.5 to 3.0 *M* and remained constant in the range 3–4 *M*. The effects of acids were the same for both reagents.

Colour formation was very rapid in acidic media (Fig. 1) but in basic media, absorbances continued to increase even after 24 h. On the basis of these tests, further work was done with 1 *M* sulfuric acid media and a development time of 5 min. Under these conditions, 2 ml of a 0.1% solution of reagent I or II provided maximum absorbance.

The absorbance spectra of the coloured compounds formed under these optimal conditions are shown in Fig. 2. It can be seen that the wavelengths of maximum absorbance occur at 560 nm with reagent I and at 430 nm with reagent II. The replacement of the hydrogen in position 6 of 3-mercapto-5-hydroxy-1,2,4-



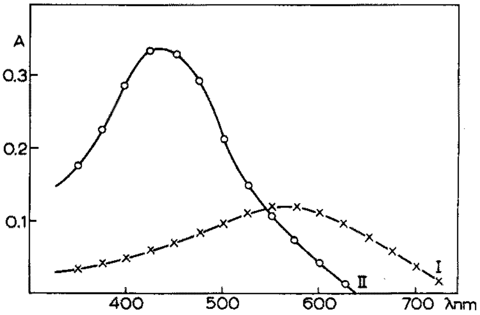


Fig. 1. The influence of time (35 μg Os/10 ml). (I-A) Os-reagent I in 1 *M* sulfuric acid at 560 nm; (I-B) Os-reagent I in 0.2 *M* sodium hydroxide at 560 nm; (II-A) Os-reagent II in 1 *M* sulfuric acid at 430 nm; (II-B) Os-reagent II in 0.2 *M* sodium hydroxide at 430 nm.

Fig. 2. Absorbance spectra (41.1 μg Os/10 ml). (I) Colored compound formed with reagent I; (II) colored compound formed with reagent II.

triazine by the benzylmercaptomethyl group causes the wavelength of maximum absorbance of the coloured osmium compound to shift from 560 nm to 430 nm, and also strongly enhances the absorbance. The hyperchromic effect for reagent II is much greater than that obtained with any other derivative of reagent I so far tested[7,9].

It was found that Beer's law is obeyed in the concentration range 1.0–22.0 μg Os/ml at 560 nm for reagent I, and in the concentration range 0.5–7.2 μg Os/ml at 430 nm for reagent II.

Composition of the coloured compound. The results obtained by the continuous variations[12] and mole ratio[13] methods were not conclusive for either reagent, owing to the appearance of anomalies when osmium was in excess. Not only complex formation but also oxidation-reduction reactions must be considered. The colour formed could be assigned both to complex formation of lower-valent forms of osmium, and to supplementary interactions between these ions and one of the possible initial or oxidized forms of the organic reagent.

Effect of foreign ions. As is well known, osmium can be separated by oxidative distillation as osmium tetroxide from most elements, hence only the effects of ruthenium, platinum, palladium and iridium were examined. Ruthenium interfered, but both reagents could be applied for the determination of osmium in the presence of a 750-fold amount of platinum, a 500-fold amount of iridium, or a 4-fold amount of palladium.

Conclusions

The colour reactions of osmium with 3-mercapto-5-hydroxy-1,2,4-triazine and 3-mercapto-5-hydroxy-6-[(benzylmercapto)-methyl]-1,2,4-triazine described above are suitable for the spectrophotometric determination of osmium. The latter compound provides the most sensitive procedure so far available with this class of reagent.

The methods can be used for 1.0–22.0 μg Os/ml and 0.5–7.2 μg Os/ml at 560 nm and 430 nm respectively.

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An ion-exchange method for the detection of nitriles

Few tests are available for the detection of nitriles[1]; detection is usually based either on some general test for several functional groups, or on the interference caused by the nitriles in a particular test. None of the tests is specific for nitriles. Hydroxamic acid has been suggested for the detection of nitriles[2]. The test is suitable for certain derivatives of carboxylic acids, such as esters, anhydrides and acid chlorides, and for trichloromethyl groups, and amides, imides and anilides provide the main interference. Nitriles have also been detected and differentiated from amides by performing two tests: the soda lime–methanolic copper sulphate test[3] gives a blue color with nitriles, if no amide is present, whereas the mercury(II) chloride–bromothymol blue test[3] is negative for nitrile if no N,N′-disubstituted amide is present and positive for unsubstituted or monosubstituted amide. This test is an improvement over the hydroxamic acid test, but amines and compounds containing olefinic and acetylenic bonds or α-hydrogen atoms interfere in both cases.

Recently, ion-exchange resins have been used for the detection of esters, amides, imides and anilides[4,5] and for the determination of aliphatic unsubstituted amides and esters[6]. The resin beads act simultaneously as catalysts and as a detection medium. In the present communication, the same technique has been successfully applied and the work has been extended for the detection of nitriles. Moreover, the test is highly selective for nitriles and can be used to differentiate nitriles from unsubstituted amides.

Chemicals

All chemicals used were of reagent grade. Solutions of nitriles were prepared in distilled ethanol. Conductivity water was prepared by first deionizing water and then distilling it from alkaline permanganate.

Dowex 50W-X8 (20–50 mesh) was used in the H^+ form. The resin was regenerated and washed several times with conductivity water until no pink color was obtained with Nessler's reagent.

Detection of nitriles

The following two tests are necessary for the detection of nitriles.

Test I. To one drop of each of the test solution and water, add two drops of concentrated sulphuric acid in a semimicro test tube. Heat the contents slowly for a few minutes on a low flame. Cool, add a few resin beads and one drop of water and heat (not boil) again. Decant, leaving behind the resin beads. Wash the beads by decantation with 4–5 portions of conductivity water. Transfer the beads to a white spot plate and dry them by blotting with filter paper. Add a drop of Nessler's reagent. A pink or red color on the resin beads indicates a positive test.

Test II. Mix a few mg of test substance with two drops of water in a semimicro test tube. Add a few resin beads and heat (not boil) on a low flame. Cool the beads and wash as described above. Transfer to a white spot plate and test with one drop of Nessler's reagent. A pink color indicates a positive test.

Nitriles give a positive response with Test I and a negative response with Test II. For unsubstituted amides and imides both tests are positive. It is therefore possible to distinguish between unsubstituted amides and nitriles. Other organic compounds give a negative response with the recommended tests.

Results

The nitriles shown in Table I were detected by the recommended method. Mandelonitrile gave the test for amide. Benzylnitrile gave a negative test.

The following unsubstituted amides and imides were detected and thus differentiated from nitriles: Oxamide, chloroacetamide, N-valeramide, formamide, succinamide, salicylamide, acetamide, propionamide, succinimide and phthalimide.

TABLE I

LIMIT OF IDENTIFICATION OF NITRILES

Nitriles	*Amount detected (mg)*	*Limiting dilution*
Acetonitrile	1.05	1 : 500
Propionitrile	0.137	1 : 500
Butyronitrile	0.307	1 : 150
Acrylonitrile	0.215	1 : 200
Benzonitrile	1.03	1 : 500
Chloroacetonitrile	0.377	1 : 150
Cyanoacetic acid	0.425	1 : 100

Negative tests were given by the following organic compounds:

Methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, glycerol, ethylene glycol.

Oxalic, formic, acetic, propionic, benzoic, tartaric, and sulphanilic acids.

Benzene, bromobenzene, nitrobenzene, chloroform, carbon tetrachloride, cyclohexane and toluene.

Acetaldehyde, crotonaldehyde and chloral hydrate.

Acetone, cyclohexanone, methyl ethyl ketone, diisobutyl ketone, methyl isobutyl ketone and acetyl acetone.

Fructose, raffinose and sucrose.

Ether, anisole and dioxane.

Ethyl acetate, ethyl acetoacetate, methyl benzoate, diethyl malonate, *n*-tributyl phosphate.

Phenol and *o*-cresol.

Acetanilide and oxanilide.

Methylamine, dimethylamine, trimethylamine, diethanolamine, triethanolamine, aniline, diethylaniline.

Pyridine.

Detection of nitrile in the presence of foreign substances. Nitriles could be detected in the presence of some foreign substances. Some results for propionitrile are quoted in Table II.

Discussion

Cation-exchange resins in the hydrogen form are very effective in the hydrolysis of unsubstituted amides and imides[5]. The corresponding acid and ammonium ion are formed, and the resin beads in the ammonium form give a red or pink color with Nessler's reagent as described in test II. Nitriles are not hydrolyzed, hence this test is negative. Nitriles can be hydrolyzed either with sodium hydroxide or with

TABLE II

DETECTION OF PROPIONITRILE IN PRESENCE OF FOREIGN SUBSTANCES

Foreign substances	*Amount added (mg)*	*Nitrile detected (mg)*	*Limiting dilution*
Formic acid	61	2.76	1 : 200
Benzene	4395	0.55	1 : 200
Chlorobenzene	73.7	0.55	1 : 200
Nitrobenzene	60.15	1.37	1 : 50
Cyclohexane	72.52	16.52	1 : 20
Sucrose	5.0	2.76	1 : 200
Phenol	53.75	2.76	1 : 200
n-Butanol	40.5	0.55	1 : 200
Ethylacetate	45.05	1.37	1 : 50
Ether	35.40	1.37	1 : 50
Pyridine	19.66	5.5	1 : 20
Methylamine	6.99	2.76	1 : 20
Acetanilide	0.5	2.76	1 : 20
Anisole	49.5	1.10	1 : 200

TABLE III

TESTS FOR NITRILES, UNSUBSTITUTED AMIDES, IMIDES AND OTHER ORGANIC COMPOUNDS

Compounds	*Test I*	*Test II*
Nitriles	Positive	Negative
Unsubstituted amides and imides	Positive	Positive
Other organic compounds	Negative	Negative

dilute sulphuric acid; the latter was chosen because it retains ammonia, and because sodium ion deactivates the resin. A positive test is obtained when a drop of Nessler's reagent is added to the resin beads. Unsubstituted amides or imides are also hydrolyzed with dilute sulphuric acid and thus also give a positive test in test I. Benzyl nitrile gives a negative test, probably because it does not hydrolyze. The indications given by the two tests are summarized in Table III. All the available nitriles were run with a number of organic compounds and the results were satisfactory.

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BOOK REVIEWS

H. B. MARK AND G. A. RECHNITZ, *Kinetics in Analytical Chemistry*, Interscience Publishers–J. Wiley & Sons, Inc., New York, 1968, xi+339 pp., price 160 s.

The growing importance of kinetic methods in chemical analysis makes the appearance of this Vol. 24 of Chemical Analysis series welcome. The first four chapters give an introduction to reaction kinetics and methods employed for catalysed and uncatalysed reactions. The next two chapters deal with simultaneous determination of closely related mixtures. In the fifth chapter, kinetic equations are discussed and the principles of the procedures used are indicated. Examples from organic analysis are then given. In the seventh chapter, written with the help of L. J. PAPA, the evaluation of reactions based on their difference in rate of reaction with a common reagent is discussed with respect to the errors involved and the selection of optimum conditions. Whereas the stress in differential analysis is laid on organic reactions, the last quarter of the book describes mechanisms and some properties of inorganic reagents which are of analytical importance. This material is of considerable interest, but its treatment at greater length would have been more valuable.

The presentation is sound and a clear picture is given. As usual, the question of what should or should not be included in a short monograph is a matter of personal preference. However, although some would perhaps prefer to see a different stress laid on the various possible techniques, and other methods of analysing the kinetic data discussed, the authors' choice is in general soundly based. The book definitely deserves reading and study by analytical chemists.

B. CAPON, M. J. PERKINS AND C. W. REES, *Organic Reaction Mechanisms 1967*, Interscience Publishers–J. Wiley and Son, Inc., New York, 1968, ix+512 pp., price 130 s.

The present volume summarizes progress in the field of organic reaction mechanisms in the same way as previous volumes of this series. In general, the limitations of this volume are also similar: there is no differentiation between reaction mechanisms based on investigations of kinetics and those based on studies of product composition; and the reviews refer predominantly to the more readily accessible journals, whereas some detail on the information in less accessible papers would be more useful.

The volume has all the advantages of the previous ones, in that if offers up-to-date information. These volumes are particularly valuable for the non-specialist and can be strongly recommended to all analytical chemists studying organic reactions.

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