ANALYTICA CHIMICA ACTA

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Papers will be published in English, French or German.

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

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1. J. J. LINGANE AND A. M. HARTLEY, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Edn., Elsevier, Amsterdam, 1966, p. 516.

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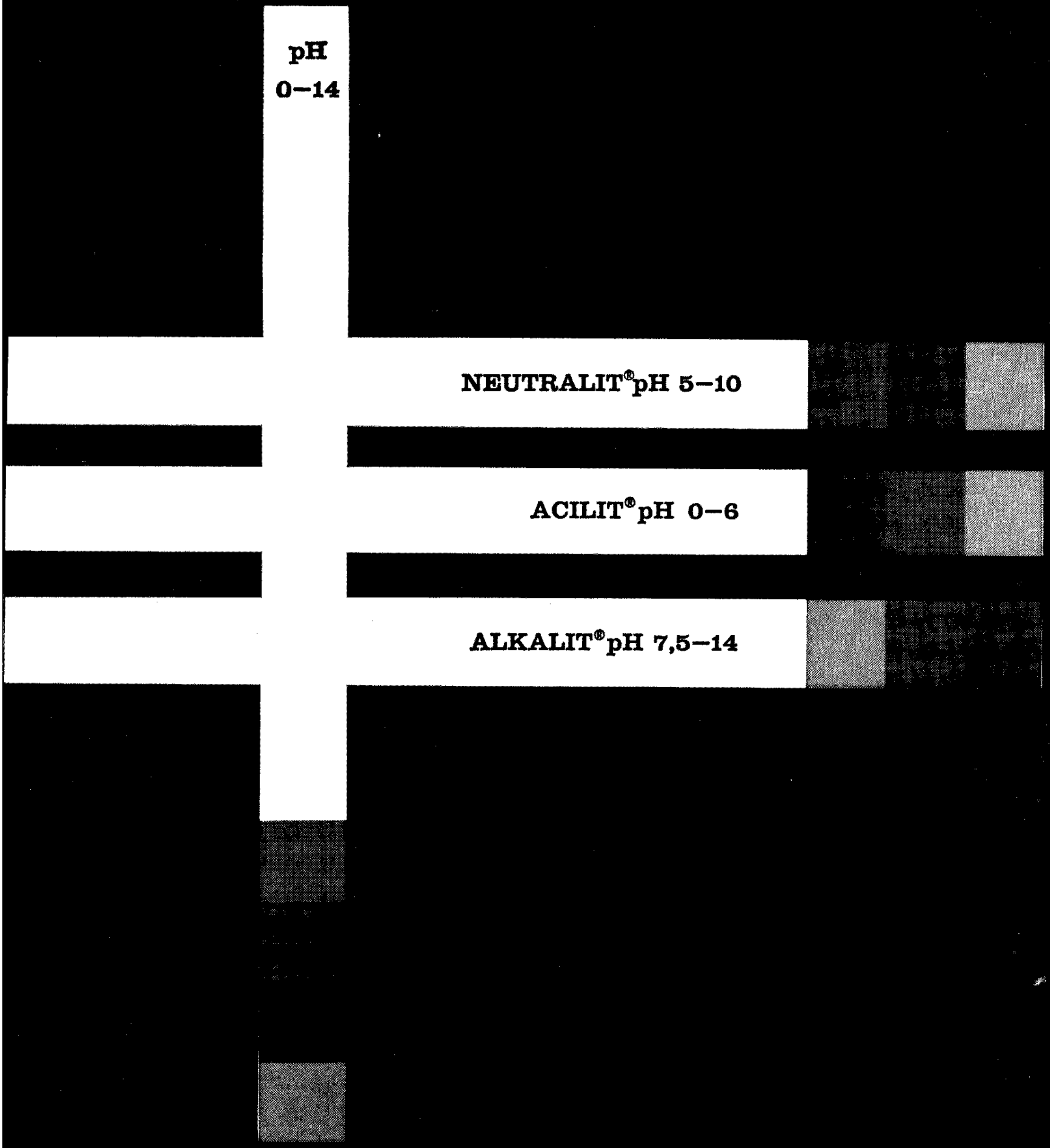
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ACILIT®pH 0–6
ALKALIT®pH 7,5–14

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 50, No. 3, June 1970

A RAPID SOLVENT EXTRACTION METHOD FOR THE DETERMINATION OF CAESIUM-137 IN ENVIRONMENTAL MATERIALS

A solvent extraction method for the quantitative determination of caesium-137 in environmental samples is described. Caesium carrier is added to the ashed sample, which is dissolved with hydrochloric acid. The solution is filtered to remove any carbon and the pH is adjusted to 2.0. Sodium dodecylbenzene sulphonate is added and the extraction is done with phenol–nitrobenzene mixture. The organic phase is washed with EDTA solution and the caesium is stripped from the washed solvent with 6 *M* hydrochloric acid. The caesium is precipitated as caesium chlorostannate to ensure absolute decontamination from potassium-40. Recovery from standard solution is about 85% and from vegetation, rainwater and effluent samples about 80%. The method is applicable in the presence of large quantities of interfering ions, and decontamination factors for many nuclides are greater than 10^3.

W. W. Flynn,
Anal. Chim. Acta, 50 (1970) 365–373

THE DETERMINATION OF LEAD BY ATOMIC FLUORESCENCE SPECTROSCOPY

The atomic fluorescence characteristics of lead are described in air–acetylene, nitrous oxide–hydrogen and argon–oxygen–hydrogen flames. An electrodeless discharge tube is used as the source of excitation. A detection limit of 0.01 μg/ml of lead in aqueous solution is obtained by measurement of the direct-line fluorescence at 405.8 nm in the argon–oxygen–hydrogen flame. The effect of 100-fold excesses of 30 cations and anions is examined: only aluminium interfered significantly. Effects of multipass optics and signal collection mirrors are examined and their effect on signal–noise ratios is discussed.

R. F. Browner, R. M. Dagnall and T. S. West,
Anal. Chim. Acta, 50 (1970) 375–381

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INTRODUCTION TO NUCLEAR CHEMISTRY

by D. J. CARSWELL

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

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

STATISTICAL THERMODYNAMICS

An Introduction to its Foundations

H. J. G. HAYMAN

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

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

THE STRUCTURE OF INORGANIC RADICALS

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

by P. W. ATKINS and M. C. R. SYMONS

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

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

FUNDAMENTALS OF METAL DEPOSITION

by E. RAUB and K. MÜLLER

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

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

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SOME OBSERVATIONS ON THE CHEMILUMINESCENCE OF ATOMS IN ACETYLENE FLAMES SUPPORTED BY AIR AND ARGON–OXYGEN MIXTURES

A study has been made of the chemiluminescent emission of As, Bi, Cd, Ge, Hg, I, Mo, Pb, Sb, Se, Sn, Te, V and Zn in the primary combustion zones of air–acetylene and argon–oxygen–acetylene flames, supported at an open burner port during the aspiration of aqueous solutions of their salts. In general, elements having excitation potentials greater than 4 eV show considerably greater atomic chemiluminescence in the primary zone than "thermal" atomic emission in the interconal region. Various mechanisms are suggested for the energy-transfer reactions between metal atoms and excited flame species, particularly carbon monoxide.

J. F. Alder, K. C. Thompson and T. S. West,
Anal. Chim. Acta, 50 (1970) 383–397

ACCURATE DETERMINATION OF TRACES OF SODIUM AND POTASSIUM IN ROCKS BY ION EXCHANGE FOLLOWED BY ATOMIC ABSORPTION SPECTROSCOPY

Sodium and potassium (5–1000 p.p.m.) in rocks such as peridotites and dunites can be determined accurately by ion-exchange separation followed by atomic absorption spectrophotometry. The samples are decomposed in sulphuric, hydrochloric and hydrofluoric acid mixtures, and after removal of hydrofluoric acid the cations are absorbed on a 90-ml column of AG50W-X8 cation-exchange resin. Vanadium and other anion-forming elements are eluted with 0.01 *M* nitric acid containing hydrogen peroxide. Then the alkali metals are eluted with 0.50 *M* nitric acid, while Mg, Mn, Ca, Ti, Al, Fe and other multivalent elements are retained by the column. The eluate fractions containing the respective alkali metals are measured directly by atomic absorption spectrophotometry against standards in 0.50 *M* nitric acid. Relevant elution curves, results for synthetic mixtures and for three international rock standards are presented and discussed.

F. W. E. Strelow, F. Von S. Toerien and C. H. S. W. Weinert,
Anal. Chim. Acta, 50 (1970) 399–405

POTENTIOMETRIC TITRATION OF LONG-CHAIN ALKYLTRIMETHYLAMMONIUM AND TETRABUTYLAMMONIUM SALTS

(in French)

A method of potentiometric titration of dodecyltrimethylammonium, tetradecyltrimethylammonium, hexadecyltrimethylammonium and tetrabutylammonium ions in aqueous solution is described. The ion-selective electrode which is used is a new liquid element electrode model. The principle of titration involves some results of the study of liquid phase electric cells.

C. Gavach and P. Seta,
Anal. Chim. Acta, 50 (1970) 407–412

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

× 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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A NEW REAGENT FOR THE DETECTION AND DETERMINATION OF SMALL AMOUNTS OF THE SULPHATE ION

An aqueous solution of 2-aminoperimidine hydrochloride is proposed as a new reagent for the detection and determination of the sulphate ion. As little as 0.05 p.p.m. can be detected by precipitation of the corresponding amine sulphate. Suspensions of the precipitate show remarkable stability and no colloidal stabilizers are needed. The reagent is applied to the nephelometric determination of 0.1–5 p.p.m. of sulphate ion; at the 0.5 p.p.m. level, the relative standard deviation is 4.5%. Although many ions form precipitates with the reagent at high concentrations, very few of the common anions provide significant interference in the nephelometric determination. The reagent seems promising for the determination of sulphate in natural waters, and for traces of sulphur in organic compounds after oxygen flask combustion.

W. I. STEPHEN,
Anal. Chim. Acta, 50 (1970) 413–422

THE GAS CHROMATOGRAPHY, THERMAL ANALYSIS AND MASS SPECTROMETRY OF FLUORINATED LEAD β-DIKETONATES

DETERMINATION OF TRACES OF LEAD BY THE INTEGRATED ION-CURRENT TECHNIQUE

Preparative details for perfluoroalkanoylpivalylmethanes and their lead chelates are given. Thermal analysis, gas chromatography and mass spectral studies all indicate high thermal stability, but strong column interaction makes successful quantitative gas chromatography difficult. The integrated ion-current technique is applied to determine lead heptafluorobutanoylpivalylmethanate in the range 10^{-9}–10^{-7} g of lead, but a lower detection limit of *ca.* 10^{-14} g is indicated.

R. BELCHER, J. R. MAJER, W. I. STEPHEN, I. J. THOMSON AND P. C. UDEN,
Anal. Chim. Acta, 50 (1970) 423–431

INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDE BY SOLVENT EXTRACTION AS TRIS(1,10-PHENANTHROLINE)IRON(II) THIOCYANATE

An indirect spectrophotometric method for the determination of small amounts of chloride in fresh waters is described. Chloride ions react with mercury(II) thiocyanate to liberate thiocyanate ions, which can be selectively extracted into nitrobenzene with tris(1,10-phenanthroline)iron(II) chelate cations. The red color (516 nm) of the organic phase measured against a reagent blank is proportional to the initial concentration of chloride ions in the aqueous phase. At least an equimolar amount of tris(1,10-phenanthroline)iron(II) chelate and a 3-fold amount of mercury(II) thiocyanate are needed; the optimal pH range is 1.5–3.5. Beer's law is obeyed over the concentration range of $0.8–5.6 \cdot 10^{-5}$ *M* of chloride. The color stability and the apparent sensitivity are better than those of the mercury(II) thiocyanate–iron(III) method. Large amounts of sulphate, phosphate, fluoride, carbonate, acetate, potassium, sodium, and ammonium ions had negligible or no effect; bromide, iodide, cyanide, sulphide, and thiocyanate interfere.

Y. YAMAMOTO, T. KUMAMARU, A. TATEHATA AND N. YAMADA,
Anal. Chim. Acta, 50 (1970) 433–438

Countercurrent Separation Processes

by H. R. C. Pratt

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

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

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

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

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

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

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1-[(5-CHLORO-2-PYRIDYL)AZO]-2-NAPHTHOL AS A NEW EXTRACTION–PHOTOMETRIC REAGENT FOR METALS

The heterocyclic azo compound, 1-[(5-chloro-2-pyridyl)azo]-2-naphthol (5-Cl-β-PAN), forms various coloured metal chelates, which can be extracted with different organic solvents. Chelate stability is greatly affected by pH. The molar absorptivities are usually considerably greater than those of the β-PAN chelate. Although the bathochromic shifts produced on chelation are no greater than those with 5-Br-β-PAN, the selectivity is increased. The reactivity of tri- and tetravalent metal ions is decreased appreciably by introduction of the chlorine. A correct choice of pH, solvent and masking reagent allows 5-Cl-β-PAN to be made reasonably selective.

S. Shibata, M. Furukawa, E. Kamata and K. Goto,
Anal. Chim. Acta, 50 (1970) 439–446

COLUMN REVERSED-PHASE PARTITION CHROMATOGRAPHY FOR THE ISOLATION OF SOME RADIONUCLIDES FROM BIOLOGICAL MATERIALS

Reversed-phase partition chromatography is a very useful tool for selective isolation of radionuclides from biological materials. Some new applications of this technique to the resolution of practical problems in radiation protection are reported. Natural thorium and enriched uranium can be determined separately and together in urine by means of a column of Microthene-710 supporting a solution of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane; batchwise extraction processes with Microthene supporting TOPO are also successful. Strontium-90 is determined in urine by a batch extraction of yttrium-90 with a slurry of Microthene supporting the liquid cation exchanger di-(2-ethylhexyl)phosphoric acid. Only a wet mineralization of the urines is required and the analyses are simple, rapid and sufficiently accurate. A method for the isolation of iodine from foodstuffs with a Microthene–benzene column is also described.

C. Testa,
Anal. Chim. Acta, 50 (1970) 447–455

EXTRACTION OF MOLYBDOSILICIC ACID BY TRIISOOCTYLAMINE NITRATE IN DICHLORO-1,2-ETHANE

EQUILIBRIA AND ANALYTICAL APPLICATION

(in French)

α-Molybdosilicic acid (α) in aqueous solution is extracted by triisooctylamine nitrate (R_3NHNO_3) in dichloro-1,2-ethane (S) according to an equilibrium which involves the dissociation of the extracted species in the organic phase:

$$\alpha_{aq} + 4(R_3NHNO_3)_S \rightleftharpoons [\alpha(R_3NH)_3]_S^- + (R_3NH)_S^+ + 4(NO_3^-)_{aq} + xH^+$$

Extraction allows separation of α from the excess of molybdenum necessary for its quantitative formation from silicate and molybdate. The direct spectrophotometric determination of the heteropolyacid in the organic phase is simple and sensitive ($\varepsilon = 28000$ l cm^{-1} mole^{-1} at 300 nm).

R. Kollar, V. Plichon and J. Saulnier,
Anal. Chim. Acta, 50 (1970) 457–464

Pigments

An Introduction to their Physical Chemistry

edited by David Patterson

Senior Lecturer, Department of Colour Chemistry, University of Leeds, Great Britai

5½ × 8½″, ix + 210 pages, 93 illus., 1967, Dfl. 32.50, 65s.

In this book the principles of physical chemistry are applied to the problems of making an using the insoluble organic and inorganic pigments manufactured for use in paints, printin inks, plastics and synthetic fibres. Development over many years has resulted in a high degre of technical quality in many of these pigments, achieved by purely empirical methods, but th use of such methods means that each case must be judged on its merits. On the other hand the application of physico-chemical theories can bring unifying concepts to a wide range o phenomena, and provide a deeper understanding of the processes involved.

It is quite insufficient to treat the making of pigments as the synthesis of certain compounds and to emphasize this the purely preparative chemistry of pigments has been left outside th scope of this book. Instead, pigments are regarded as substances produced to exert particula optical effects on certain media by colouring and opacifying them. The ways in which pigments can be prepared to carry out these functions, together with the appropriate technique for appraising their performance of them are consequently the main content of the book. Al the problems cannot be solved at present, but this book by showing what can be achieve and attempting to provide signposts to some of the unexplored areas, will undoubtedly stimulate and encourage further work in a field that is of considerable industrial importance.

Contents

1. Introduction
2. The theory of the colour of inorganic substances
3. The colour and constitution of organic molecules
4. The colour of pigment crystals
5. Photoconduction and the degradation of organic molecules
6. The nucleation and growth of particles
7. Particle size measurements and their significance
8. Instrumental methods of colour measurement
9. Instrumental colour match prediction
10. The theory of surface activity
11. The theory of dispersion, flocculation and flotatio phenomena

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COMPLEXES FORMED IN THE CHLOROFORM EXTRACTION OF COBALT(II) WITH OXINE

Absorption spectra of cobalt oxine complexes extracted into chloroform indicate that two cobalt(II) and one cobalt(III) complexes can be extracted depending on pH and the initial concentrations of oxine in the organic phase or cobalt(II) ion in the aqueous phase. The oxidation state of cobalt in the complexes was determined by treatment of organic extracts with an 0.001 *M* EDTA solution at pH 4–5; cobalt(II) complexes were back-extracted, and the cobalt(III) complex was not. The equilibrium distribution ratios of cobalt(II) between aqueous perchlorate solutions and oxine solutions in chloroform were determined at 20°. A plot of $\log D_{Co}$–$\log [HOx]_o$ *vs.* pOx gave a single curve for different concentrations of oxine; it was concluded that cobalt(II) is extracted as $CoOx_2HOx$.

S. Ōki,
Anal. Chim. Acta, 50 (1970) 465–474

THE STABILITY CONSTANTS OF SOME METAL CHELATES OF TRIETHYLENETETRAMINEHEXAACETIC ACID (TTHA)

Stability constants for Al(III), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), La(III), Nd(III), Er(III), Mg(II), Mn(II), Ni(II), Pb(II), Th(IV) and Zn(II) complexes of triethylenetetraminehexaacetic acid (TTHA) have been evaluated from data obtained by pH and pM measurements. The pM method based on measurements with the mercury electrode and the redox system Fe(III)/Fe(II) proved to be very useful when binuclear complexes are formed.

L. Harju,
Anal. Chim. Acta, 50 (1970) 475–489

COULOMETRIC PRODUCTION OF SULFHYDRYL REAGENTS

TITRATIONS OF LEAD(II) AND COPPER(II)

The efficiency of generation of 1-propanethiol and thiophenol from the electrodes Ag/AgSR (R = Pr,Ph) was tested. Coulometric titrations of lead(II) and copper(II) with electrically generated sulfhydryl reagent are reported. The reaction between copper(II) and sulfhydryl ions was studied.

F. Magno and V. Peruzzo,
Anal. Chim. Acta, 50 (1970) 491–497

DIFFRACTION OF X-RAYS BY CHAIN MOLECULES

by B. K. VAINSHTEIN

Foreword by M. F. PERUTZ

6 x 9″, xiii + 414 pages, 3 tables, 258 illus., 256 lit.refs., 1966,
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AN AUTOMATIC METHOD FOR INJECTION ENTHALPIMETRY

(in French)

A completely automatic apparatus based on injection enthalpimetry is described. The sample is taken automatically and reagent is added by means of pneumatic pipettes. The detector is a thermistor, and automation is achieved by means of a new servomechanism; a digital read-out can be provided. Typical applications were tested with oxidation–reduction, complexing and neutralisation reactions. The precision of the analyses was about 1%. Analyses are performed sequentially, either discontinuously or repetitively.

PH. GUILLOT,
Anal. Chim. Acta, 50 (1970) 499–504

THE DETERMINATION OF NICKEL, ZINC, COBALT AND MANGANESE IMPURITIES IN CADMIUM BY PULSE POLAROGRAPHY

A pulse-polarographic method for the simultaneous determination of traces of nickel, zinc, cobalt and manganese in cadmium and its compounds is described. Interference from the reduction of the cadmium matrix was eliminated by a prior electrolytic deposition of cadmium on a mercury cathode at a controlled potential of −0.90 V *vs.* S.C.E. Iron in excess interfered with the determination of cobalt and was therefore extracted from the electrolysed solutions. The polarographic determination was performed in 0.1 *M* lithium acetate–0.025 *M* lithium thiocyanate as supporting electrolyte. A sample weight of 10 g and a final volume of 10 ml allowed the determination of about 0.08 p.p.m. nickel, 0.01 p.p.m. zinc, 0.02 p.p.m. cobalt and 0.003 p.p.m manganese. Less than 0.01 p.p.m. nickel could be determined with a 0.25 *M* pyridine–0.05 *M* potassium chloride supporting electrolyte. Several synthetic samples and commercially available cadmium products were analysed.

E. TEMMERMAN AND F. VERBEEK,
Anal. Chim. Acta, 50 (1970) 505–514

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

PART VIII. THE ANALYSIS OF SULFIDE MINERALS AND ORES

(Short Communication)

F. J. LANGMYHR AND P. E. PAUS,
Anal. Chim. Acta, 50 (1970) 515–516

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

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

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Second International Symposium organized by the Chromatography
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SOME OBSERVATIONS ON THE DETERMINATION OF ZINC BY ATOMIC FLUORESCENCE SPECTROMETRY UNDER CONDITIONS FAVOURABLE FOR ANALYSIS

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M. S. Cresser and T. S. West,
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THE DETERMINATION OF CALCIUM IN STEEL BY OPTICAL EMISSION SPECTROMETRY

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A. C. Knott and C. B. Belcher,
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(Short Communication)

P. J. De Bièvre and G. L. Del Bino,
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A RAPID SOLVENT EXTRACTION METHOD FOR THE DETERMINATION OF CAESIUM-137 IN ENVIRONMENTAL MATERIALS

W. W. FLYNN

Australian Atomic Energy Commission Research Establishment, Lucas Heights, N.S.W. 2232 (Australia)

(Received February 18th, 1970)

It is customary to monitor the environment around any atomic energy activity to ensure that the level of discharge of radio-nuclides is controlled and kept below certain permissible values. One of the principal radio-nuclides involved in such a monitoring programme is caesium-137, which constitutes a danger because of its half-life (30 years) and the ease with which it enters the food-chain.

At present most methods for the determination of caesium-137 use either precipitation or ion exchange. Precipitation methods are mostly unsuitable for environmental analyses because of the difficulty in obtaining efficient separation in the presence of relatively large amounts of foreign ions, and ion-exchange methods are time-consuming. The need for a rapid solvent extraction method has long been apparent, but the difficulties in extracting the large caesium ion (effective radius 2.54 Å) and separating it from large amounts of potassium and sodium have so far proved a barrier to general use.

NIESE *et al.*[1] succeeded in extracting caesium from 0.5 *M* sodium nitrate solution at pH 1.7 with mono(2,9-diethyl-tridecyl-6)phosphoric acid in kerosene; but the distribution factor was only 3, and separation from potassium and sodium was poor. KYRS AND PODEŠVA[2] used nitrobenzene to extract the polyiodides, obtaining a separation factor of only 30–40 from potassium. BRAY AND ROBERTS[3] used dipicrylamine for the extraction of caesium-137 into nitrobenzene to obtain a highly selective separation at pH 9–13. At this pH, precipitation would present a problem when dealing with environmental samples.

RAIS *et al.*[4] extracted caesium with nitrobenzene in the presence of phosphomolybdic acid, but the distribution ratio was only 9.1 with an initial pH of 7.0. EGAN *et al.*[5] used 4-*sec.*-butyl-2-(α-methylbenzyl)phenol (BAMP), with various diluents to extract caesium, but required a pH of about 11.0 for good separation. A further study by BRAY[6] showed that a mixed extractant of BAMP with di(2-ethylhexyl)phosphoric acid (HDEHP) made the extraction of caesium possible at a lower pH.

An investigation of this synergetic effect with HDEHP was carried out at this laboratory to try to find a rapid solvent extraction method for the determination of caesium-137 in environmental materials. During the investigation, it was found that phenol had a synergetic effect with HDEHP similar to BAMP, enabling extraction to take place at about pH 2.0. However, the separation from potassium and sodium was poor. Subsequent investigation of possible extraction effects with phenol alone in various diluents showed that there was practically no extraction of caesium-137. A partial extraction with diluents of high dielectric constant led to further study which showed that the glassware had been contaminated with a small amount of an anionic detergent and that this was responsible for the extraction of caesium-137. On investigating this effect it was found that the addition of sodium dodecylbenzene sulphonate (the active agent in many anionic detergents) gave a distribution coefficient of above 1000 for caesium-137 at an optimum temperature of 15°. Phenol in nitrobenzene was used as the extractant at pH 2.0–10.0. Dimethyl sulphate could also have been used as an extractant but it undergoes hydrolysis and is more toxic than nitrobenzene.

With 0.01 *M* EDTA in 0.1 *M* lithium hydroxide as a wash, decontamination factors were 5000 for potassium and greater than 10,000 for sodium. Caesium-137 was effectively stripped from the organic phase with 6 *M* hydrochloric acid, and after evaporation to near dryness, caesium carrier was precipitated by the tin(IV) chloride method[7] to ensure complete decontamination from potassium-40 and sodium.

Quantitative recovery from standard solution was 80–85%. The accuracy of the method was established by comparative analyses of various types of environmental samples by the ammonium molybdophosphate ion exchange method[8] and by γ-spectrometry with an 8 x 4 in sodium iodide (Tl-activated) crystal.

EXPERIMENTAL

Apparatus

Intertechnique β-counter RA12 (2π gas flow, Geiger-Müller with end-window, anti-coincidence). When helium gas with 1.3% isobutane was used, the efficiency with a standard ^{137}Cs source was 35%. The background was 35 counts per h.

EKCO well-type γ-scintillation counter N664A, with sodium iodide phosphor (Tl-activated), and an EKCO 580F automatic scaler.

Reagents

^{137}Cs standard solution. 11.0 pCi ml^{-1}, obtained from the A.A.E.C. Radioisotopes Standards Section.

^{137}Cs tracer solution. Ca. $1.2 \cdot 10^3$ d.p.m. ml^{-1}.

Caesium carrier, 10.0 mg ml^{-1}. Dry caesium chloride at 110° for about 30 min. Weigh accurately 1.267 g, dissolve in demineralised water and dilute to 100 ml.

Phenol–nitrobenzene extractant. Weigh 376 g of A.R.-grade phenol into a 1-l beaker, dissolve in nitrobenzene with mechanical stirring, and dilute to 1.0 l.

EDTA stock solution. Weigh 37.2 g of A.R.-grade ethylenediaminetetraacetic acid (disodium salt) into a 1-l beaker, and dissolve in about 500 ml of demineralised water. Weigh 21.0 g of lithium hydroxide monohydrate and dissolve in the EDTA solution. Dilute to 1.0 l.

EDTA wash solution. Dilute 100 ml of stock solution to 1 l with demineralised water.

Tin(IV) chloride solution. Saturate a 1:1 mixture (v/v) of 10 *M* hydrochloric acid and ethanol with A.R.-grade tin(IV) chloride.

Sample pretreatment

Effluent, rainwater, riverwater. Add 20.0 mg of caesium carrier to an aliquot of the sample (usually about 2 l), then add 10 ml of concentrated nitric acid and 10 ml of 70% perchloric acid. Evaporate to about 20 ml, transfer to a 250-ml beaker and take to near dryness. Add 50 ml of 1.0 *M* hydrochloric acid, heat to dissolve, and cool.

Vegetation (grass, leaves, seaweed, vegetables). Dry in an air oven, and ash at 450° in a muffle furnace until the sample is free from excessive carbon. Weigh accurately 2–5 g of ashed sample into a 250-ml beaker, and add 20.0 mg of caesium carrier and 50 ml of 5 *M* hydrochloric acid. Cover with a watch glass and heat to boiling. Simmer for 30 min, filter through a sintered glass filter (porosity 4) to remove any carbon, and evaporate the filtrate to near dryness. Add 50 ml of 1.0 *M* hydrochloric acid, heat to dissolve, then cool.

Milk, oyster flesh, fish. Dry, ash in a muffle furnace at 450° until the sample is free from excessive carbon. Weigh accurately about 10 g of ashed sample into a 250-ml beaker, add 20.0 mg of caesium carrier and 100 ml of 5 *M* hydrochloric acid, and treat in the same manner as vegetation. Evaporation must be carried out cautiously to avoid spattering.

Extraction

Add 5 ml of aqueous 10% (w/v) ascorbic acid to the solution. Adjust the pH to 2.0 with aqueous 5% (w/v) lithium hydroxide. Transfer to a 250-ml separating funnel in a fume hood and add 25 ml of 5% (w/v) sodium dodecylbenzene sulphonate in demineralised water. Shake for about 15 sec. Add 50 ml of phenol–nitrobenzene extractant, shake for 1 min and allow to settle. Transfer the organic phase to another 250-ml separating funnel, and repeat the extraction of the aqueous phase by adding another 25 ml of 5% dodecylbenzene solution and shaking again with 50 ml of phenol–nitrobenzene extractant. Allow to settle, and discard the aqueous phase.

To the combined organic solutions add 100 ml of EDTA wash solution. Shake for 1 min and allow to settle. Transfer the organic phase to another 250-ml separating funnel and discard the aqueous solution. Wash with a further 100 ml of EDTA solution and again allow to settle. Discard the aqueous phase.

Add 50 ml of 6 *M* hydrochloric acid to the organic phase and shake for 1 min. Allow to settle, then run the organic phase into another separating funnel, and repeat the stripping step. Discard the organic phase.

Wash the combined hydrochloric acid solutions with 50 ml of diethyl ether (A.R. grade) by shaking for 1 min. Allow to settle and run the aqueous phase into a 250-ml beaker. Discard the ether. Place the beaker on a water bath and evaporate off any ether before transferring to a hot plate. Evaporate to about 2 ml, and add 5 ml of concentrated hydrochloric acid. If necessary, heat to dissolve, then cool and transfer to a 40-ml centrifuge tube. Wash the beaker with 5 ml of ethanol, and add 2 ml of saturated tin(IV) chloride solution to the combined hydrochloric acid–ethanol solution. Stir with a glass rod and allow to stand for 5 min. Centrifuge and discard the supernate. Add 10 ml of 10 *M* hydrochloric acid–ethanol (1:1) solution, stir with a glass rod, and centrifuge. Discard the supernate.

Add about 5 ml of 0.4 *M* hydrochloric acid in ethanol, stir with a glass rod and filter through a previously weighed Whatman No. 42 filter paper, using a special filter stick[9]. Wash with a further 5 ml of the ethanolic 0.4 *M* hydrochloric acid solution, and then with 10 ml of diethyl ether. Allow to suck dry and remove the filter paper. Transfer to a special mount[10] and dry under an infrared lamp for about 30 sec. Cool, weigh and then count in a low-background β-counter.

DISCUSSION

To conserve reagents the original investigations were carried out on a reduced scale. Extractions from 25 ml of aqueous solution with 10 ml of solvent were done in a 40-ml centrifuge tube to facilitate separation. A caesium-137 tracer was used to determine distribution ratios by counting the barium-137m daughter in a well γ-scintillation counter. A delay of 20 min was necessary before counting to enable the barium-137 m to reach equilibrium.

At the start of the investigation of the effect of a small amount of anionic detergent on extraction, a commercially available laboratory detergent with sodium dodecylbenzene sulphonate as its active agent was used. The acquisition of the actual reagent gave no improvement in extraction compared to the commercial product. Almost complete extraction of caesium was obtained with 5–14 mg of sodium dodecylbenzene sulphonate per ml of aqueous solution (Fig. 1). A 2.0 *M* phenol concentration in nitrobenzene gave good extraction and no improvement was found with higher concentrations. In the pH range 2.0–10.0, recovery of caesium was con-

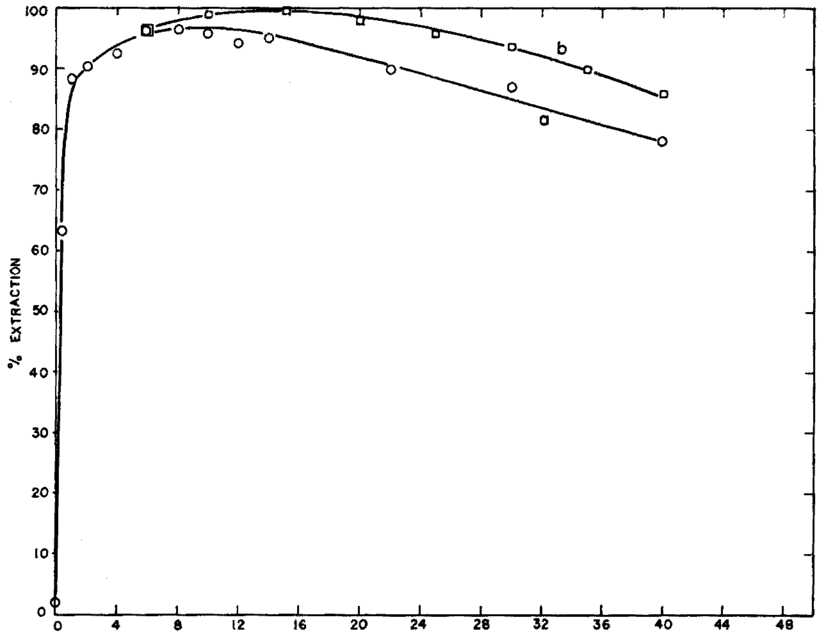

Fig. 1. (a) Effect of sodium dodecylbenzene sulphonate on extraction of ^{137}Cs from 25 ml of aqueous solution containing 0.1 g of ascorbic acid and 2 mg of caesium carrier at pH 3.2, with 10 ml of 4.0 *M* phenol in nitrobenzene (○). (b) Effect of temperature on extraction of ^{137}Cs from 25 ml of aqueous solution containing 0.1 g of ascorbic acid, 0.25 g of dodecylbenzene sulphonate, and 2 mg of caesium carrier at pH 3.2, with 10 ml of 4.0 *M* phenol in nitrobenzene (□).

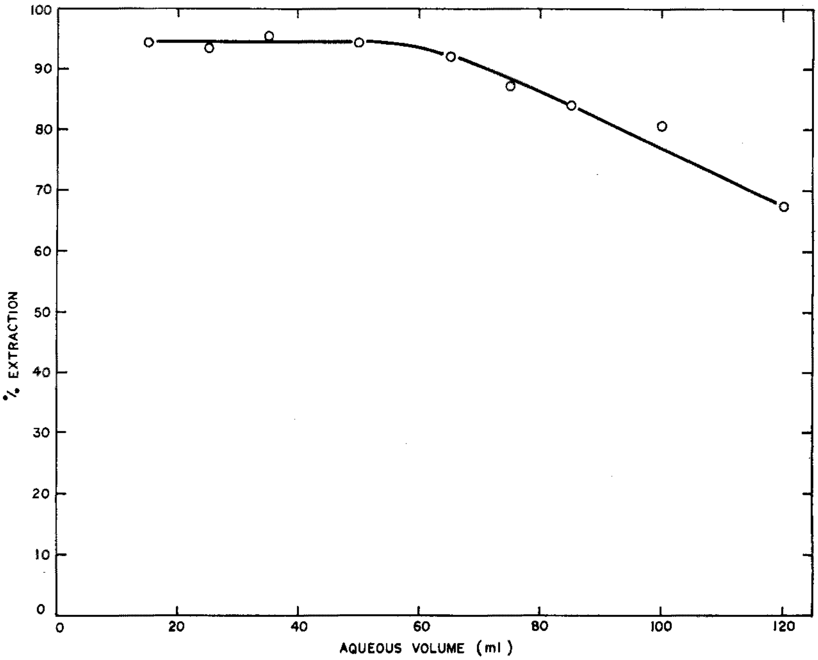

Fig. 2. Effect of aqueous volume on extraction of ^{137}Cs. Conditions as for Fig. 1, curve b.

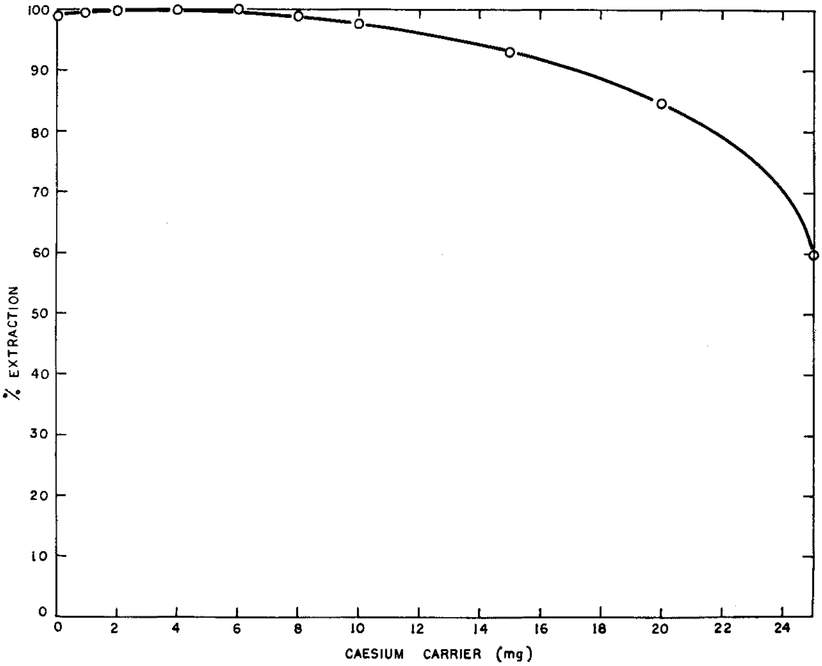

Fig. 3. Effect of caesium carrier on extraction of ^{137}Cs from 25 ml of aqueous solution. Conditions as for Fig. 1, curve b.

TABLE I

DECONTAMINATION FACTORS FOR VARIOUS RADIO-NUCLIDES

Radio-nuclide	*Decontamination factor*	*Radio-nuclide*	*Decontamination factor*	*Radio-nuclide*	*Decontamination factor*
^{133}Ba	$>$ 10,000	^{22}Na	$>$ 10,000	^{85}Sr	$>$ 5,000
^{144}Ce	$>$ 1,000	^{231}Pa	$>$ 2,000	^{90}Sr–^{90}Y	$>$ 10,000
^{60}Co	$>$ 3,000	^{226}Ra	$>$ 300	^{234}Th	$>$ 5,000
^{203}Hg	$>$ 800	^{87}Rb	3	^{238}U	$>$ 10,000
^{40}K	$>$ 10,000	^{106}Ru	$>$ 1,000	^{95}Zr–^{95}Nb	$>$ 3,000

TABLE II

EFFECT OF VARIOUS ELEMENTS ON ^{137}Cs EXTRACTION

(Extraction from 25 ml of aqueous solution at pH 2.5–3.5 containing ^{137}Cs solution, 0.1 g of ascorbic acid, 2 mg of caesium carrier, 0.25 g of sodium dodecylbenzene sulphonate and foreign ion with 10 ml of 4.0 *M* phenol in nitrobenzene)

Foreign ion	*Amount present (mg)*	*Added as*	*^{137}Cs recovery (%)*[a]
Al^{3+}	50	$Al_2(SO_4)_3$	85.1
	25		88.7
Ba^{2+}	100	$BaCl_2$	95.8[b]
Br^-	250	HBr	89.1
	125		95.5
Ca^{2+}	50	$CaCl_2$	85.8
	25		91.9
Cl^-	250	LiCl	86.6
	125		91.8
Co^{2+}	50	$Co(NO_3)_2$	92.6
	25		94.9
Cr^{2+}	50	$CrCl_2$	78.5
	25		85.7
Cu^{2+}	50	$Cu(NO_3)_2$	89.7
	25		95.6
Fe^{3+}	50	$FeCl_3$	86.3
F^-	50	HF	95.4
Hg^{2+}	50	$HgCl_2$	95.0
I^-	250	HI	94.4
K^+	25	KCl	87.4
	10		94.5
La^{3+}	25	$La(NO_3)_3$	86.4
Li^+	50	LiCl	86.6
	25		91.3
Mg^{2+}	50	$MgCl_2$	82.5

Foreign ion	*Amount present (mg)*	*Added as*	*^{137}Cs recovery (%)*[a]
Mn^{2+}	50	$MnCl_2$	84.6
Na	50	NaCl	90.5
	25		96.3
Ni^{2+}	50	$NiSO_4$	87.6
Pb^{2+}	50	$Pb(NO_3)_2$	96.4[b]
Rb^+	50	RbCl	84.2
	10		94.9
Sb^{3+}	10	$SbCl_3$	92.4[b]
Sn^{2+}	10	$SnCl_2$	89.2[b]
Sr^{2+}	50	$Sr(NO_3)_2$	88.1
Y^{3+}	10	$Y(NO_3)_3$	88.7[b]
Zn^{2+}	50	$ZnCl_2$	81.6[b]
Zr^{4+}	50	$Zr(SO_4)_2$	94.5
H_3BO_3	1000		95.5
$HClO_4$	100		96.8
NH_4Cl	100		36.8
NO_3^-	200	HNO_3	95.5
PO_4^{3-}	200	H_3PO_4	95.1
SO_4^{2-}	200	Na_2SO_4	92.6
Acetic acid	250		98.4
Ascorbic acid	500		96.3
	0		99.5
Citric acid	100		89.4
Oxalic acid	100		89.2
Tartaric acid	100		97.9

[a] Corrected for temperature.

[b] Precipitate present on extraction.

stant, lithium hydroxide being used to adjust the pH. An investigation of the effect of temperature showed that the optimum for extraction was 15° (Fig. 1), and that the discrepancies in recovery from day to day were mainly due to fluctuations in room temperature. An aqueous-to-organic ratio of 5:1 was found possible before loss of caesium became evident (Fig. 2), and the presence of as much as 0.6 mg of caesium carrier per 1.0 ml of extractant did not reduce the recovery (Fig. 3).

Two washes with 0.01 *M* EDTA in 0.1 *M* lithium hydroxide were used to ensure the complete removal of any interfering ions and radio-nuclides. Phase separation was slow but only about 2% of the caesium was lost in each wash. The presence of a small amount of the wash solution in the organic phase gave sodium contamination in the final solution, but the use of the tin(IV) chloride precipitation ensured a sodium-free precipitate.

Two strips of the washed organic phase with hydrochloric acid gave full recovery of caesium. The use of ether to remove traces of organic phase from the hydrochloric acid scavenges proved effective.

The tin(IV) chloride method for the precipitation of caesium gave decontamination from as much as 200 mg of sodium and potassium. This procedure enabled the final decontamination factor for potassium-40 to reach 10^4 or more (Table I). A study of some of the radio-nuclides commonly encountered showed decontamination factors in excess of 10^3 for most.

Recovery from grass and effluent samples was in the range 70–80%, but the larger sample aliquot necessary to determine caesium-137 in milk, fish and oyster flesh (10–15 g) reduced the recovery to 40–50%. Precipitation on addition of the sodium dodecylbenzene sulphonate did not interfere with the extraction. Ashing was carried out at 450° to avoid loss of caesium-137.

The time taken for extraction and precipitation of six samples was 3–4 h. The efficiency of the 2π gas flow β-counter with a standard caesium-137 source was 32% with a caesium chlorostannate precipitate of 0.1–0.2 mg/mm^2.

TABLE III

COMPARATIVE ANALYSES OF SOME ENVIRONMENTAL MATERIALS

Sample	*Weight of ash (g)*	*Extraction recovery (%) of Cs carrier*	*^{137}Cs activity (pCi g^{-1} ash)*		
			γ-Spectrometry[a]	*Ion exchange*[b]	*Phenol extraction*
Grass	2.0	73.0	8.4	5.5	4.8
		72.4	7.4	4.4	3.2
		66.8	2.1	1.2	0.9
Milk	10.0	50.3	0.76	0.78	0.58
		46.3	1.53	0.71	0.70
		41.4	0.71	0.92	0.94
	5.0	60.5	0.71	0.92	1.0
Sand	100	74.0	1.50	—	1.90
Effluent	1.0	80.3	—	33.1[c]	32.1[c]
	litre	75.7	—	113[c]	113[c]
		63.4	—	62.2[c]	59.8[c]

[a] Analyses by A. DUDAITIS, A.A.E.C. Lucas Heights, Australia.
[b] Ammonium molybdophosphate method.
[c] pCi l^{-1}.

The method is suitable for samples which contain large quantities of various ions (Table II) and good agreement was found with results obtained by other methods for various types of environmental samples (Table III).

SUMMARY

A solvent extraction method for the quantitative determination of caesium-137 in environmental samples is described. Caesium carrier is added to the ashed sample, which is dissolved with hydrochloric acid. The solution is filtered to remove any carbon and the pH is adjusted to 2.0. Sodium dodecylbenzene sulphonate is added and the extraction is done with phenol–nitrobenzene mixture. The organic phase is washed with EDTA solution and the caesium is stripped from the washed solvent with 6 *M* hydrochloric acid. The caesium is precipitated as caesium chlorostannate to ensure absolute decontamination from potassium-40. Recovery from standard solution is about 85% and from vegetation, rainwater and effluent samples about 80%. The method is applicable in the presence of large quantities of interfering ions, and decontamination factors for many nuclides are greater than 10^3.

RÉSUMÉ

Une méthode par extraction dans un solvant est décrite pour le dosage du césium-137 dans des échantillons d'environnement. Du césium marqué est ajouté à l'échantillon incinéré, que l'on dissout dans l'acide chlorique. La solution est filtrée pour éliminer le carbone; le pH est ajusté à 2.0. On ajoute du dodécylbenzène-sulfonate de sodium et on effectue l'extraction à l'aide d'un mélange phénol–nitrobenzène. La phase organique est lavée au moyen d'une solution d'EDTA; le césium est séparé du solvant par l'acide chlorhydrique 6 *M*. On précipite ensuite le césium sous forme de chlorostannate pour garantir une décontamination absolue d'avec le potassium-40. Cette méthode est applicable en présence de grandes quantités d'ions gênants; les facteurs de décontamination pour de nombreux nucléides sont supérieurs à 10^3.

ZUSAMMENFASSUNG

Es wird eine Extraktionsmethode für die quantitative Bestimmung von Cäsium-137 in Umgebungsproben beschrieben. Zu der veraschten Probe, die in Salszäure gelöst wird, wird Cäsium als Träger gegeben. Die Lösung wird zur Entfernung von Kohlenstoff filtriert und der pH-Wert auf 2.0 eingestellt. Nach Zugabe von Natriumdodecylbenzolsulfonat wird mit einem Phenol–Nitrobenzol-Gemisch extrahiert. Die organische Phase wird mit EDTA-Lösung gewaschen und das Cäsium mit 6 *M* Salzsäure aus dem gewaschenen Lösungsmittel reextrahiert. Das Cäsium wird als Cäsiumchlorostannat gefällt, um eine absolute Dekontamination von Kalium-40 sicherzustellen. Der wiedergewonnene Anteil einer Standardlösung beträgt etwa 85% und der von Pflanzen- und Regenwasserproben etwa 80%. Die Methode ist auch bei grossen Mengen störender Ionen anwendbar, die Dekontaminationsfaktoren für viele Nuklide sind grösser als 10^3.

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THE DETERMINATION OF LEAD BY ATOMIC FLUORESCENCE SPECTROSCOPY

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With a double beam system and an air–hydrogen flame maintained on a triple-slot burner, a detection limit of 0.02 p.p.m. of lead has been reported by atomic absorption measurements at 217.00 nm[1], whilst in flame photometry in a nitrous oxide–acetylene flame a detection limit of 0.2 p.p.m. at 405.8 nm is obtainable[2]. However, the determination of lead is frequently required at concentration levels below these. Atomic fluorescence signals for lead in flames have previously been recorded using electrodeless discharge tubes[3,4] or a demountable hollow-cathode lamp[5] as source. The best of these systems[4] gave a limit of detection of 0.06 p.p.m. lead in aqueous solution.

This paper describes a detailed investigation of the atomic fluorescence spectrum of lead in a number of analytically useful flames and also evaluates the effectiveness of adding argon as a diluent to the flames in order to improve the sensitivity. Furthermore, a study of the analytical growth curves for resonance and direct-line fluorescence emissions shows the slope and shape of the curves to be highly dependent on the nature of the optics used in the experimental arrangement.

EXPERIMENTAL

The apparatus used was similar to that described in previous communications[6,7]. A Perkin-Elmer 290 atomic absorption spectrophotometer was used in its emission mode in conjunction with a microwave-excited (2450 MHz) electrodeless discharge tube source, electronically modulated at 50 Hz in phase with the a.c. amplifier of the spectrophotometer.

Certain refinements were made to the optical system.

(*a*) Focussing of the source onto the flame is accomplished with a set of four spherical lenses of "Spectrosil" grade B, giving an effective focal length in combination of *ca.* 30 mm and producing an image of the source in the flame at a 1:1 magnification. A double pass of this beam back through the flame is obtained with a 65-mm diameter front-silvered concave mirror (source mirror) positioned 82 mm behind the flame with the centre of the flame falling at the centre of curvature of the mirror.

(*b*) A cone of fluorescent radiation emitted at right angles to the incident beam is reflected back into the monochromator, the light path taking it first through the flame, by another mirror of 125 mm diameter (field mirror). Again, the flame lies at the centre of curvature of the (field) mirror.

The mirrors and lenses are all rigidly mounted to the spectrophotometer, but spring seatings allow variable tilt for fine control of the optical alignment.

Electrodeless discharge lamp

The detailed preparation of these sources for lead has been described previously[8]. A few of the sources examined showed a tendency to decrease in intensity by up to a factor of three over a 100-h running period; this is probably caused by the use of too large an excess of free metal in their construction. The excess of metal plates-out on the inside of the tube and shields the plasma from the exciting microwave field. The majority of sources, however, showed little change in output over extended running periods and these were quite suitable for use in atomic fluorescence measurements. A 3/4 wave cylindrical (Broida) cavity was used throughout this study.

A recent development of a version of this cavity, which incorporates provision for more efficient tuning, gives a strong emission spectrum characteristic of lead from tubes containing lead metal alone[9]. It is likely that problems involving efficient coupling previously experienced with lead and lead iodide tubes may thus be overcome.

RESULTS AND DISCUSSION

Sensitivities in different flames

The relative intensities of all the measurable fluorescent lines were examined in the $A/O_2/H_2$, air/acetylene and nitrous oxide/hydrogen flames. These results are shown in Table I, together with the relative source intensity at each wavelength. A consideration of earlier studies[7] with theoretical expressions[10] leads to the expectation that the best detection limits for a readily atomised element such as lead should

TABLE I

ATOMIC FLUORESCENCE INTENSITIES FOR LEAD IN DIFFERENT FLAMES[a]

Wavelength (nm)	*Spectral term values (K)*		*Relative source intensity*[b]	*Relative fluorescence signal*[b]		
	Lower state	*Upper state*		*$A/O_2/N_2$*[c]	*Air/C_2H_2*[d]	*N_2O/H_2*[e]
283.3	0	35287	34.3	52.5	18.1	6.63
364.0	7819	35287	14.7	16.1	5.21	2.31
368.3	7819	34960	70.5	7.61	0.82	1.25
405.8	10650	35287	100	100	36.3	15.0
722.9	21458	35287	77.1	65.2	14.1	3.52
217.0	0	46069	0.41	3.21	2.90	1.40
261.4[f]	7819	46069	18.8	4.00	2.75	1.15
280.2	10650	46329	17.2	2.65	2.25	1.02
282.3	10650	46061	32.8	2.23	1.38	0.75
287.3	10650	45443	4.43	1.31	0.54	—
402.0	21458	46329	4.75	0.65	—	—
406.2	21458	46069	5.33	—	—	—

[a] Solution of 5 μg/ml lead sprayed. Spectral bandpass of 0.2 nm. All intensities corrected for spectral response of system from manufacturer's data.
[b] Taken relative to 405.8 nm as 100.
[c] H_2 8.0 l min^{-1}; O_2 0.65 l min^{-1}; A 7.7 l min^{-1}.
[d] C_2H_2 1.6 l min^{-1}; air 9.0 l min^{-1}.
[e] H_2 16.5 l min^{-1}; N_2O 7.5 l min^{-1}.
[f] Sum of two unresolved lines at 261.37 and 261.42 nm.

occur in the $A/O_2/H_2$ flame. This was confirmed experimentally. However, an observation of some interest is that the most intensely emitted line in all flames occurs at 405.8 nm, which is a direct-line fluorescence emission and would be expected[11] to be less intense than the resonance line at 283.3 nm according to the relationship:

$$I\,(\text{d.l.f.}) = \frac{\lambda_a}{\lambda_f}\, I\,(\text{r.f.})$$

where λ_a and λ_f are the wavelengths of the absorbed and fluoresced light, respectively. In fact, the direct line at 405.8 nm is 1.9 times more intense than the resonance line at 283.3 nm in the $A/O_2/H_2$ flame, 2.0 times more intense in an air/C_2H_2 flame and 2.3 times more intense in a N_2O/H_2 flame.

This divergence from the results which would be expected by application of the above formula can be accounted for in several ways. When an electrodeless discharge source is focussed onto a flame, such that the image size is less than the flame diameter, then the expression for the intensity ratios of the direct and resonance fluorescence processes must take into account the differential absorption by the atoms in the unirradiated part of the flame at the two wavelengths considered. Thus:

$$\frac{I\,(\text{d.l.f.})}{I\,(\text{r.f.})} = \frac{\lambda_a}{\lambda_f}\,\frac{fz\,(\text{d.l.f.})}{fz\,(\text{r.f.})}$$

where fz (d.l.f.) and fz (r.f.) are factors to allow for the re-absorption of the direct-line and resonance fluorescence emissions, respectively. The atomic absorption coefficient at the wavelength of the direct-line emission will be small and so fz (d.l.f.) may be taken as unity. But as $fz\,(\text{r.f.}) < 1$, then I (d.l.f.)/I (r.f.) will be greater than predicted from the ideal case.

A further complicating factor is that the focussed radiation from such a source is not truly isotropic, an assumption implicit in all expressions for fluorescence intensity[12]. This will be less important where the source image size is greater than the flame diameter or where the radiation is not focussed. However, a quantitative evaluation of this effect is difficult.

It would also be expected that the ratio (I 405.8 nm)/(I 283.3 nm) should increase with increasing flame temperature. This may be partially accounted for by the rise with increasing temperature in the thermal population of the $^3P_2$ level (*cf.* the fluorescence characteristics of Ga, In and Tl[11] and Sn[7]), which lies 1.320 eV above the ground state. At 2100°, the ratio N^3P_2/N^3P_0 will be 0.0017, and at 2800° this will rise to 0.0061. Resonance fluorescence should then occur at 405.8 nm, after excitation from this thermally populated level.

Addition of argon to flame gases

The replacement of atmospheric nitrogen in the flame gases, which may quench fluorescence, produces an increase in the atomic fluorescence signal; thus the use of an $A/O_2/H_2$ mixture is to be preferred to the air/hydrogen flame. Lead is considerably atomised even in low temperature flames[13] and the substitution of argon in the flame gas mixture gives a reduction in quenching without implications arising from changes in the free atom fraction; however, the addition of argon is restricted by the flame stability. The addition of 40% of argon (by volume in the unburned flame gases) also produces an almost exactly corresponding percentual increase in the atomic fluorescence emission in both air/acetylene and nitrous oxide/hydrogen flames.

The relative fluorescence intensities at 405.8 nm in these flames containing an optimal volume of argon are shown in Table II; the values for the air/hydrogen and air/propane flames are also given, together with the corresponding gas flow rates.

The atomic fluorescence signal varies only slightly with fuel flow or height of measurement in the flame; generally measurements were taken 20 mm above the top of the burner head.

TABLE II

EFFECT OF FLAME GASES ON ATOMIC FLUORESCENCE AT 405.8 nm COMPARED TO $A/O_2/H_2$ FLAME

Flame	*Relative signal*
$A/O_2/H_2$	1.00
Air/H_2[a]	0.33
$A/N_2O/H_2$[b]	0.29
$A/Air/C_2H_2$[c]	0.45
Air/C_3H_8[d]	0.36

[a] H_2 8.0 l min^{-1}; air 3.5 l min^{-1}.
[b] H_2 11.2 l min^{-1}; N_2O 7.5 l min^{-1}; A 12.5 l min^{-1}.
[c] C_2H_2 1.6 l min^{-1}; air 9.0 l min^{-1}; A 8.0 l min^{-1}.
[d] C_3H_8 1.5 l min^{-1}; air 9.5 l min^{-1}.

Analytical curves and the influence of mirrors

In spite of the wide use of optical arrangements similar to that described above, no previous mention appears to have been made of the influence of the mirrors on the shape of the analytical atomic fluorescence curves. Metal atoms in the flame will absorb resonance radiation from the source preferentially compared with the other wavelengths. Consequently, the light reflected from the source mirror will be weaker in this component than the original radiation reaching the flame. Neglecting thermally assisted processes, this will produce an equal fractional reduction in the intensities of the resonance and direct-line fluorescence emissions reaching the detector which result from the second pass of the same light through the flame. Accordingly, only at low atomic concentrations in the flame will the source mirror approximately double the atomic fluorescence signal. This improvement will therefore tend to reduce with increasing concentration, but equally at all wavelengths. The incidence of curvature is advanced by the use of a source mirror.

Similarly, the light reflected from the field mirror will lose more of its resonance component than its direct-line component on passing through the flame. However, in contrast to the previous case, radiation then passes directly into the monochromator and that portion of the radiation reaching the detector from the field mirror will have a resonance component which reduces in intensity, with respect to the direct-line component, with increasing atom concentration in the flame.

In summary, the analytical curves obtained using the source mirror only, are initially of a steeper gradient than without the mirror, but they bend more rapidly towards the concentration axis; with the field mirror this effect is more marked for the resonance than for the direct-line atomic fluorescence emissions. The results obtained for lead are clearly shown in Fig. 1.

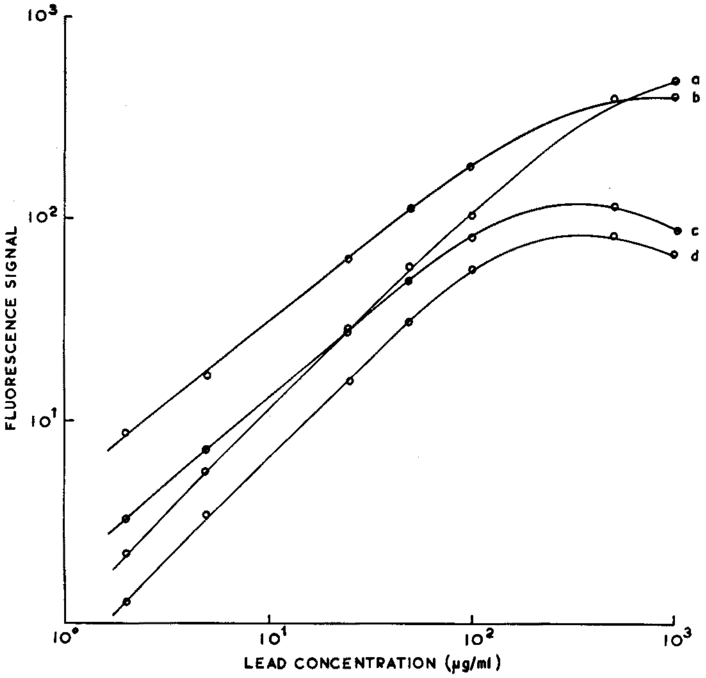

Fig. 1. Analytical curves for atomic fluorescence of lead in $A/O_2/H_2$ flame. (a) Without field mirror at 405.8 nm; (b) with field mirror at 405.8 nm; (c) with field mirror at 283.3 nm; (d) without field mirror at 283.3 nm.

Detection limit

In a separated $A/O_2/H_2$ flame, at 405.8 nm, a detection limit (defined as signal: noise = 1) of 0.01 p.p.m. of lead in aqueous solution was obtained. This compares with an atomic absorption detection limit of 0.1 p.p.m. achieved using the same instrument in its normal absorption mode with an optimised 5-cm air/hydrogen flame and measuring at the most sensitive absorption line at 217.0 nm. For the atomic fluorescence of lead, a better detection limit (*ca.* 4-fold) is obtained with the above mirrors in position. However, it must be remembered that the mirrors will influence the detection limit to a varying degree depending on the level of the background emission from the flame.

The total noise in the final signal may be represented as the sum:

$$NE + NP.M. + NF + NS + NR = N\ TOTAL$$

where NE is the electronic noise in amplifier etc., NP.M. is the photomultiplier noise (essentially shot noise), NF is the noise caused by local fluctuations in the atomic concentration in the flame (flame turbulence, statistical fluctuations in the spray supply to flame, etc.), NS is the noise on the fluorescence signal caused by source fluctuations, and NR is the noise contribution associated with the background radiation from the flame.

Under analytical conditions, the use of the source mirror will not alter the noise components NS or NF as a percentage of the total signal; NP.M., being essentially due to shot noise, will increase as the square root of the increased signal. The field mirror, however, as it collects unwanted background radiation at the analytical wavelength in addition to the modulated atomic fluorescence signal will cause an increase in NP.M., not only as the square root of the increased atomic fluorescence, but also with a component arising as the square root of the increased background. The noise NF will also contribute where there is appreciable re-absorption by the flame (see above); NE and NR will remain constant. This means that at all levels of background radiation, the use of both mirrors is advantageous to the detection limit, but the usefulness of the field mirror will decrease with increasing flame background radiation and increasing noise (NR) associated with it.

Interferences

The effects of 500 p.p.m. of 30 cations and anions on 5 p.p.m. of lead were studied under optimised conditions (Table III). At a $H_2:O_2$ ratio of 8.4:1 ($H_2:A = 1:1$) only aluminium interfered significantly (43% drop in signal). By lowering the $H_2:O_2$ ratio to 5.3:1 ($H_2:A$ kept constant) this interference was removed, but only at the expense of introducing interferences from calcium (−20%) and magnesium (−4%).

TABLE III

INTERFERENCES IN THE $A/O_2/H_2$ FLAME

(5 p.p.m. of lead and 500 p.p.m. of diverse ions)

No interference[a]	*Interference signal change (%)*	
Ba, Ca, Cd, Co, Cs,	Na	+ 5
Cu, Fe(III), Hg, Li, Mg,	K	+ 5
Mn, Ni, NH_4, Sn, Rb,	Al	−43
Ti(IV), Tl, Zn, Zr,	SO_4^{2-}	− 4
Br^-, citrate, Cl^-,		
I^-, MnO_4^-, NO_3^-, PO_4^{3-}		

[a] Producing a change less than twice the standard deviation at this concentration level (2%).

Conclusions

This study confirms that lead can be determined more sensitively by atomic fluorescence than by atomic absorption or flame photometry. The fact that the direct-line fluorescence signal at 405.8 nm is more sensitive than the best signal quoted for flame photometry even at this wavelength, which is well clear of the ultraviolet region, illustrates one instance where the superiority of the fluorescence technique is not restricted exclusively to the ultraviolet region. The freedom of the fluorescence technique from interatomic quenching and chemical interferences is again demonstrated in this study.

We are grateful to the S.R.C. for the award of a C.A.P.S. grant to one of us (R.F.B.) and to Perkin Elmer (Beaconsfield) for the loan of the apparatus used in this study.

SUMMARY

The atomic fluorescence characteristics of lead are described in air–acetylene, nitrous oxide–hydrogen and argon–oxygen–hydrogen flames. An electrodeless discharge tube is used as the source of excitation. A detection limit of 0.01 μg/ml of lead in aqueous solution is obtained by measurement of the direct-line fluorescence at 405.8 nm in the argon–oxygen–hydrogen flame. The effect of 100-fold excesses of 30 cations and anions is examined: only aluminium interfered significantly. Effects of multipass optics and signal collection mirrors are examined and their effect on signal-noise ratios is discussed.

RÉSUMÉ

On décrit les caractéristiques de fluorescence atomique du plomb dans les flammes air–acétylène, oxyde nitreux–hydrogène et argon–oxygène–hydrogène. Un tube à décharge sans électrode est utilisé comme source d'excitation. On obtient une limite de détection de 0.01 μg/ml de plomb en solution aqueuse, en mesurant la raie de fluorescence directe à 405.8 nm, dans une flamme argon–oxygène–hydrogène. On a examiné l'influence de 30 cations et anions en proportion 100:1. Seul l'aluminium interfère. On a examiné également l'optique de l'appareil et son influence.

ZUSAMMENFASSUNG

Es wird das Atomfluoreszenzverhalten von Blei in Luft–Acetylen-, Distickstoffoxid–Wasserstoff- und Argon–Sauerstoff–Wasserstoff-Flammen beschrieben. Eine elektrodenlose Entladungsröhre wird als anregende Strahlungsquelle benutzt. In wässriger Lösung beträgt die Nachweisgrenze des Bleis 0.01 μg/ml, wenn die Resonanzfluoreszenz bei 405.8 nm in der Argon–Sauerstoff–Wasserstoff-Flamme gemessen wird. Der Einfluss eines 100-fachen Überschusses von 30 Kationen und Anionen wurde geprüft, wobei nur Aluminium störte. Die Wirkung von Optiken für mehrfachen Durchgang und von Signal-Sammelspiegeln wurde untersucht und deren Einfluss auf das Signal:Rausch-Verhältnis erörtert.

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SOME OBSERVATIONS ON THE CHEMILUMINESCENCE OF ATOMS IN ACETYLENE FLAMES SUPPORTED BY AIR AND ARGON–OXYGEN MIXTURES

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Thermal emission measurements of atomic radiations in flames are usually taken from the interconal region where the flame gases are effectively in thermal equilibrium and the intensity of the emission of metal atoms can be calculated by means of the Boltzmann equation. The emission of lines with excitation energies >4.0 eV is usually very weak unless a very hot flame is used. Even with an air-diluted premixed oxy–acetylene flame, FASSEL AND GOLIGHTLY[1] obtained limits of detection for the far u.v. lines of arsenic, antimony and bismuth that were relatively high (>20 p.p.m.).

DEAN AND CARNES[2] have observed chemiluminescent emission of all these elements in the primary reaction zone of turbulent oxy–acetylene flames used in conjunction with organic solvents, obtaining detection limits of 2.2, 1.0 and 6.4 p.p.m. respectively. GILBERT[3] has observed chemiluminescent emission of many elements from turbulent air–hydrogen flames with solutions containing isopropanol. ZHITKEVICH *et al.*[4] have observed chemiluminescence from the primary reaction zone of an air–acetylene flame burning on a 120-mm slot burner by using aqueous solutions in conjunction with a spectrograph and a photographic plate. Chemiluminescence was observed from 25 elements, but no limits of detection were reported. MAVRODINEANU AND BOITEUX have also observed chemiluminescent emission of many elements from the primary cone of an air–acetylene flame[5].

This paper deals with the chemiluminescent emission of aqueous solutions of various elements from the reaction zones of air–acetylene (AA) and 85% argon–15% oxygen–acetylene (AOA) flames maintained on open tube burner ports. Good limits of detection were obtained for a number of elements.

The limits of detection in the AOA flame showed a decrease as the argon: oxygen ratio was decreased, thus causing the temperature to increase. This probably arises because chemiluminescent emission from metal species is usually the result of highly energetic reactions occurring in the primary reaction zone of the flame. The energy liberated by these reactions is transferred to a third body, *i.e.* either directly to a metal atom, or initially to a flame gas molecule or free radical which then transfers its energy, by collision, to a metal atom[5].

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For example

$$C_2H_2+O_2 \xrightarrow[\text{various reactions}]{M} Q+R+M^*$$

and/or

$$\begin{aligned} C_2H_2+O_2 &\rightarrow Q+R+S^* \\ S^*+M &\rightleftharpoons M^*+S \\ M^* &\rightarrow M+h\nu \end{aligned}$$

where M is a metal species and Q, R and S are flame gas molecules.

The excitation of metal atoms by these processes would not be expected to be very dependent on the overall temperature of the flame. In hydrogen flames the relatively weak chemiluminescence observed for certain metal additives has been explained by radical recombination reactions[6]:

$$\begin{aligned} H+H+M &\rightarrow H_2+M^* \ (+4.5 \text{ eV}) \\ H+OH+M &\rightarrow H_2O+M^* \ (+5.1 \text{ eV}) \end{aligned}$$

The strengths of the H_2O and H_2 bonds limit the amount of energy liberated to *ca.* 5 eV[5]. Thus negligible chemiluminescence is observed with excitation energies greater than 5 eV in hydrogen flames.

The intensity of any emission that is in thermal equilibrium should be independent of the nature of the flame gases (assuming negligible compound formation in the flame), and should increase exponentially with temperature. Thus an increase in temperature will tend to increase the flame background signal and the very small thermal emission signal of the metal species, but hardly increase the chemiluminescent emission.

Chemiluminescent emission from the primary reaction zone would be expected to be more prone to interference than thermal emission from the interconal region. However, it is possible to obtain excitation of chemiluminescence of elements in the primary zone which are difficult to excite by equilibrium processes in the interconal region, without recourse to high temperature (high background) flames. Furthermore, we have observed that the type of flame which possesses the most desirable characteristics for excitation of chemiluminescence usually has a relatively low burning velocity and can best be supported on the open burner port of a simple tube burner.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 900 A thermal emission–atomic absorption flame spectrometer, which has a quartz prism monochromator of high light gathering power (f 7), and a resolution of 0.4 nm/0.1 mm slit width at 250.0 nm, was used. The photodetector was an eleven stage E.M.I. 9601 B, u.v.-sensitive photomultiplier with a Corning glass window. The output was connected to a Servoscribe recorder used on the 0–10 mV range.

Most solutions were prepared by dissolving the pure metal or the oxide in a small volume of hydrochloric acid, nitric acid or aqua regia and diluting to volume.

The germanium solution was prepared by heating 0.288 g of germanium dioxide with *ca.* 0.5 g of potassium hydroxide and 5 ml of water until dissolution, then diluting to *ca.* 200 ml with water and adding a slight excess of *M* sulphuric acid. The iodide solution was a standardised 1 *M* solution of analytical reagent grade hydriodic acid.

Burner design

The primary reaction zone from the conventional Unicam air–acetylene emission head consisted of 13 small cones. The maximum chemiluminescent emission was usually observed in slightly fuel-lean flames. Under these conditions the 13 cones were only 2–3 mm high and the background was not very stable. This instability was attributed to heating of the burner head by the fuel-lean flame. When the air–acetylene flame was maintained on a stainless steel tube (with an internal diameter of 3–6 mm), the primary reaction zone of the slightly fuel-lean flame consisted of a single cone of height 1–3 cm (depending on the diameter of the tube). Optimum results were obtained for the AA and AOA flames with a burner tube of internal diameter 3.2 mm and length 32 mm. The burner tube was screwed into a modified burner top (Fig. 1). The primary reaction cone of the slightly fuel-lean air–acetylene flame was 20 mm

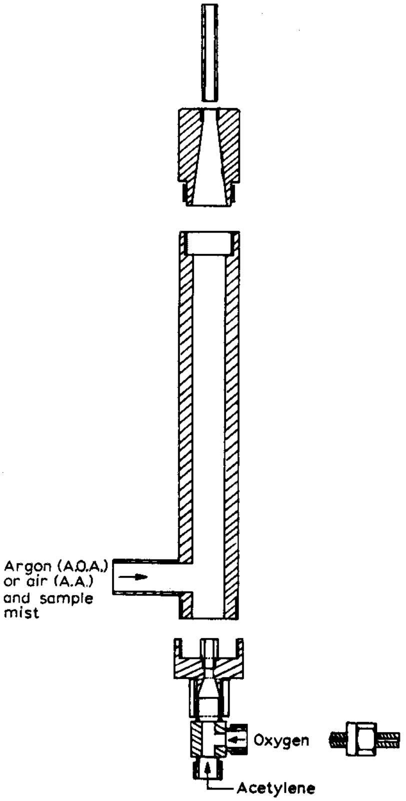

Fig. 1. The burner. For the argon–oxygen–acetylene flame, the oxygen and acetylene enter at the base of the burner and the mixture is then diluted by the argon in the burner barrel. For the air–acetylene flame the acetylene is fed into the base and mixes with the aspirating air in the barrel.

in length and that of the slightly fuel-lean AOA flame was slightly shorter. The length of the monochromator entrance slit was 25 mm.

The addition of a third gas (oxygen) was achieved by means of an adapted burner base (Fig. 1). The 80% carbon dioxide–20% oxygen–acetylene flame tended to lift off the 3.2-mm burner, owing to its lower burning velocity. When the carbon dioxide:oxygen ratio was lowered to give a 67% carbon dioxide–33% oxygen–acetylene flame, the flame could easily be maintained on the burner.

Optimum flame conditions

For all studies in the primary reaction zone, the burner was set so that the top of the tube was 1 mm below the bottom of the monochromator entrance slit.

Air–acetylene flame. The air nebulisation pressure was set at 15 p.s.i.g. (5100 cm^3 min^{-1}). The acetylene flow rate was then optimised for each element to give the maximum signal:background ratio. This optimum emission was usually observed in a slightly fuel-lean flame (acetylene flow rate 475 cm^3 min^{-1}), although molybdenum, vanadium and germanium required a slightly more fuel-rich flame (Fig. 2). The flame lifted off when the acetylene flow rate was reduced to *ca.* 360 cm^3 min^{-1}.

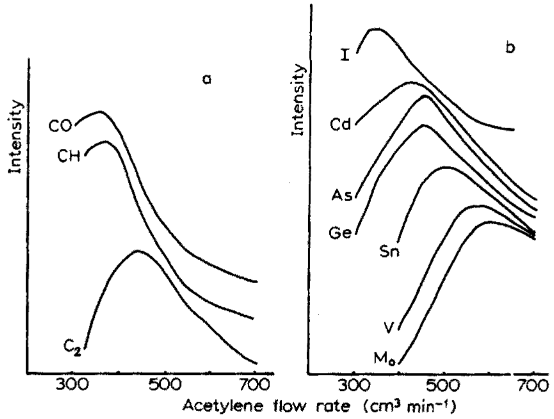

Fig. 2. Diagram showing the dependence of the emission intensity of (a) CO, CH and C_2, and of (b) As, Cd, Ge, I, Mo, Sn, V on the acetylene flow rate, with argon flow rate 4800 cm^3 min^{-1}. Oxygen flow rate 800 cm^3 min^{-1}.

85% Argon–15% oxygen–acetylene flame. The argon nebulisation pressure was set at 15 p.s.i.g. (4800 cm^3 min^{-1}). The oxygen flow rate was then set at 800 cm^3 min^{-1} and the acetylene flow rate was optimised for each element. This usually occurred in a slightly fuel-lean flame (acetylene flow rate 425 cm^3 min^{-1}), although molybdenum, vanadium and germanium required a slightly more fuel-rich flame. The flame lifted off the burner when the acetylene flow rate was reduced to *ca.* 280 cm^3 min^{-1}.

The argon:oxygen ratio was found to be quite critical. Hot flames (75% argon–25% oxygen) exhibited very high background emission and consequently gave poorer limits of detection from the primary reaction zone than the cooler AOA flame. When the argon:oxygen ratio was increased further, the flame tended to lift off and had to be supported on a wider burner thus giving a more unstable flame. The 85%

argon–15% oxygen–acetylene flame was slightly more stable than the air–acetylene flame; this was attributed to better mixing of the acetylene and oxygen of the former flame (Fig. 1).

67% *Carbon dioxide–33% oxygen–acetylene flame.* The carbon dioxide nebulisation pressure was set at 15 p.s.i.g. (4100 cm^3 min^{-1}). The oxygen flow was set at 2000 cm^3 min^{-1} and the acetylene flow rate was then optimised for each element. This flame exhibited a higher continuous background emission than the other flames (Fig. 3), and gave very poor limits of detection for all the elements tested. The low burning velocity of the carbon dioxide flame meant that fuel-lean flames could not be maintained satisfactorily on the burner.

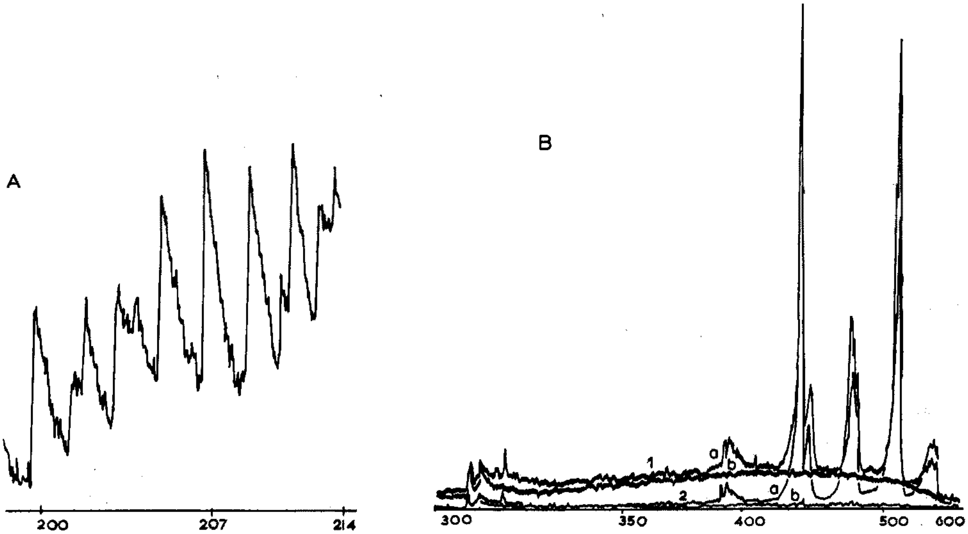

Fig. 3. Emission profiles. (A) Fourth positive CO band system in the primary region of the AOA flame. The intensity scale is not the same as for Fig. 3B.
(B) (1) (a) Emission of CO_2OA flame in primary zone.
(1) (b) Emission of CO_2OA flame in interconal zone.
(2) (a) Emission of AOA flame in primary zone.
(2) (b) Emission of AOA flame in interconal zone.
(Slit width = 0.008 mm)

RESULTS

The limits of detection, defined as signal:noise = 2, are shown in Table I for a number of elements. The acetylene flow rate was optimised for each element.

Antimony

Emission from the 206.8, 217.6, 231.1, 259.8 nm, and other weaker lines was observed. The resonance emission at 231.1 nm gave the best signal:background ratio, and showed an intensity that was quite dependent on the acetylene flow rate and reached a maximum in slightly fuel-lean flames. The calibration curve in the AOA flame was linear over the range 10–1000 p.p.m.

TABLE I

LIMITS OF DETECTION FROM THE PRIMARY REACTION ZONE

Element	*Line*[a] *(nm)*	*Energy of excited state above ground state (eV)*	*Limit of detection*[b] *(p.p.m.)*	
			AA	*AOA*
Antimony	231.1	5.4	3	1
Arsenic	235.0	6.6	7	5
Bismuth	223.0	5.6	3	1
Cadmium	228.8	5.4	1.5	0.5
Germanium	265.1	4.7	7	3
Iodine	206.2	7.0	2500	1000
Lead	261.4	5.7	4	1
Mercury	253.7	4.9	1	1
Mercury + ascorbic acid	253.7	4.9	0.15	0.15
Molybdenum	379.8	3.3	80	10
Selenium	204.0	6.4	50	25
Tellurium	214.3	5.8	5	3
Tin	235.5	5.5	2	1
Vanadium	318.4	3.9	1000	25
Zinc	213.9	5.8	7	1

[a] Only the most intense line is listed for each element, other observed lines are mentioned in the text.
[b] Signal: noise = 2:1.

Arsenic

Emission was observed from the 189.0, 193.7, 228.8 and 235.0 nm lines, as well as some weak longer wavelength lines. The 235.0-nm non-resonance line gave the optimum signal:background ratio and its intensity was also quite dependent on the acetylene flow rate (Fig. 2).

Linear calibration curves were obtained in the AOA flame over the region 10–2000 p.p.m. The 193.7-nm resonance line gave a calibration curve that became convex with respect to the concentration axis above 500 p.p.m. The limit of detection at 235.0 nm in the AOA flame is similar to that obtained with atomic absorption using conventional flames.

Bismuth

Emission was observed from many bismuth lines in the far u.v. The 223.0-nm resonance line gave the best signal:background ratio and its intensity was quite dependent on the acetylene flow rate, reaching a fairly sharp maximum in the slightly fuel-lean flame. The calibration curve in the AOA flame was linear over the range 10–500 p.p.m. and became convex at higher concentrations.

Cadmium

Relatively intense emission was observed from the 228.8 and 326.1-nm resonance lines and very weak emission from the unresolved 346.6–346.8 and 361.1–361.3-nm non-resonance lines. The 326.1-nm line was overshadowed by the intense OH emission. The intensity of the cadmium emission at 228.8 nm was quite dependent on the acetylene flow rate (Fig. 2), reaching a maximum in the slightly fuel-lean flames. The calibration curve in the AOA flame was almost linear up to 100 p.p.m., but rapidly became convex at higher concentrations.

The upper energy levels of the 346.6, 346.8, 361.1, and 361.3-nm lines are 7.4 eV above the ground state. Even though the emission intensity was low, this indicates that there must be highly energetic reactions taking place in the primary reaction zone.

Germanium

Emission was observed from the 259.2, 265.1, 269.1, 271.0 and 275.5-nm resonance lines. The emission at 265.1 nm which was the sum of two unresolved lines at 265.12 and 265.16 nm[7] was the most intense and was again dependent on the acetylene flow rate, reaching a maximum at a higher value than for other elements. This was attributed to the stability of the Ge–O bond. The calibration curve was almost linear over the range 25 to 250 p.p.m., but rapidly became convex at higher concentrations.

Iodine

Emission was observed from the 206.2-nm non-resonance iodine atomic line. The intensity of the emission attained a maximum in a more fuel-lean flame than for most other elements (Fig. 2). The emission intensity showed a similar dependence on the acetylene flow rate to that of the fourth positive carbon monoxide band system. The calibration curve in the AOA flame was almost linear over the range 2000 to 50000 p.p.m. iodine. The poor limit of detection may be ascribed to the high energy of the excited state above the ground state (7.0 eV, *cf.* cadmium) and a poor response of the photomultiplier at that wavelength.

Lead

Emission from the 217.0, 261.4, 283.3, 363.4, 405.8-nm and other weaker lines was observed. The 261.4-nm non-resonance line (which consists of the unresolved 261.37 and 261.42-nm lines[7]) gave the best signal:background ratio. The intensity of the emission attained a maximum in the slightly fuel-lean flames. The calibration curve in the AOA flame was linear between 20 and 1000 p.p.m.

Mercury

Emission was observed from the 253.7-nm resonance line only, the optimum signal being from a slightly fuel-lean flame. The calibration curve in the AOA flame was linear over the range 25–500 p.p.m. The limits of detection in the AOA and AA flames were the same in this instance.

The intensity of the emission increased *ca.* 20 times in the presence of ascorbic acid. This large increase is due to an increase in the ground state population of mercury atoms, because a similar increase was observed in atomic fluorescence studies on mercury using the same nebulisation system in conjunction with an air–acetylene flame. HINGLE *et al.*[8] have observed a similar increase in atomic absorption studies on mercury; the emission from mercury solutions containing ascorbic acid was dependent on the nitric acid concentrations, and was not very stable. Accordingly, although the signal increased *ca.* 20 times, the limit of detection decreased only 7 times.

Molybdenum

Emission was observed from the 379.8 and 390.3-nm resonance lines. The best detection limits were obtained from the 379.8-nm line and the optimum emission occurred at higher acetylene flow rates than those of other elements. This indicates the refractory nature of molybdenum oxide species (*cf.* germanium). The limits of detection for molybdenum (Table I), were higher than those for most other elements in the Table. This was attributed to the high flame background, low dispersion of the quartz prism at 379.8 nm, and poor atomisation of molybdenum in the flame.

Selenium

Emission was observed from the 196.1, 204.0, and 206.3-nm resonance lines. The emission at 204.0 nm gave the best signal: background ratio and the intensity of emission reached a maximum in slightly fuel-lean flames. The relatively poor limit of detection may be attributed to the high energy (6.4 eV) of the excited state above the ground state. The higher sensitivity observed for arsenic (excitation energy 6.6 eV) can be ascribed partly to the better response of the photomultiplier at 235.0 nm and partly to the higher transition probability of the 235.0-nm arsenic line.

Tellurium

Emission was observed from the 214.3, 238.3 and 238.6-nm lines. The intensity of emission reached a maximum in slightly fuel-lean flames. The 214.3-nm resonance line gave a slightly better limit of detection than the 238.6-nm non-resonance line, although the latter gave more linear calibration curves.

Tin

Emission was observed from a multitude of tin lines[3]. The intensity of the emission reached a maximum at a higher acetylene flow rate than for most other elements (Fig. 2). The non-resonance emissions at 235.5 and 242.9 nm gave the best signal:background ratios. The calibration curve at 235.5 nm in the AOA flame was linear between 50 and 1000 p.p.m.

Vanadium

Emission was observed from the 318.4-nm resonance line. The intensity of the emission reached a maximum in fuel-rich flames, indicating the refractory nature of the oxide. The calibration curve in the AOA flame was linear over the range 50–250 p.p.m., but became convex at higher concentrations.

Zinc

Emission was observed from the 213.9, 277.1, 280.1, and 334.5-nm lines. The 307.6-nm intercombination line was obscured by the intense OH background emission. The 213.9-nm emission intensity reached a maximum in a slightly fuel-lean flame. The calibration curve at 213.9 nm in the AOA flame was almost linear over the range 5–50 p.p.m. but rapidly became convex above this concentration. The emission from the 334.5-nm line was very weak. This was attributed to the very high energy of the excited state above the ground state (7.8 eV). Emission was also observed at 330.3 nm which corresponds to a highly energetic zinc line (7.8 eV), but this wavelength also corresponds to the wavelength of a relatively strong sodium resonance line. The emission observed from the 277.09–277.10-nm and 280.09–280.11-nm doublets was extremely weak (excited states 8.5 eV above the ground states), and could only be observed with concentrated zinc solutions (50,000 p.p.m.). The emission was checked by setting the monochromator just off the lines and nebulising the zinc solution again.

No lines with excited states more than 8.5 eV above the ground state were observed in this study.

Comparison of the emission in and above the primary reaction zone

The ratios of the chemiluminescent emission intensity in the primary reaction zone to the chiefly thermal emission intensity 30 mm above the primary zone ($I_{pr}:I_{int}$) are shown in Table II. It can be seen that, in general, the ratio $I_{pr}:I_{int}$ increases as the energy of the excited state above the ground state increases. The emission from the primary reaction cone can be expressed as:

TABLE II

RATIO OF THE EMISSION IN AND ABOVE THE PRIMARY REACTION CONE OF THE AOA FLAME

(Argon: 4800 $cm^3 min^{-1}$. Oxygen: 800 $cm^3 min^{-1}$)

Element	*Line (nm)*	*Concn. (p.p.m.)*	*Energy of excited state above ground state (eV)*	*C_2H_2 flow rate ($cm^3 min^{-1}$)*	$I_{pr}:I_{int}$
As	235.0	100	6.6	425	>500
Bi	223.0	100	5.6	425	40
Ca	422.7	100	2.9	425	0.5
Cd	228.8	100	5.4	425	20
Cd	326.1	500	3.8	425	1.0
Ge	265.1	200	4.7	475	>500
Hg	253.7	100	4.9	425	120
I	206.2	10000	7.0	425	>500
K	766.5	10	1.6	425	0.5
Mo	379.8	200	3.3	475	>500
Na	330.2	100	3.8	425	0.5
Na	589.0 589.6	2	2.1	425	0.3
Pb	261.4	100	5.7	425	70
Sb	231.1	200	5.4	425	100
Se	204.0	100	6.4	425	>500
Sn	235.5	200	5.5	475	>500
Sn	242.9	200	5.5	475	>500
V	318.4	200	3.9	475	>500
Zn	213.9	100	5.8	425	>500

$$I_{pr} = I_{ch} + I_{th}$$

where I_{pr} = total observed emission intensity of a line; I_{ch} = chemiluminescent intensity; and I_{th} = thermal emission intensity.

The emission from the interconal zone (I_{int}) is thought to consist only of thermal emission. If complete atomisation and no self-absorption are assumed, then

$$I_{th} \propto N_0 \exp - \frac{E}{RT}$$

where E = energy of the excited state above the ground state; N_0 = number of ground state atoms; R = gas constant; and T = temperature of the flame gases.

The thermal emission intensity is exponentially dependent on the temperature and the energy of the excited state above the ground state. The chemiluminescent energy is not, however, very dependent on the maximum interconal temperature of the flame and should not be so dependent on the energy of the excited state[9]. For lines with excitation energies less than about 4 eV, the thermal emission intensity is generally much greater than the chemiluminescent emission intensity (*e.g.* Ca, K, Na), whilst for lines with greater excitation energies the chemiluminescent emission intensity is much greater than the thermal emission intensity except in very hot flames. The $I_{\text{pr}}:I_{\text{int}}$ values for the main resonance lines of calcium, potassium and sodium are less than unity because the volume of gas emitting from the primary reaction zone is less than that emitting from above the zone.

The elements forming refractory oxides did not give any emission above the primary reaction zone in these flames. This was attributed to poor atomisation rather than absence of thermal excitation. For example, the thallium 377.6-nm line has a lower transition probability than the nearby molybdenum 379.8-nm line but, instead of stronger molybdenum emission (which would be expected assuming similar atomisation efficiency) the reverse situation is observed.

The effect of temperature on chemiluminescent emission

The effect of altering the oxygen:argon ratio on the arsenic and lead emission is shown in Table III. It was found that increasing the temperature of the flame only slightly increased the intensity of the chemiluminescent emission from the primary cone, but considerably increased the intensity of the background emission. Table IV shows the effect of altering the oxygen:argon ratio on the sodium and cadmium emission intensities in the primary reaction zone and the interconal zone. The sodium and cadmium emissions from the interconal zone can be considered to be in effective thermal equilibrium and are very dependent on temperature. The sodium emission from the primary cone is still effectively thermal rather than chemiluminescent,

TABLE III

THE EFFECT OF INCREASING THE OXYGEN:ARGON RATIO ON THE CHEMILUMINESCENT EMISSION INTENSITY OF ARSENIC AND LEAD

(Argon: 4800 cm^3 min^{-1}. AOA flame)

Oxygen flow rate (cm^3 min^{-1})	*Acetylene flow rate (cm^3 min^{-1})*	*Oxygen: argon ratio*	*Signal: background ratio*
Arsenic 235.0 nm, slit width, 0.020 mm			
720	350	0.150	2.5
800	450	0.167	1.5
1200	900	0.250	0.95
Lead 261.4 nm, slit width 0.013 mm			
720	350	0.150	2.5
800	450	0.167	2.1
1200	900	0.250	1.1

TABLE IV

THE EFFECT OF INCREASING THE ARGON:OXYGEN RATIO ON EMISSION FROM THF PRIMARY REACTION CONE AND INTERCONAL ZONE

(AOA flame)

Element	*Concn. (p.p.m.)*	*Line (nm)*	*Energy of excited state above ground state (eV)*	*Ratio of emission intensities hot: normal*[a]
Primary reaction zone				
Cd	50	228.8	5.4	1.0
Na	2	589.0 589.6	2.1	2.3
Na	2	330.2	3.8	3.9
Interconal zone				
Cd	200	228.8	5.4	4.0
Na	2	589.0 589.6	2.1	1.9
Na	2	330.2	3.8	3.3

[a] *"Normal" flame:* argon, 4800 $cm^3 min^{-1}$; oxygen, 800 $cm^3 min^{-1}$; acetylene, 425 $cm^3 min^{-1}$. *"Hot" flame:* argon, 4800 $cm^3 min^{-1}$; oxygen, 1150 $cm^3 min^{-1}$; acetylene, 875 $cm^3 min^{-1}$.

because the emission is still very dependent on temperature. On the other hand, there was little temperature-dependence for the cadmium signal from the primary cone, thus showing that it is still effectively chemiluminescent in nature. As well as this, the cadmium emission is much more intense from the primary cone than from the interconal region (Table II).

Maximum energy available for chemiluminescence

Very weak emission was observed from the zinc 277.09–277.10-nm and 280.09–280.11-nm lines when a 50,000 p.p.m. zinc solution was nebulised. The excited states of these lines are 8.5 eV above the ground state[10]. No emission could be observed from the 365.0-nm line of mercury when a 20,000 p.p.m. solution was nebulised into the flame. This line has a high transition probability[10] and the excited state is 8.85 eV above the ground state. Thus it would appear that at least one of the reactions responsible for the chemiluminescent emission must have an energy of reaction of about 8.5 eV.

DISCUSSION

Possible mechanisms of excitation

The background emission from the primary reaction cones of the flames was far more intense than that from the interconal regions (Fig. 3B). Intense C_2, CH and OH emission was observed in the visible and the near u.v. regions. In the far u.v. the main emission was from the fourth positive band system of carbon monoxide. Of the three flames, the AOA flame gave the most intense C_2, CH, OH and fourth positive CO band emissions. The spectrum of the AA flame was very similar to that of the AOA flame, but the bands were approximately half as intense. The carbon dioxide flame gave much more of a continuum beneath the C_2, CH, OH and CO emissions and also the C_2:CH intensity ratio was much lower than with the other two flames.

The fourth positive band system of carbon monoxide (Fig. 3A) was surprisingly intense in view of the maximum temperature of only 2600°K; this was established for the air–acetylene flame by line reversal measurements[5]. Since the upper energy levels of the fourth positive bands are *ca.* 7–9 eV above the ground state[5], it must be assumed that some very energetic chemical reactions occur in the primary reaction zone. The fact that the fourth positive band system ($A^1\pi$) of carbon monoxide was observed, indicates that other highly excited states of the carbon monoxide molecules (*e.g.* $a^3\pi$) could also be excited[5]. The reason that no emission was observed from these other excited states is probably due to their low transition probability (*i.e.* they are spin forbidden and, therefore, metastable).

The carbon monoxide molecule is the only molecule in the AOA flame with a dissociation energy greater than 7.0 eV (the carbon monoxide dissociation energy is 11.1 eV[5]). It would seem reasonable, therefore, to assume that the high energy of this bond is responsible for the chemiluminescent excitation. Possibly the excitation could result from the following mechanism:

$$C_2H_2+M \xrightarrow{O_2} \text{intermediates} \rightarrow CO+M^*+S \tag{1}$$

$$C_2H_2 \xrightarrow{O_2} \text{intermediates} \rightarrow CO^*+S \tag{2}$$

(CO^* is in an excited electronic state or a high vibrational energy level of the ground state.)

$$CO^*+M \rightarrow M^*+CO \tag{3}$$

$$CO^*+S \rightarrow S^*+CO \tag{4}$$

$$M^* \rightarrow M+h\nu \tag{5}$$

$$CO^* \rightarrow CO+h\nu \tag{6}$$

(S represents a flame gas molecule.)

As the metal additive is highly diluted in the flame gases, the probability that the metal atoms will undergo three body collisions (*i.e.* $CH+O+M \rightarrow CO+H+M^*$) is low[5]. Thus reaction (1) is unfavourable and it is more probable that the excitation occurs in two stages: first reaction (2) produces excited carbon monoxide molecules and then the energy is transferred to metal atoms by reaction (3). It is unlikely however, that the excited carbon monoxide molecules in the fourth positive state are solely responsible for the chemiluminescence emission. This is because the vibrational levels of the observed bands in this electronic state range from 8.2 to 8.9 eV above the ground state, and the few lines observed with excited energy levels greater than *ca.* 7.0 eV, were extremely weak. The fact that the singlet $A^1\pi$ state can combine with the singlet ground state ($X^1\Sigma^+$) would tend to give a relatively low population of this excited state compared to the lower triplet metastable $a^3\pi$ state. This is the lowest excited electronic state of carbon monoxide and being a triplet state cannot combine with the singlet ground state ($X^1\Sigma^+$), hence the absence of the Cameron bands ($a^3\pi \rightarrow X^1\Sigma^+$) in the flame. A relatively high concentration of carbon monoxide molecules could therefore possibly persist in the long-lived triplet-excited state within the reaction cone. The energy of the state $a^3\pi$ $(v=8)$ is 7.6 eV and that of $a^3\pi$ $(v=6)$ is 7.2 eV[5]. The energy requirements for nearly all of the observed chemiluminescent emission would appear satisfied with the metal atoms acting as convenient vehicles for quenching of the triplet state carbon monoxide molecules.

It is also possible that, by some energetic reaction, carbon monoxide molecules are formed in the ground electronic state, but with high vibrational energy. Since the upper vibrational levels of the ground electronic state extend up to 11 eV, they could also be responsible for the chemiluminescent emission.

The nitrogen molecule has a high dissociation energy (9.76 eV). In the air–acetylene flame, nitrogen is not thought to participate in any of the reactions occurring within the flame, but the high dissociation energy and also the occurrence of high-energy metastable states could allow the nitrogen molecules to act as energy carriers:

$$CO^* + N_2 \rightarrow N_2^* + CO$$

The fact that the argon flame gave more intense chemiluminescence than the nitrogen-containing flame indicates, however, that the number of excited carbon monoxide and excited metal atoms quenched by nitrogen molecules is greater than the number of atoms excited by the excited nitrogen molecules. The difference in the chemiluminescent emission intensities between the AA and AOA flames cannot be attributed to the small temperature difference between them. (A 2-p.p.m. sodium solution gave similar emission intensities from both the flames, and flame temperature measurements by MORGAN AND KANE[11] suggest that the AOA flame used in this study has the same line reversal temperature as the AA flame.)

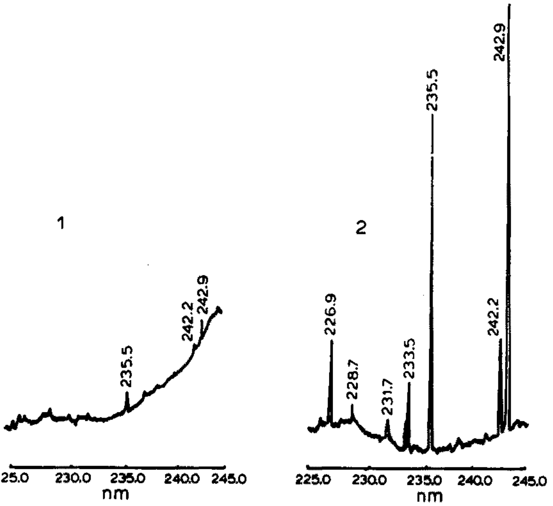

Fig. 4. Comparison of the signal and background emissions of some tin lines from the primary reaction cones of the (1) C_2H_2–O_2–CO_2 and (2) C_2H_2–O_2–A flames with the same instrumental settings.

The poor limits of detection observed in the carbon dioxide flame can be explained by quenching of the excited metal atoms and excited carbon monoxide molecules by carbon dioxide (Fig. 4). The dissociation energy of carbon dioxide to carbon monoxide and atomic oxygen is 5.46 eV and no excited level of carbon dioxide above 5 eV is known[12], thus unlike nitrogen, it cannot act as a carrier of energy more than 5 eV. Carbon dioxide molecules have a large collisional cross-section and quenching processes such as these can be envisaged:

$$CO^* + CO_2 \rightarrow CO + CO + O$$

$$M^* + CO_2 \rightarrow CO + M + O$$

The variation in the emission intensity of the 206.8-nm fourth positive band of carbon monoxide *versus* acetylene flow rate is shown in Fig. 2. It can be seen that the maximum emission intensity and, therefore, maximum concentration of excited carbon monoxide molecules in all excited states, occurred in fuel-lean flames. The CH emission at 431 nm showed a similar dependence on the acetylene flow rate, but the C_2 emission at 516 nm reached a maximum in less fuel-lean flames than did either the CH or CO emission (Fig. 2). The iodine emission intensity showed a similar dependence on the acetylene flow rate as the 206.8-nm fourth positive band intensity, whilst most metal emission intensities reached a maximum in slightly fuel-lean flames (*e.g.* Cd, Hg, Pb, Se, Te, and Zn) and then decreased in very fuel-lean flames. This decrease could be due to incomplete atomisation in the cool, very fuel-lean flames. Iodine, however, forms an unstable oxide and hydrogen iodide is not very stable. This behaviour tends to indicate that excited carbon monoxide molecules could be responsible for most of the observed chemiluminescent excitation.

It would appear unlikely that the oxides are directly excited by reaction with atomic carbon[13]:

$$MO + C \rightarrow M^* + CO$$

as the atomic carbon line at 247.8 nm was not observed under any conditions and the slightly fuel-lean flames used in this study would be unlikely to produce atomic carbon.

The reaction[14]

$$MO + CO^* \rightarrow CO_2 + M^*$$

is considered unlikely because the elements forming refractory oxides (Ge, Mo, Sn, and V), required more fuel-rich flames than the other elements (Fig. 2), thus indicating that breakdown of the oxide is necessary before chemiluminescent excitation. It is also probable that the energy liberated in the above reaction would be split between the carbon dioxide molecule and the metal atom.

The addition of a 1000-fold excess of potassium did not affect the arsenic or lead emission, indicating that the excitation mechanism does not involve ions[3,14].

We are grateful to B.P. Ltd for the provision of a scholarship to J.F.A.

SUMMARY

A study has been made of the chemiluminescent emission of As, Bi, Cd, Ge, Hg, I, Mo, Pb, Sb, Se, Sn, Te, V and Zn in the primary combustion zones of air–acetylene and argon–oxygen–acetylene flames, supported at an open burner port during the aspiration of aqueous solutions of their salts. In general, elements having excitation potentials greater than 4 eV show considerably greater atomic chemiluminescence in the primary zone than "thermal" atomic emission in the interconal region. Various mechanisms are suggested for the energy-transfer reactions between metal atoms and excited flame species, particularly carbon monoxide.

RÉSUMÉ

Une étude est effectuée sur l'émission chimiluminescente de As, Bi, Cd, Ge, Hg, I, Mo, Pb, Se, Sn, Te, V et Zn dans les zones de combustion primaires des flammes air–acétylène et argon–oxygène–acétylène. En général, les éléments ayant des potentiels d'excitation supérieurs à 4 eV présentent une chimiluminescence atomique considérablement plus grande dans la zone primaire que l'émission atomique "thermique" dans la région interconique. Divers mécanismes sont proposés pour ces réactions de transfert d'énergie entre atomes métalliques et particules excitées, en particulier l'oxyde de carbone.

ZUSAMMENFASSUNG

Es wurde die Chemilumineszenz-Emission von As, Bi, Cd, Ge, Hg, J, Mo, Pb, Sb, Se, Sn, Te, V und Zn untersucht, die in den primären Verbrennungszonen von Luft–Acetylen- und Argon–Sauerstoff–Acetylen-Flammen bei offenen Brennern während des Versprühens wässriger Salzlösungen auftritt. Im allgemeinen zeigen die Elemente mit Anregungspotentialen grösser als 4 eV eine erheblich grössere atomare Chemilumineszenz in den primären Zonen als "thermische" atomare Emission im Bereich des inneren Kegels. Für die Energieübertragung zwischen Metallatomen und angeregten Flammen-Spezies, insbesondere Kohlenmonoxid, werden verschiedene Mechanismen vorgeschlagen.

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ACCURATE DETERMINATION OF TRACES OF SODIUM AND POTASSIUM IN ROCKS BY ION EXCHANGE FOLLOWED BY ATOMIC ABSORPTION SPECTROSCOPY

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The reliable determination of sodium and potassium in silicate rocks still appears to be a problem when these elements are present in trace amounts. This is pertinently demonstrated by recent results for the U.S. geological survey standards PCC-1 and DTS-1[1]. The reason for the wide spread of the results—about an order of magnitude and more—is not quite clear. Inhomogeneous sample composition, interference by the large amount of a complex mixture of other elements, losses in separation procedures, contamination before or during analysis, or a combination of these factors could be responsible. The second and third of these factors can be eliminated by employing an effective method for separation and concentration before the final determination step. In addition this also would increase the sensitivity of the method, a feature which appears to be welcome when looking at the published results[1]. An ion-exchange procedure for the separation of silicate rock elements which has been described recently[2] is not satisfactory because of relatively high reagent blank values. A special procedure therefore was developed for the determination of trace amounts of alkalies. This incorporated the following features. Only specially purified reagents were employed. The eluting agent, 0.50 *M* nitric acid, for separating the alkalies from multivalent elements[2,3] was retained, but only that fraction of the eluate which contained the relatively narrow peak of one particular alkali metal was taken for analysis. Because dunites and peridotites contain between 40 and 50% of magnesium oxide, the peak positions had to be determined in the presence of large and varying amounts of magnesium, which caused a shift to a lower elution volume. Predominantly anionic elements such as vanadium(V), molybdenum(VI) and tungsten(VI) were eluted with 0.01 *M* nitric acid containing hydrogen peroxide[2]. Perchloric or sulphuric acid of the same concentration could be used instead[4]. The alkali metals were retained according to their distribution coefficients[5] and then eluted with 0.5 *M* nitric acid. The separated alkali metals were determined by atomic absorption spectroscopy.

EXPERIMENTAL

Reagents and apparatus

Water was redistilled and all solutions were kept in polyethylene containers. Hydrochloric, hydrofluoric, sulphuric, perchloric and nitric acid were "suprapur" grade (E. Merck A. G., Darmstadt,Germany). Phosphoric acid (A.R. grade) was diluted with 4 volumes of redistilled water and purified by passing through a cation-exchange column. The resin was AG50W-X8 cation exchanger (200–400 mesh, BIO.RAD Laboratories, Richmond, Calif.). Borosilicate glass tubes of 2.5 cm inner diameter fitted with a No. 2 porosity glass sinter and a stopcock at the bottom and a B19 joint at the top were used as columns. All glassware was purified by washing with hot 1:1 nitric acid (A.R.) and resin columns were cleaned by passing through 500 ml of 3 *M* nitric acid (A.R.), followed by 50 ml of 1 *M* nitric acid "suprapur" before use. A Perkin Elmer 303 instrument was used for atomic absorption measurements. Alkali metal determinations were carried out with a propane–butane–air flame and a special flat water-cooled burner[6].

Elution curves

A solution containing 1 mg of each vanadium(V), lithium, sodium and potassium, 2 mg of cesium, 300 mg of magnesium, 55.8 mg of iron(III), 10 ml of 2.0 *M* hydrochloric and 10 ml of 2.5 *M* sulphuric acid and 10 ml of 0.3% (w/v) hydrogen peroxide in a volume of 100 ml, to simulate conditions after decomposition of a rock sample, was passed onto the exchange column and washed onto the resin with 0.01 *M* nitric acid containing 0.03% (w/v) hydrogen peroxide. Vanadium was eluted with 100 ml of the same solution. Then the alkali metals were eluted with 0.50 *M* nitric acid. A flow rate of 3.0±0.5 ml min^{-1} was maintained throughout. Fractions (25 ml) were taken with an automatic fractionator and analysed. Vanadium was determined spectrophotometrically as the 4-(2-pyridylazo)-resorcinol complex[7] and the alkali metals and magnesium were determined by atomic absorption spectrometry using the following lines: 6708 Å for Li, 5890 Å for Na, 7665 Å for K, 8521 Å for Cs, 2852 Å for Mg. A propane–butane–air flame was used for lithium, sodium, potassium and cesium and an acetylene–air flame for magnesium.

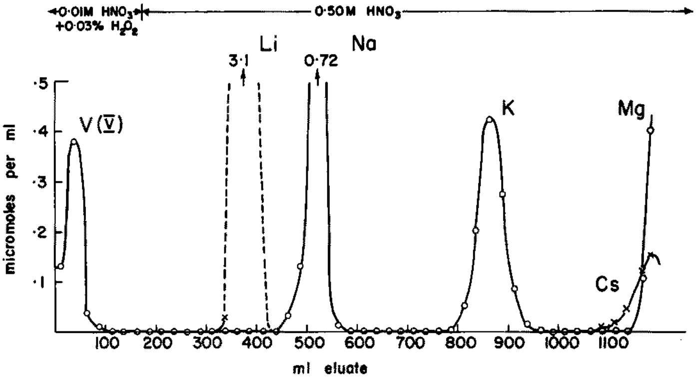

Fig. 1. Elution curve for V(V), Li, Na, K, Cs and Mg with 0.01 *M* HNO$_3$ and 0.50 *M* HNO$_3$. 90 ml (30 g) AG50W-X8 resin, 200–400 mesh.

The experimental elution curve for a 90-ml (30-g) resin column (Fig. 1) shows that sodium in microgram amounts will be collected quantitatively in the 250–500 ml fraction of the 0.50 *M* nitric acid eluting agent. The only possible contaminant is lithium, but trace amounts of lithium will not interfere in the determination of sodium. Potassium is collected in the 600–850 ml fraction of the eluting agent. The only possible contaminant, rubidium, which is eluted between the potassium and cesium peaks, is unlikely to be present in observable amounts and will not interfere in the determination unless present in fairly large amounts.

Titanium and beryllium are eluted later than cesium and are separated quantitatively unless present in large amounts (more than 1 mmole). All other di- and multivalent cationic elements such as Ca, Sr, Ba, Cu(II), Co(II), Zn, Cd, Mn(II), Ni(II), Al, Ga, In(III), Fe(III), rare earths(III), Zr(IV) and Th(IV) are more strongly retained than magnesium. As much as 12 mmoles of these elements can be present without interfering.

Figure 2 shows a similar curve for a 75-ml (25-g) resin column to demonstrate the effect of column size. Lithium, rubidium and cesium were not included. The Figure shows that with this column size, separation of 1 mg of potassium from 300 mg of magnesium is too marginal for quantitative work. A good separation can be obtained when only 200 mg of magnesium are present. No magnesium could be detected in the first 1000 ml of 0.5 *M* nitric acid in this case, while the last traces of potassium were eluted with 750 ml.

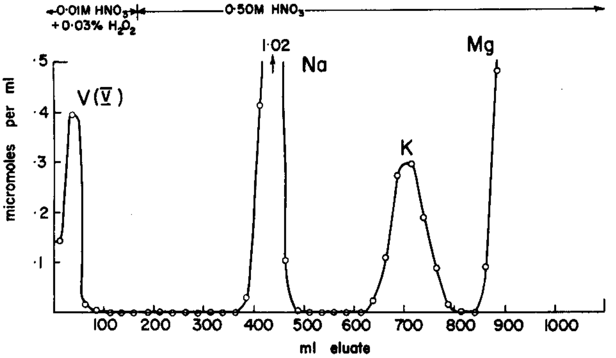

Fig. 2. Elution curve for V(V), Na, K and Mg with 0.01 *M* HNO_3 and 0.50 *M* HNO_3. 75 ml (25 g) AG50W-X8 resin, 200–400 mesh.

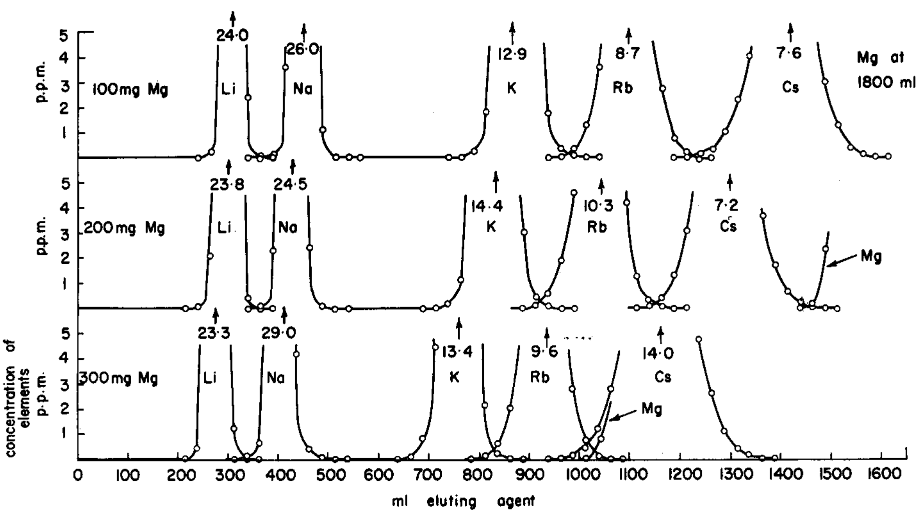

Fig. 3. Elution curve for Li, Na, K, Rb, S and Mg with 0.50 *M* nitric acid at various amounts of Mg. 90 ml (30 g) AG50W-X8 resin, 200–400 mesh.

Effect of column load on alkali peak position

Figure 3 shows the effect of column loading on the position of the sodium and potassium peaks for a 90-ml (30-g) resin column. Only 1 mg of each sodium and potassium and 100, 200 or 300 mg of magnesium, respectively, were present. The cations were absorbed from 0.01 *M* hydrochloric acid in this case. Equivalent loads of iron, calcium and aluminium cause considerably less shifting of the alkali metal peaks. The effect of manganese is similar to that of magnesium. Other divalent heavy metals such as Cu, Co, Zn, Ni and Cd were not investigated, but from their known distribution coefficients[5] it can be expected that their effect will be similar to that of magnesium.

Analysis of synthetic mixtures

Accurate amounts of standard solutions containing known amounts of the alkali metals and magnesium or other elements were measured out, mixed and absorbed on a 90-ml resin column of 2.5 cm diameter and 21 cm length from 0.01 *M* nitric acid or from 0.10 *M* hydrochloric acid when iron(III) or aluminium were present. The cations were washed onto the resin with the same reagent, and the alkalies were then eluted with 0.50 *M* nitric acid. A flow rate of 3.0 ± 0.5 ml min^{-1} was used. The eluate fraction from 300 to 550 ml was taken for the analysis of sodium and that from 650 to 900 ml for the analysis of potassium when 300 mg of magnesium or 700 mg manganese were present (Fig. 3). The same fraction was taken for the determination of sodium when 300 mg of aluminium, 500 mg of calcium or 700 mg of iron were present, but for potassium the fraction from 750 ml to 1000 ml was taken.

The eluates containing the alkali metals were received in acid-cleaned 250-ml volumetric flasks and the concentrations of the alkali metals were measured by atomic absorption spectrophotometry under the conditions described above. The concentrations were read from a calibration curve prepared from standards in 0.50 *M* nitric acid. The results were corrected by subtracting the average of a duplicate blank run and are shown in Table I.

TABLE I

SEPARATION OF SYNTHETIC MIXTURES

Taken		*Found*[a]
μg alkali metal	*mg other element*	*μg alkali metal*
102 Na	300 Mg	101 ± 1
20.4 Na	300 Mg	20.1 ± 0.8
5.1 Na	300 Mg	4.9 ± 0.6
501 Na	300 Mg	499 ± 3
102 Na	500 Ca	100 ± 2
102 Na	700 Mn	101 ± 1
102 Na	300 Al	102 ± 1
102 Na	700 Fe	101 ± 1
104 K	300 Mg	103 ± 2
20.8 K	300 Mg	20.6 ± 1.3
5.2 K	300 Mg	5.0 ± 0.9
502 K	300 Mg	501 ± 3

[a] The results are means of quadruplicate determinations.

Procedure for analysis of dunites and peridotites

About 1-g samples of dunite or peridotite were weighed out and dissolved by heating with mixtures of hydrofluoric, hydrochloric and sulphuric acid as described before[2]. The solution was adjusted to a volume of about 100 ml containing 10 ml of 2 *M* hydrochloric acid and 10 ml of 2.5 *M* sulphuric acid, and passed through a 90-ml (30-g) resin column of 2.5 cm inner diameter. It was washed onto the resin with 0.01 *M* nitric acid containing 0.03% (w/v) hydrogen peroxide. Vanadium(V), molybdenum(VI), tungsten(VI), phosphate and other anionic elements were eluted with another 100 ml of the same reagent. Sodium and potassium then were eluted with 0.50 *M* nitric acid taking the fraction 250–500 ml for the determination of sodium, and the fraction 600–850 ml for the determination of potassium. The fractions were received in 250-ml volumetric flasks and the amounts of the elements were determined by atomic absorption spectrophotometry as described above; scale expansion was used for low concentrations. Specpure potassium (500 p.p.m.) was added to sodium samples and standards. Duplicate runs on reagent and procedure blanks were carried out and the averages subtracted from the results. The results are presented in Table II.

TABLE II

DETERMINATION OF SODIUM AND POTASSIUM IN ROCK SAMPLES

Sample	*p.p.m. found*[a]		*"Average" literature value*[b]	
	Na	*K*	*Na*	*K*
PCC-1	16.2 ± 0.7	30.9 ± 0.8	~ 390	~ 160
DTS-1	36.9 ± 0.9	14.0 ± 1.9	~ 340	~ 190
NIM-D	524 ± 3	226 ± 2	Not available	Not available

[a] The results are means of quadruplicate determinations.
[b] From ref. 1.

DISCUSSION

The described method provides a useful means for the determination of trace amounts of sodium and potassium in silicate rocks. Between 5 and 1000 μg of sodium and potassium can be determined in a 1-g rock sample. In the range 100–1000 μg (0.01–0.1%) results are quite precise (coefficient of variation about ±1 to ±2%), and from the results obtained with synthetic standards (Table I), it is believed that the accuracy is of the same order as the precision. A very small negative bias may be present. At lower amounts, the precision slowly declines to about ±10 to ±20% at the 5-μg level. This is due to low atomic absorption readings and variable blank values. The blank values for sodium were of the order of 2–3 μg, and those for potassium of the order of 0.5–1.0 μg. First attempts to obtain higher accuracy through higher absorption readings by evaporating the sample solutions and reading in a smaller volume failed. Evaporation in glass led to very high and variable blank values (>20 μg sodium) and even evaporation in teflon and platinum gave blank values which were increased by 50 to 100%. Apparently this was due to uptake of alkali metals from dust particles in the air.

The results obtained for the international rock standards PCC-1 and DTS-1 are an order of magnitude lower than the average value (Table II) given by FLANAGAN[1], but FLANAGAN already has pointed out that the "averages" given in his paper for sodium and potassium in PCC-1 and DTS-1 are very much higher than the neutron activation results and probably are much too high. Because the proposed sample decomposition procedure is simple and is included in the blank runs, and because good results were obtained with synthetic mixtures (Table I), it is felt that the results presented are reliable. They also show good agreement with the newest results obtained by neutron activation analysis[7].

The described method is very simple and lends itself to rationalization, because only a small amount of actual work is involved. As much as 20 and even more samples can be done in a working day, provided that an adequate battery of exchange columns is available. The position of the peaks in the ion-exchange separation is critical; apart from resin loading (Fig. 3), it also may vary with long-term variations in the effective cross-linkage of different resin batches. Although no significant variations could be detected when 3 different batches of AG50W-X8 resin were tested, for obtaining reliable results it is advisable to establish the peak positions of sodium and potassium for the kind and amount of sample and the resin batch and column size used before the analysis is started. It may be pointed out that Dowex 50W-X8 cation exchangers will give similar peak positions to AG50W-X8 resin, but Amberlite 120H or other cation exchangers, even with 8% cross-linkage according to their designation, do not.

SUMMARY

Sodium and potassium (5–1000 p.p.m.) in rocks such as peridotites and dunites can be determined accurately by ion-exchange separation followed by atomic absorption spectrophotometry. The samples are decomposed in sulphuric, hydrochloric and hydrofluoric acid mixtures, and after removal of hydrofluoric acid the cations are absorbed on a 90-ml column of AG50W-X8 cation-exchange resin. Vanadium and other anion-forming elements are eluted with 0.01 *M* nitric acid containing hydrogen peroxide. Then the alkali metals are eluted with 0.50 *M* nitric acid, while Mg, Mn, Ca, Ti, Al, Fe and other multivalent elements are retained by the column. The eluate fractions containing the respective alkali metals are measured directly by atomic absorption spectrophotometry against standards in 0.50 *M* nitric acid. Relevant elution curves, results for synthetic mixtures and for three international rock standards are presented and discussed.

RÉSUMÉ

Il est possible de doser avec précision 5 à 1000 p.p.m. de sodium et potassium dans des roches telles que péridotites et dunites, par séparation au moyen d'échangeurs d'ions et spectrophotométrie par absorption atomique. Les échantillons sont décomposés par des mélanges d'acides sulfurique, chlorhydrique et fluorhydrique. Après élimination de l'acide fluorhydrique les cations sont absorbés sur une colonne de résine cationique AG50W-X8. Le vanadium et d'autres éléments pouvant former des anions sont élués avec de l'acide nitrique 0.01 *M* renfermant du peroxyde d'hydrogène. Les métaux alcalins sont ensuite élués avec acide nitrique 0.5 *M*; alors que Mg, Mn, Ca, Ti, Al, Fe et autres éléments multivalents sont retenues sur la colonne.

Les fractions d'éluat contenant les métaux alcalins sont mesurés directement par spectrophotométrie par absorption atomique, en utilisant des étalons en milieu acide nitrique 0.5 *M*. Des résultats sont présentés et discutés.

ZUSAMMENFASSUNG

Natrium und Kalium (5–1000 p.p.m.) in Gesteinen wie Peridotiten und Duniten können durch Ionenaustausch-Trennung und anschliessende Atomabsorptionsspektrophotometrie genau bestimmt werden. Die Proben werden in Mischungen von Schwefel-, Salz- und Flusssäure zersetzt und die Kationen nach Entfernung der Flusssäure in einer 90 ml-Säule vom Kationenaustauscher AG50W-X8 absorbiert. Vanadin und andere anionenbildende Elemente werden mit 0.01 *M* Wasserstoffperoxid enthaltender Salpetersäure eluiert. Dann werden die Alkalimetalle mit 0.50 *M* Salpetersäure eluiert, während Mg, Mn, Ca, Ti, Al, Fe und andere mehrwertige Elemente von der Säule zurückgehalten werden. Die die jeweiligen Alkalimetalle enthaltenden Eluatfraktionen werden direkt durch Atomabsorptionsspektrophotometrie gegen Standards in 0.50 *M* Salpetersäure gemessen. Die Elutionskurven sowie die Ergebnisse von künstlichen Mischungen und von drei internationalen Standardgesteinen werden vorgelegt und diskutiert.

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DOSAGE POTENTIOMETRIQUE DES IONS ALKYL-TRIMETHYL-AMMONIUM A LONGUE CHAINE ET TETRABUTYL-AMMONIUM

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(Reçu le 26 janvier, 1970)

L'acidimétrie en milieu non aqueux[1] qui constitue la méthode la plus générale de dosage des sels d'amines ou d'ammonium quaternaire ne paraît pas applicable aux ions de la série alkyl-triméthyl-ammonium. Ces derniers ions ont pu être dosés soit par colorimétrie[2,3], après précipitation par un colorant anionique suivie d'une extraction par un solvant organique; soit par néphélométrie[4] après addition d'une solution iodo–iodurée. Par ailleurs, la possibilité de précipiter en solution aqueuse les hexacyanoferrates(III) des ions ammonium quaternaire a été utilisée dans la mise au point d'un dosage potentiométrique indirect[5] de ce type d'ion.

Le présent mémoire décrit une méthode de dosage potentiométrique direct des ions dodécyl-triméthyl-ammonium (DTA^+), tétradécyl-triméthyl-ammonium (TTA^+), hexadécyl-triméthyl-ammonium (HTA^+) et tétrabutyl-ammonium (TBA^+) en solution aqueuse. Le principe du dosage est issu de certains résultats de notre étude des piles à phases liquides et sa réalisation pratique fait intervenir une électrode spécifique de ces types d'ions.

Principe

Tout système constitué d'une phase non aqueuse interposée entre deux solutions aqueuses électrolytiques constitue une pile à phases liquides, s'il existe une différence des potentiels de Galvani entre les deux phases aqueuses.

Parmi les divers types de piles à phases liquides étudiés jusqu'ici on retiendra les deux cas particuliers suivants:

Système I:

R^+X^-	$R^+R'^-$	R^+X^-
dans H_2O	dans nitrobenzène	dans H_2O
(e_1)	(n)	(e_2)

Système II:

R^+X^-	$R^+R'^-$	R'^-Na^+ ou R'^-K^+
dans H_2O	dans nitrobenzène	dans H_2O
(e_1)	(n)	(e_2)

R^+: ion ammonium quaternaire.
X^-: ion halogénure.

R'^- désigne un anion organique tel que l'ion picrate (Pi^-) ou l'ion tétraphényl-borate (TPB^-).

Le composé $R^+R'^-$, insoluble dans l'eau, est soluble et presque totalement dissocié dans le nitrobenzène. Les indices (e) et (n) se réfèrent respectivement à l'eau et au nitrobenzène. Le système I appartient au type des piles à membrane liquide à effet de concentration, car la solution non aqueuse joue le rôle d'une membrane sélectivement perméable à l'ion R^+ et imperméable aux ions X^- [6–8]; le second système est une pile à double distribution[8,9].

La différence des potentiels de Galvani E des deux solutions aqueuses d'un même système que l'on dénomme aussi f.é.m. du système de piles à phases liquides a pour expression:

dans le cas du système I: $$E = \frac{RT}{F} \ln \frac{a_{R^+(e_1)}}{a_{R^+(e_2)}} \qquad (1)$$

dans le cas du système II:

$$E = \frac{1}{F}\left[\mu^\circ_{R^+(e)} + \mu^\circ_{R'^-(e)} - \mu^\circ_{R^+(n)} - \mu^\circ_{R'^-(n)}\right] + \frac{RT}{F} \ln \frac{a_{R^+(e_1)} \cdot a_{R'^-(e_2)}}{a_{R^+(n)} \cdot a_{R'^-(n)}} \qquad (2)$$

R = constante des gaz parfaits, a = activité ionique individuelle, μ° = potentiel chimique standard.

L'addition à la solution aqueuse (e_2) du système I d'une volume V d'une solution de titre connu de R'Na ou R'K entraîne la formation d'un précipité de $R^+R'^-$, insoluble dans l'eau, et la nouvelle valeur de E peut être évaluée, d'après la relation (1), en fonction du volume V de solution de R'Na ou R'K. Lorsque la totalité des ions libres R^+ de la solution e_2 aura ainsi disparu, toute nouvelle addition de R'Na transformera le système en un système II dont la ddp peut être également évaluée, d'après la relation (2), en fonction de la nouvelle concentration en ions R'^- présent dans la solution e_2. Il est donc possible, en appliquant successivement les relations (1)

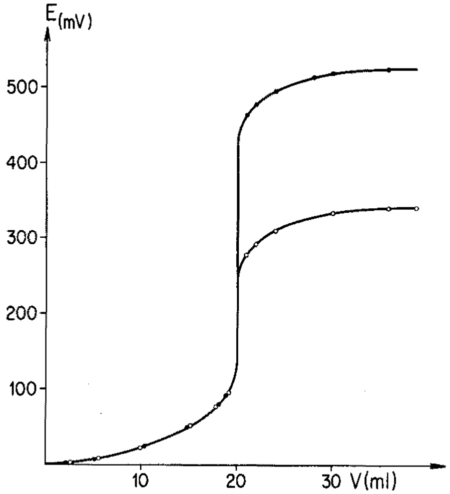


Fig. 1. Courbe de titrage calculée à partir des relations (1) et (2), relative à 20 ml de solution de DTA^+X^- 10^{-3} M (solution e_2). Solution titrante: (○) K^+Pi^- ou Na^+Pi^- 10^{-3} M. (●) Na^+TPB^- 10^{-3} M. Electrolyte de la phase organique (solution n): (●) DTA^+Pi^- 10^{-3} M dans nitrobenzène, (○) DTA^+TPB^- 10^{-3} M dans nitrobenzène. Solution e_1: DTA^+X^- 10^{-3} M dans l'eau.

et (2), de connaître les diverses valeurs de E en fonction du volume V de solution de R'Na ou R'K ajoutée à e_2 et de la concentration initiale en RX.

Les variations des valeurs de E ainsi calculées, lorsque R^+ est l'ion DTA^+, sont représentées dans la Fig. 1 en fonction du volume de solution titrante de picrate de potassium ou de tétraphényl-borate de sodium. La variation de E de part et d'autre du point équivalent est nettement plus brutale dans le cas de l'ion tétraphényl-borate.

Cette propriété est liée au fait que l'enthalpie libre standard de transfert du nitrobenzène à l'eau a une plus grande valeur dans le cas de l'ion TPB^- que dans le cas de l'ion Pi^-.

DISPOSITIF EXPÉRIMENTAL

Les solutions (n) et (e_1) sont placées dans un prototype d'électrode à élément actif liquide, spécifique des ions dosés[10]. Ce dispositif répond à la nécessité de réaliser une aire de contact extrêmement faible entre les solutions (n) et (e_2) qui réduit à l'extrême la redissolution dans le nitrobenzène du précipité de $R^+R'^-$ formé, en cours de dosage, dans la solution (e_2). D'autre part ce type d'électrode assure la possibilité de renouveler très facilement la phase organique en contact avec la solution aqueuse étudiée. Ceci constitue un avantage appréciable dans le cas présent où les espèces dosées ont la propriété de s'adsorber à divers interfaces.

Le montage utilisé est absolument analogue à celui des dosages potentiométriques classiques: dans la solution contenant l'ion ammonium quaternaire dont on veut déterminer la concentration (solution e_2), se trouvent immergées, d'une part, l'extrémité inférieure de l'électrode spécifique à élément actif liquide, et d'autre part, une jonction saline au chlorure de sodium reliée à une électrode de référence au calomel.

La solution est agitée à l'aide d'un barreau aimanté durant tout le temps de l'addition de la solution titrante.

La jonction électrique entre la solution e_1 et l'autre borne d'entrée de l'appareil de mesure est assurée par une électrode du type Ag–AgX qui représente l'un des éléments de l'électrode complexe indicatrice de l'ion à doser.

L'appareil de mesure est un millivoltmètre Tacussel type 90 AS/N.

Comme dans tout autre dosage potentiométrique, les courbes de titrage représentent les variations de ddp lues sur le millivoltmètre en fonction du volume de solution titrante ajouté à la solution à doser. Les modes d'obtention et de purification des produits utilisés ont été décrits antérieurement[8].

Le picrate de sodium est obtenu par neutralisation de l'acide picrique par la soude et ce composé est ensuite recristallisé dans le méthanol.

Le tétraphényl-borate de sodium est un produit Merck pour analyse et le nitrobenzène un produit UCB pour analyse chromatographique.

RÉSULTATS ET DISCUSSION

Ion dodécyl-triméthyl-ammonium (DTA^+)

On a pu ainsi réaliser le dosage de l'ion dodécyl-triméthyl-ammonium en solution aqueuse de chlorure et de bromure de DTA^+ au moyen d'une solution titrée de tétraphényl-borate de sodium (Fig. 2).

La limite du dosage se situe vers une concentration en ion DTA^+ de l'ordre de $10^{-6}\,M$. Dans le Tableau I sont présentés des résultats relatifs à des séries de dosage de l'ion DTA^+ lorsque l'électrolyte DTABr est seul présent en solution. La précision moyenne du dosage dépend des concentrations en DTABr comme l'indique le Tableau I.

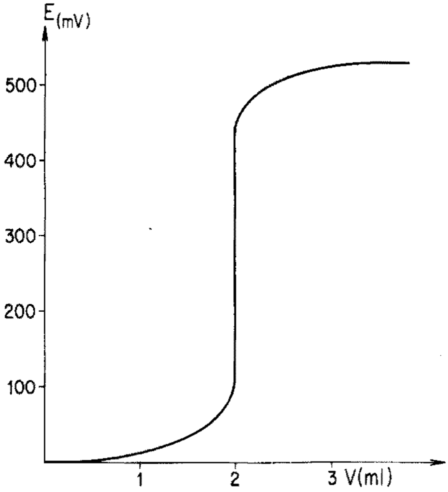


Fig. 2. Courbe de titrage de 20 ml de solution de DTABr $10^{-3}\,M$ par une solution de NaTPB $10^{-2}\,M$ (concentration DTA^+TPB^- dans le nitrobenzène: $10^{-3}\,M$).

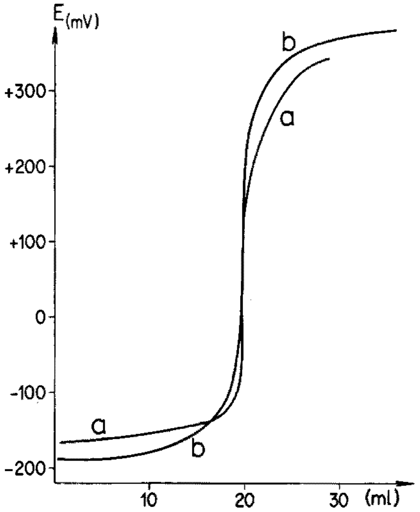


Fig. 3. Courbes de titrage de 20 ml de solution de DTABr $10^{-3}\,M$ + sel minéral par une solution de NaTPB $10^{-3}\,M$. (a) + NaCl 1 M. (b) + KBr $10^{-3}\,M$.

TABLEAU I

PRÉCISION MOYENNE DU DOSAGE DE DTABr

Concentration en DTABr (M)	*Précision moyenne (%)*
10^{-3}	± 0.1
10^{-4}	± 0.1
$5 \cdot 10^{-5}$	± 0.2
$2 \cdot 10^{-5}$	± 0.2
$5 \cdot 10^{-6}$	± 0.3
$2 \cdot 10^{-6}$	± 0.5

TABLEAU II

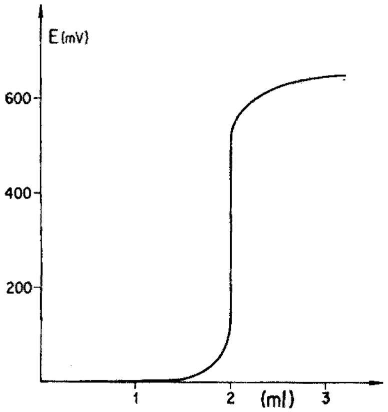
PRÉCISION MOYENNE DU DOSAGE DE HTACl

Concentration en HTACl (M)	*Précision moyenne (%)*
10^{-3}	± 0.5
$3 \cdot 10^{-4}$	± 1
10^{-4}	± 1.5
$5 \cdot 10^{-5}$	± 2

Le dosage de l'ion dodécyl-triméthyl-ammonium peut être également réalisé, de cette façon, en présence d'un fort excès de sel minéral—tel que le chlorure de sodium— dont le cation ne forme pas de précipité avec l'ion tétraphényl-borate (Fig. 3, courbe a). Cependant, dans ce cas, la courbe de titrage est légèrement différente de celle qu'on obtient avec DTABr en l'absence de sel minéral en solution aqueuse. Toutefois, bien que le tétraphényl-borate de potassium soit un composé insoluble dans l'eau, il est possible d'effectuer le dosage de l'ion DTA^+ en présence d'ion K^+ à faible concentration (Fig. 3, courbe b).

Ion tétradécyl-triméthyl-ammonium (TTA^+)

Le dosage de cet ion en solution aqueuse a été réalisé selon le même mode opératoire que celui de l'ion dodécyl-triméthyl-ammonium. Les résultats obtenus sont comparables. La différence des potentiels chimiques standard de cet ion dans l'eau et dans le nitrobenzène étant supérieure en valeur absolue à celle de l'ion DTA^+, à cause du caractère lipophile plus marqué de l'ion TTA^+, lié à une plus grande longueur de sa chaîne hydrocarbonée; la courbe de titrage, au voisinage du point équivalent, indiquera une variation de ddp plus importante (Fig. 4).



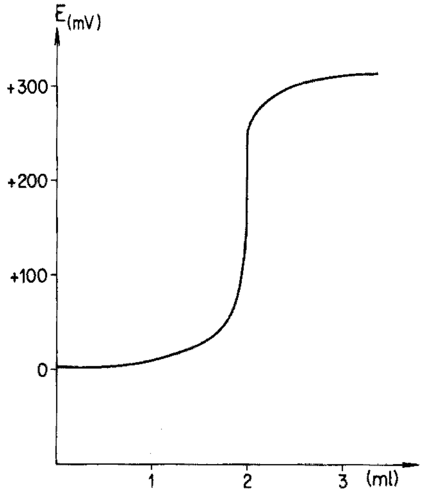


Fig. 4. Courbe de titrage de 20 ml de TTABr 10^{-3} *M* par une solution de NaTPB 10^{-2} *M*. Phase organique: solution de TTA TPB $5 \cdot 10^{-4}$ *M* dans le nitrobenzène.

Fig. 5. Courbe de titrage de 20 ml de bromure d'hexadécyl-triméthyl-ammonium (HTABr). Composition électrode spécifique:

AgAgCl	HTACl- 10^{-3} *M* dans H_2O	HTA Pi 10^{-3} *M* dans nitrobenzène + 20% benzène

Ion tétrabutyl-ammonium (TBA^+)

La méthode de dosage des ions DTA^+ et TTA^+ par une solution de tétraphényl-borate de sodium décrite ci-dessus peut être appliquée à l'ion tétrabutyl-ammonium (TBA^+). La précision obtenue reste dans un ordre de grandeur absolument analogue, car le facteur prépondérant, qui est l'enthalpie libre standard de transfert du nitrobenzène à l'eau, a une valeur du même ordre de grandeur pour ces trois types d'ions.

Ion hexadécyl-triméthyl-ammonium (HTA^+)

Le dosage potentiométrique de l'ion hexadécyl-triméthyl-ammonium par une solution de tétraphényl-borate de sodium n'a pas pu être réalisé à cause du caractère trop lipophile de ce cation. Mais on a pu appliquer la présente méthode potentiométrique modifiée sur les deux points suivants: la solution titrante est une solution aqueuse de picrate de sodium et le solvant de la solution (n) est du nitrobenzène additionné de 20% de benzène (Fig. 5). Dans ces conditions, la limite inférieure de dosage est de l'ordre de $3 \cdot 10^{-5}\,M$ et la précision est moins satisfaisante que celle des dosages des trois ions précédents comme l'indique le Tableau II relatif à plusieurs séries de dosages.

RÉSUMÉ

On décrit une méthode de dosage potentiométrique des ions dodécyl-triméthyl-ammonium, tétradécyl-triméthyl ammonium, hexadécyl triméthyl-ammonium et tétrabutyl ammonium en solution aqueuse. L'électrode indicatrice utilisée est un nouveau modèle d'électrode à élément actif liquide. Le principe du dosage fait intervenir certains résultats de l'étude des piles à phase liquides.

SUMMARY

A method of potentiometric titration of dodecyltrimethylammonium, tetradecyltrimethylammonium, hexadecyltrimethylammonium and tetrabutylammonium ions in aqueous solution is described. The ion-selective electrode which is used is a new liquid element electrode model. The principle of titration involves some results of the study of liquid phase electric cells.

ZUSAMMENFASSUNG

Eine Methode zur potentiometrischen Titration von Dodecyl-trimethyl-ammonium-, Tetradecyl-trimethylammonium-, Hexadecyl-trimethylammonium- und Tetrabutyl-ammonium-Ionen in wässrigen Lösungen wird beschrieben. Die ionenselektive Elektrode, die hier angewandt wird, ist ein neues Modell einer Elektrode mit Flüssigkeitszelle. Das Prinzip der Titration schliesst einige Ergebnisse der Untersuchung von elektrischen Flüssigkeitszellen ein.

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A NEW REAGENT FOR THE DETECTION AND DETERMINATION OF SMALL AMOUNTS OF THE SULPHATE ION

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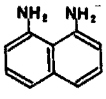
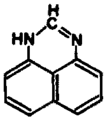
The determination of small amounts of the sulphate ion in aqueous solution is of importance in many fields of applied analysis but particularly in connection with the analytical problems of air and water pollution, and other environmental aspects of chemical analysis. Of the available methods, the recent nephelometric method described by MARTIN AND STEPHEN[1], in which the sensitive 4-amino-4′-chlorobiphenyl reagent is utilised as the precipitant for sulphuric acid, would appear to be amongst the most satisfactory. This reagent was described several years ago[2] as part of extended studies of benzidine and its derivatives as precipitants for the sulphate ion. In these same studies[3], the efficacy of 1,8-naphthylenediamine (I) as a precipitant for sulphate ions was also demonstrated; no analytical use was made of this finding because the solubility of the diamine sulphate at room temperature is more than twice that of benzidine sulphate. At that time, the search was for a diamine with a sulphate less soluble than benzidine sulphate, and this aim was realised with the synthesis and examination of 4,4′-diaminotolane[4].



I



II

Closely related to 1,8-naphthylenediamine and readily derived from it, is the series of organic bases known as perimidines which have been described in detail by SACHS[5]. The parent heterocycle, perimidine (II), is characterised by its readiness to form sparingly soluble salts with several acids, but this behaviour is much more marked with the 2-amino derivative. SACHS remarks on the unusually low solubility of the normal sulphate of this base and states that the salt is soluble to the extent of 1 part in 2000 parts of water[6]. Although this is not particularly low by comparison with other amine sulphates (Table I), it is sufficiently low to justify preparation of 2-aminoperimidine and its examination as a potential analytical reagent. Previous experience has shown that the solubility of a precipitated salt is only a rough guide to its analytical utility and a much more significant factor is the sensitivity of the precipitant towards the ion being precipitated. With 4-amino-4′-chlorobiphenyl hydrochloride, this has been effectively demonstrated both in the earlier studies and in the nephelometric applications.

Accordingly, 2-aminoperimidine has been prepared by SACHS' directions and has

TABLE I

SOLUBILITIES OF VARIOUS AMINE SULPHATES

Amine	*Solubility of normal sulphate ($g\ l^{-1}$ at 25°)*	*Ref.*
Benzidine	0.098	3
1,8-Diaminonaphthalene	0.222	3
4-Amino-4′-chlorobiphenyl	0.155	2
4,4′-Diaminotolane	0.059	4
2-Aminoperimidine	0.020[a]	This work

[a] Measured at 18°.

been purified and isolated as its hydrochloride salt as described below. This salt is quite soluble in warm water and provides a 0.5%(w/v) solution at room temperature. The amine is susceptible to oxidation and care must be taken to avoid undue exposure to oxidising conditions, but the solution is perfectly satisfactory for several days of normal usage.

When the reagent solution is added to known amounts of sulphate solution, initially of 10 p.p.m. concentration, quite heavy silky white precipitates are obtained. Surprising features of these precipitates are their unusually small particle size (microscopic examination shows most particles to be no more than 2 μm across), their extremely regular shape in the form of a right-angled cross (Fig. 1), and their apparent unwillingness to ripen or aggregate on standing for several hours. Even at 1 p.p.m. of sulphate, the precipitation is readily observed, and it is possible to detect by direct visual examination of the solution as little as 0.05 p.p.m. of sulphate in a test volume of 10 ml. This is a considerable improvement over the 4-amino-4′-chlorobiphenyl

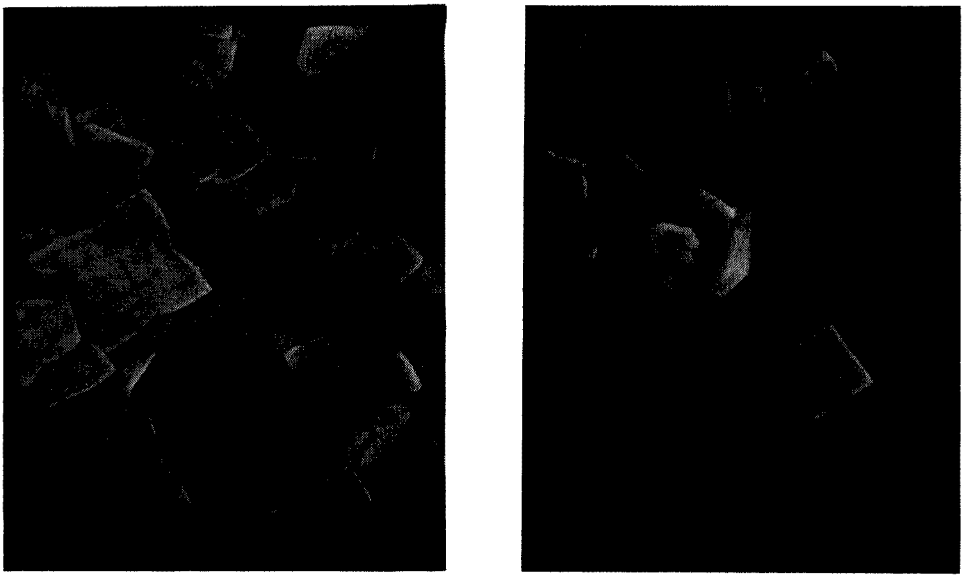


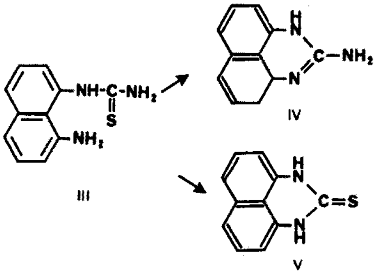
Fig. 1. Scanning electron photomicrographs of 2-aminoperimidine sulphate (magnification 10,000 ×).

reagent, which has hitherto been the most sensitive reagent known for the precipitation of the sulphate ion.

These findings indicate a distinct possibility that 2-aminoperimidine may be exploited as a reagent for the nephelometric determination of small amounts of sulphate. A thorough examination has shown that as little as 0.2 p.p.m. of sulphate can be determined by an extremely simple procedure.

PREPARATION OF REAGENT

The reaction of 1,8-diaminonaphthalene with ammonium thiocyanate is a special case of the more general reaction of this diamine with isothiocyanates as established by Sachs[5]. Initially, 8-amino-1-naphthylthiourea (III) is formed and this loses either hydrogen sulphide or ammonia to give either 2-aminoperimidine (IV) or 2-thioperimidone (V).



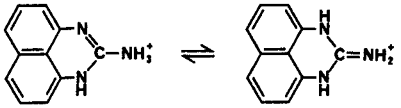
In practice, both 2-aminoperimidine and 2-thioperimidone are formed. The latter is quite insoluble in hot water and is easily separated from the water-soluble amino derivative. Little difficulty is experienced in scaling up the original directions of Sachs for the preparation by twenty times. The isolation and purification of the free base is, however, less convenient than isolation and purification of the hydrochloride, and the preparation in the EXPERIMENTAL part describes only the purification of this salt, which is used as the reagent. The amine has, however, been adequately characterised in the form of the free base and as its salts with hydrochloric, nitric, sulphuric and picric acids.

It is a fairly straightforward matter to convert the sparingly soluble amine sulphate to the hydrochloride. Thus, it is worthwhile to retain all solutions and precipitates containing 2-aminoperimidine for purposes of reagent recovery.

SOLUBILITY AND NATURE OF 2-AMINOPERIMIDINE SULPHATE

The nephelometric measurement of a saturated aqueous solution of 2-aminoperimidine sulphate by the method described below, indicates that the salt is soluble in water to the extent of 20 mg l^{-1} at 18°. This is by far the lowest solubility yet recorded for an amine sulphate in water (*cf.* Table I), and is considerably lower than the value given by Sachs who does not discuss how his value was obtained. If, as is indicated by the analytical data, the normal sulphate is obtained, it is reasonable to suppose that this salt dissociates completely in solution; a measurement of the sulphate concentration in the saturated aqueous solution is sufficient to indicate the solubility of the amine salt. The new nephelometric method is ideally suited to this measurement, particularly as the only other ion present (other than those of the solvent) is the amine cation, present in very much larger concentration in the precipitating agent.

The amine sulphate is unusual in many ways. It cannot apparently be titrated with alkali like 4-amino-4′-chlorobiphenyl sulphate or benzidine sulphate. The free base is liberated from its salts by addition of strong alkali, but the base is strongly hydrated in aqueous solution and is not readily extracted into solvents such as ether. A complete study has not yet been made of the acid–base equilibria involved with solutions of this perimidine, but it does seem that the basic nature of 2-aminoperimidine is somewhat conditioned by the presence of the imino group in the molecule. The imino hydrogen may be weakly acidic and in some way may participate in salt formation. The sulphate is an unusual one and is sparingly soluble not only in water, but in water–ethanol and water–acetone mixtures. In general, the addition of these hydrophilic organic solvents results in an increase in the solubility of the amine salts. It may be that 2-aminoperimidine behaves as a guanidine derivative as a result of tautomeric changes in the molecule, and this may account for the ease with which the amine forms well-defined crystalline salts.



NEPHELOMETRY OF THE SULPHATE ION

The very low solubility of 2-aminoperimidine sulphate and its unwillingness to form aggregates when precipitated at room temperature seemed to make it ideal for nephelometric applications. A detailed examination has therefore been carried out.

Effect of pH

A preliminary examination of the precipitation of the sulphate ion has shown that the best characteristics for the precipitate are obtained when the pH of the solution is about 5.0. The reagent solution usually has a pH of 4.8 and if the unbuffered test solution is between pH 5.0. and 7.0, there is no problem with the precipitation.

Effect of reagent concentration

The procedure for the determination of sulphate simply involves addition of the aqueous 0.5% 2-aminoperimidine hydrochloride solution to a suitable amount of sulphate solution, dilution to 10 ml with water, and measurement of the light scattering. For the precipitation of 1 p.p.m. of sulphate (with respect to the final volume of solution), a 4-ml volume of reagent solution is optimal for complete precipitation and for reproducible galvanometer readings. This amount of reagent is also satisfactory for both higher and lower ranges of sulphate concentrations at different sensitivity settings of the nephelometer used. The 4.0-ml reagent addition corresponds to a reagent concentration of $4 \cdot 10^{-3}$ *M* in the final 10-ml measurement volume.

Effect of time on the precipitate

Direct observation of the precipitate of 2-aminoperimidine sulphate indicates that precipitation of the sulphate ion is practically complete within 1–2 min of adding the reagent solution. Detailed nephelometric measurements substantiate this fact; for sulphate concentrations in the range 0.25–1 p.p.m., the light scattering increases up to 5 min and then remains essentially constant for some hours, provided that the suspension is inverted once or twice just before the measurement. Even on standing overnight, the suspensions only partially settle out and on shaking assume essentially the same nephelometric characteristics as are obtained shortly after their preparation.

Accordingly, no great emphasis is placed on time of measurement; for practical purposes, it is convenient to measure the suspensions 10–15 min after their preparation. The remarkable stability of the precipitate and its ideal nephelometric characteristics obviate the necessity of protective colloids and other stabilising chemicals; therefore no examination of such additives has been made.

Preparation of standard curves

When the simple procedure outlined in the EXPERIMENTAL part is applied, linear calibration graphs can be achieved over several ranges of sulphate concentration, depending on the sensitivity setting of the instrument used. At maximum sensitivity of the EEL nephelometer used in the present work, a suspension containing 0.1 p.p.m. of sulphate produces a response of about 30% f.s.d., but the readings are not then stable. With lower sensitivity settings varying from 30 to 80% of the available sensitivity range, measurements are very stable, and it is possible to set up calibration curves over the ranges 0–0.5 p.p.m., 0–1 p.p.m. and 0–5 p.p.m. of sulphate ion (Fig. 2).

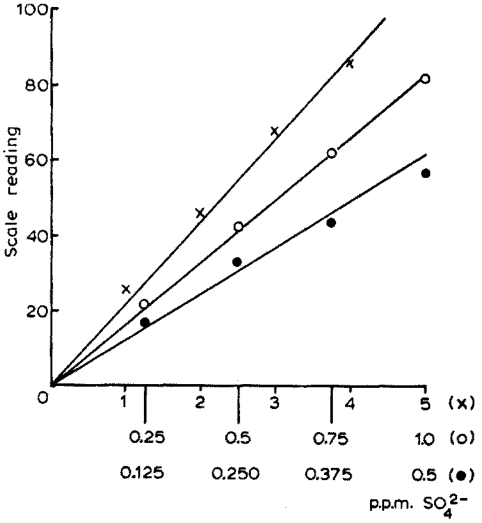


Fig. 2. Calibration graphs at different instrumental sensitivities: (×) 0–5 p.p.m. sulphate, (○) 0–1 p.p.m. sulphate, (●) 0–0.05 p.p.m. sulphate.

These ranges correspond to 0–1, 0–2, and 0–10 p.p.m. of sulphate ion in the original sample solution, if a 5-ml portion is taken. A properly prepared reagent solution shows the same blank deflection as distilled water except at high sensitivity settings of the instrument.

With regard to the reproducibility of the method, a series of 11 determinations of 0.5 p.p.m. of sulphate showed a relative standard deviation from the mean of 4.5%.

Effect of foreign ions on the nephelometric procedure

An examination of the effect of known amounts of the ions, chloride, bromide, iodide, fluoride, fluorosilicate and phosphate on the nephelometric determination of sulphate at the 0.25, 0.50 and 0.75 p.p.m. levels, has shown that there are few serious interferences from moderate amounts of these ions. There is no interference from 10 or 100 p.p.m. of nitrate ion. Bromide causes no interference when 10 p.p.m. is present, but the presence of 100 p.p.m. introduces a positive error of *ca.* 20%. Iodide at both the 10 and 100 p.p.m. levels causes a positive error of about 10%. The interference of fluoride or fluorosilicate is more severe, amounting to about 10% at the 1 p.p.m. level, though the error increases to only 15% when the mixture contains 10 p.p.m. of fluoride. There is an appreciable interference from phosphate; even 1 p.p.m. leads to a positive error of 25%.

The effect of chloride is very dependent on its concentration. The reagent solution is about 0.01 *M* with respect to chloride, and is almost saturated, hence the presence of a large amount of chloride ion results in the gradual precipitation of the amine hydrochloride by common ion effect; this happens with 500 or 1000 p.p.m. of chloride present. There is no interference from 10 p.p.m. of chloride, but 100 p.p.m. leads to variable positive errors of 5–15%. It might be possible to overcome this by lowering the concentration of the reagent in the final solution; for particular applications, such as the examination of sea waters, it may be advantageous to develop particular procedures to cope with unusually high chloride contents. For the examination of natural fresh waters, high ionic concentrations of interfering ions are unlikely, and the general procedure described in the EXPERIMENTAL section should be readily applied.

Analytical applications

The existence of an unequivocal test of this nature for the sulphate ion should prove useful for qualitative and quantitative applications. The detection of trace sulphur in hydrocarbon oils should be readily effected by a flask combustion process which leads to a relatively unadulterated test solution of sulphate. In cases where the amount of sulphate in solution is very small, the limit of detection could be improved by centrifuging off the precipitate of 2-aminoperimidine sulphate and examining this microscopically for the characteristic crystal form. Similarly, atmospheric pollutants containing inorganic sulphates and sulphur trioxide could well be identified by simple drop reactions followed by microscopic identification of 2-aminoperimidine sulphate.

The determination of very small amounts of sulphate in natural waters can be simplified by the use of the proposed method, as can the determination of sulphate in any other relatively unadulterated test solution.

THE REACTION OF 2-AMINOPERIMIDINE HYDROCHLORIDE IN AQUEOUS SOLUTION WITH OTHER ANIONS

The addition of aqueous 0.5% 2-aminoperimidine hydrochloride solution to aqueous solutions of other anions has shown that this base readily forms slightly soluble salts with very many acids. When equal volumes of the reagent solution and of 0.01 M solutions of bromide, iodide, iodate, cyanate, sulphite, sulphide, dithionate, thiosulphate, selenate, tellurate, oxalate, benzoate, salicylate, formate, acetate, citrate, tartrate, molybdate, tungstate, dichromate, vanadate, permanganate, perrhenate, chloroplatinate, hexacyanoferrate(II) and (III), arsenate, arsenite, borate, fluoroborate, silicate, fluorosilicate, dihydrogen phosphate, hydrogen phosphate, phosphite, hypophosphite, pyrophosphate or trimetaphosphate, are mixed, quite heavy precipitates are obtained. Slight precipitates occur with chlorate, perchlorate and thiocyanate at the same concentration. Fluoride, chloride, bromate and nitrate do not react except at higher concentrations, whereas nitrite, carbonate or hydrogen carbonate do not yield precipitates at any of the concentrations tested. Persulphate gives an initial white precipitate which rapidly turns green and finally black as a result of the oxidation of the amine, but the dichromate and vanadate salts appear to be quite stable at room temperature. The reactions reported indicate that 2-aminoperimidine behaves like several other salt-forming reagents, for example, benzidine and nitron, in exhibiting a rather poor selectivity. Nevertheless, this fact has not prevented their considerable application as analytical reagents. The study of interferences of common anions on the nephelometric determination indicates that at least 10-fold amounts of most common anions can be tolerated without undue error.

EXPERIMENTAL

Preparation of 2-aminoperimidine hydrochloride

1,8-Diaminonaphthalene (100 g) and ammonium thiocyanate (54 g) are dissolved in pure ethanol (650 ml) and the mixture is heated under reflux in a 1-l flanged two-piece reaction vessel on a steam bath for about 8 h. During this time, hydrogen sulphide and ammonia are evolved and a yellow sublimate appears in the condenser. The condenser and the lid of the vessel are removed and heating is continued for about 16 h, by which time almost all the solvent has been removed and the reaction mixture has become a dark pasty mass. It is more convenient for the subsequent operations to transfer the material to a 500-ml wide-mouthed conical flask which is then set in an oil-bath at 100°. The temperature is raised gradually (1–2 h) to 150° and is held at this temperature for about 8 h until the evolution of hydrogen sulphide has virtually ceased (lead acetate test paper). The reaction mixture has now become a hard black amorphous mass which is broken up with a stout spatula and boiled up in the flask with several portions (250 ml) of already boiling water. The boiling aqueous extracts are filtered from the black insoluble residue and are collected together. (The extraction is apparently complete when the black residue assumes a fine crumbly structure.)

When cool, the aqueous solution deposits a curdy yellow substance which is filtered off on a large sintered glass funnel, washed with a little cold water, drained well and then dissolved from the filter in the minimal amount of hot acetone. The acetone solution is then treated with sufficient 4 M hydrochloric acid to precipitate completely the hydrochloride of the base; this is filtered off, drained well, washed on the filter with a small volume of acetone followed by diethyl ether, and finally air-dried on the filter. About 30 g of a pale yellow finely crystalline powder are obtained.

This material should not contain any sulphur (by qualitative oxygen flask combustion), but it is advantageous to purify the hydrochloride by dissolving 10 g in 400 ml of water with warming, filtering the hot solution and treating with a saturated aqueous solution of potassium chloride until precipitation is complete. The precipitate is filtered off, washed with a little dilute potassium chloride solution and then with acetone and diethyl ether as previously. The hydrochloride is obtained as a greyish-white crystalline powder which dissolves readily in warm water. The solution gives an immediate silky white precipitate when treated with 0.05% potassium sulphate solution.

2-Aminoperimidine hydrochloride melts at 282°; elemental analyses of a sample dried at 110° *in vacuo* gave 59.8%C, 4.8% H and 19.4% N ($C_{11}H_{10}N_3Cl$ requires 60.1% C, 4.6% H, 19.1% N).

2-Aminoperimidine sulphate has no melting point. A sample dried at 110° *in vacuo* gave 57.0% C, 4.4% H, 17.8% N, 7.1% S; $(C_{11}H_{10}N_3)_2SO_4$ requires 56.9% C, 4.3% H, 18.1% N, 6.9% S.

Nephelometric determination of sulphate

2-Aminoperimidine hydrochloride solution. Dissolve 0.5 g of the amine salt in 100 ml of warm distilled water, filter the hot solution and store in an amber-coloured reagent bottle. The reagent is sensitive to oxidants, and some deterioration of the reagent solution occurs if it is left exposed to air and light for some days. If it is stored in a stoppered dark glass bottle, little or no change occurs for some time, and the reagent can be used for at least 4 days, giving exactly the same calibration graph.

Stock potassium sulphate solution, 10 p.p.m. Dissolve 18.14 mg of freshly dried A.R.-grade salt in 1 l of freshly distilled water.

Apparatus. An "EEL" nephelometer comprising the EEL nephelometer head and EEL Unigalvo Type 20 (Evans Electroselenium Ltd., Essex, England) is suitable. Test tubes (10 mm i.d., capacity 12 ml) provided with the instrument are used for holding the suspensions in the nephelometer.

General procedure. For 0–5 p.p.m. of sulphate, transfer 1.0... 5.0 ml of standard sulphate solution to each of five 10-ml volumetric flasks. Dilute to about 5 ml with distilled water, add 4 ml of the 2-aminoperimidine hydrochloride solution, and dilute the contents to the mark. Mix well by inverting the flask several times and leave the suspensions for 5–10 minutes. Transfer to the nephelometer tube and measure the light scattering of each solution, after setting the zero reading on a blank solution and the sensitivity to give a reading of about 80% f.s.d. for the most concentrated sulphate solution. At the lower sensitivity settings of the instrument, distilled water and a reagent blank solution give essentially the same reading. Plot the galvanometer readings against the concentration of sulphate in the 10-ml test solution.

For 0–1 p.p.m. or 0–0.5 p.p.m. of sulphate, proceed in exactly the same way but use higher instrumental sensitivities.

Recovery of reagent

All solutions and suspensions containing the reagent may be stored in a residues bottle to which a quantity of 5% sodium sulphate solution has been added. On standing, the precipitate of the amine sulphate settles out and the supernatant liquid is periodically decanted off. More sulphate solution is added to maintain a sufficient concentration in the aqueous phase. When an appreciable amount of precipitate has been collected, it is filtered off on a large sintered glass filter funnel, washed with water and then is suspended in water. After addition of 4 *M* sodium hydroxide, the mixture is thoroughly shaken up and the free base is filtered off. This is dissolved in acetone and worked up to give the hydrochloride salt as described for the preparation of the reagent.

The author expresses his thanks to Mr. HOWARD M. HECK of the Marathon Oil Company, Littleton, Colorado for providing the scanning electron photomicrographs of 2-aminoperimidine sulphate.

SUMMARY

An aqueous solution of 2-aminoperimidine hydrochloride is proposed as a new reagent for the detection and determination of the sulphate ion. As little as 0.05 p.p.m. can be detected by precipitation of the corresponding amine sulphate. Suspensions of the precipitate show remarkable stability and no colloidal stabilizers are needed. The reagent is applied to the nephelometric determination of 0.1–5 p.p.m. of sulphate ion; at the 0.5 p.p.m. level, the relative standard deviation is 4.5%. Although many ions form precipitates with the reagent at high concentrations, very few of the common anions provide significant interference in the nephelometric determination. The reagent seems promising for the determination of sulphate in natural waters, and for traces of sulphur in organic compounds after oxygen flask combustion.

RÉSUMÉ

Un nouveau réactif, le chlorhydrate d'amino-2-périmidine est proposé pour l'identification et le dosage des sulfates. On peut déceler ainsi jusqu'à 0.05 p.p.m. par précipitation sous forme du sulfate d'amine correspondant. Les suspensions de ce précipité présentent une stabilité remarquable; aucun stabilisateur colloïdal n'est nécessaire. Ce réactif permet un dosage néphélométrique de 0.1 à 5 p.p.m. de sulfate. Il semble intéressant pour l'analyse des eaux naturelles et pour le dosage de traces de soufre dans des substances organiques après combustion dans l'oxygène.

ZUSAMMENFASSUNG

Als neues Reagenz für den Nachweis und die Bestimmung von Sulfationen wird eine wässrige Lösung von 2-Aminoperimidinhydrochlorid vorgeschlagen. So geringe Mengen wie 0.05 p.p.m. können durch Fällung des korrespondierenden Aminsulfats nachgewiesen werden. Suspensionen des Niederschlags zeigen eine bemerkenswerte Stabilität; Kolloid-Stabilisatoren werden nicht benötigt. Das Reagenz wird für die nephelometrische Bestimmung von 0.1–5 p.p.m. Sulfationen verwendet; bei 0.5 p.p.m. beträgt die relative Standardabweichung 4.5%. Obwohl viele Ionen mit dem Reagenz bei hohen Konzentrationen Niederschläge ergeben, stören von den gewöhnlichen Anionen sehr wenige ernsthaft bei der nephelometrischen Titration. Das Reagenz erscheint vielversprechend für die Bestimmung von Sulfat in natür-

lichen Wässern und Schwefelspuren in organischen Verbindungen nach deren Verbrennung in Sauerstoff.

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THE GAS CHROMATOGRAPHY, THERMAL ANALYSIS AND MASS SPECTROMETRY OF FLUORINATED LEAD β-DIKETONATES

DETERMINATION OF TRACES OF LEAD BY THE INTEGRATED ION-CURRENT TECHNIQUE

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Considerable attention has been given to the preparation of numerous metal β-diketonates[1] and to their possible applications[2], but little work has been done on the lead derivatives of β-diketones. COMBES[3] prepared lead bis(acetylacetonate) in 1887, and later MENZIES[4] reported the ready hydrolysis of this chelate and its partial volatilisation on heating. FERNELIUS *et al.*[5] determined the formation constants of the lead chelates of acetylacetone, benzoylacetone, dibenzoylmethane and 2-furoyl-2-thenoylmethane in 75% (v/v) dioxane solution and BERG *et al.* reported the preparation and partial sublimation of lead bis(thenoyltrifluoroacetonate)[6] and lead bis-(trifluoroacetylacetonate)[7]. X-Ray crystallographic studies have shown lead bis-(benzoylacetonate) to be planar[8]. The most comprehensive survey of lead β-diketonates was conducted by SCHWEITZER *et al.*[9], who studied the behaviour of a number of fluorinated and non-fluorinated chelates on sublimation.

The perfluoroalkanoylpivalylmethanes form complexes with a wide range of metal ions to give volatile, thermally stable chelates, and these have been used successfully in gas chromatography[10,11] and mass spectrometry[12,13] for trace metal analysis. In the work described below, lead chelates were prepared by direct reaction of aqueous solutions of lead(II) with trifluoroacetylpivalylmethane, pentafluoropropanoylpivalylmethane and heptafluorobutanoylpivalylmethane, and their analytical potential in gas chromatography and mass spectrometry was examined.

EXPERIMENTAL

General nomenclature

The β-diketones are referred to by the trivial names given below, which in metal complexes refer to the enolate ion of the parent β-diketone.

1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione (trifluoroacetylpivalylmethane), TPM.

1,1,1,2,2-Pentafluoro-6,6-dimethylheptane-3,5-dione (pentafluoropropanoylpivalylmethane), PPM.

1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyloctane-4,6-dione (heptafluorobutanoylpivalylmethane), HPM.

Preparation of organic ligands

The three β-diketones were synthesized by the Claisen condensation of pinacolone with the ethyl ester of the appropriate fatty acid, with powdered sodium hydride (Koch-Light Ltd) as the condensing agent. Liquid reagents obtained commercially were purified by distillation from phosphorus pentoxide. The preparative procedure for trifluoroacetylpivalylmethane was as follows: dry ethyl trifluoroacetate (228.5 g; 1.62 mole) was added to 1 l of ether (dried over sodium wire) and sodium hydride powder (39 g; 1.62 mole) in a 2-l flask fitted with a double condenser, dropping funnel and "gago" sealed stirrer. The ether solution was stirred and brought to gentle reflux on an electric heating mantle. Dry pinacolone (162.4 g; 1.62 mole) was added continuously over a period of 1.5 h and the reaction mixture was stirred under reflux for a further 4.5 h. The yellow reaction mixture was then cooled in an ice bath and treated carefully with 50 ml of water to destroy any remaining sodium hydride. Concentrated hydrochloric acid (140 ml) was then added with vigorous stirring and the precipitated sodium chloride was dissolved by adding 100 ml of water. The contents of the reaction vessel were poured into a 5-l separating funnel and the lower aqueous layer was removed and extracted with fresh ether (2 x 50 ml). The combined wet ether extracts were evaporated to a volume of about 300 ml, and dried with two separate batches of anhydrous magnesium sulphate. The ether was distilled off at atmospheric pressure and the remaining liquid was fractionally distilled at 30 mm Hg through a 10-in column packed with Fenske helices to give (a) ether, (b) material boiling up to 54° (6 g), (c) trifluoroacetylpivalylmethane (210 g; yield 66%; b.p. 55–56°), and (d) a dark brown residue (4 g).

Gas chromatography of fraction (c) gave a single peak and mass spectral analysis showed a fragmentation pattern with a top mass peak at *m/e* 196, corresponding to the molecular ion of $CF_3COCH_2COC(CH_3)_3$. The β-diketone was collected as a colourless liquid (b.p. 146–147°) at 750 mm Hg.

The other two fluorinated β-diketones were prepared in the same way and had the following characteristics: pentafluoropropanoylpivalylmethane, b.p. 152–153° at 750 mm Hg (50–50.5° at 20 mm Hg), yield 63%; heptafluorobutanoylpivalylmethane, b.p. 165–166° at 748 mm Hg (44–45° at 7 mm Hg), yield 68%.

Preparation of lead chelates

The chelates were prepared by adding a slight excess of the appropriate ligand in ether to an aqueous lead acetate solution in a separatory funnel. After vigorous shaking, the aqueous phase was removed and the lead chelate was obtained by evaporation of the ether. The lead chelates of trifluoroacetylpivalylmethane and pentafluoropropanoylpivalylmethane were obtained readily as white crystalline needles, but lead heptafluorobutanoylpivalylmethanate crystallised only on standing for 12 h at 0°. The conditions of sublimation for the chelates together with melting points and microanalytical data are summarised in Table I.

Sublimation procedure

The dried chelates were sublimed at 0.5 mm Hg in a sublimation apparatus immersed in an oil bath and the sublimates were collected on a cold finger. Chloroform was used in the cold finger for the lead chelates of trifluoroacetylpivalylmethane and pentafluoropropanoylpivalylmethane, but liquid air was used for lead heptafluoro-

TABLE I

PHYSICAL DATA FOR LEAD PERFLUOROALKANOYLPIVALYLMETHANATES

Chelate	*Initial sublim. temp. at 0.5 mm Hg (°)*	*Purification sublim. temp. at 0.5 mm Hg (°)*	*M.p. (°)*	*Carbon–hydrogen (%)*	
				Calculated	*Found*
$Pb(TPM)_2$	112–114	150	194	C, 32.2 H, 3.4	C, 32.4 H, 3.7
$Pb(PPM)_2$	73–74	120	132	C, 31.0 H, 2.9	C, 31.2 H, 2.6
$Pb(HPM)_2$	62–63	110	74	C, 30.1 H, 2.5	C, 30.1 H, 2.5

butanoylpivalylmethanate. The initial sublimation temperature of the chelates was taken as the temperature of the oil bath corresponding to the first appearance of solid material on the cold finger of the sublimation apparatus, but for the purifications the temperature was maintained above this level to ensure a preparative sublimation rate.

Thermal analysis

Thermogravimetric analysis was carried out on a Perkin-Elmer TGS-1 Thermobalance with 4-mg samples at scan rates of 16 and 32° min^{-1} in both direct and derivative modes. A nitrogen atmosphere was employed.

The chelates were also examined by differential scanning calorimetry with the Perkin-Elmer DSC-1B Calorimeter, with scanning rates of 16 and 32° min^{-1}.

Mass spectrometry

The mass spectra were recorded on an A.E.I. MS9 double-focusing mass spectrometer, operating at an ionizing voltage of 70 eV and an accelerating potential of 8 kV. The source temperature was maintained at $250 \pm 10°$ and samples were evaporated into the source with the direct insertion probe. The integrated ion-current curves were recorded as described previously[13].

Gas chromatography

A Philips PV 4000 (Pye R) chromatograph equipped with a hydrogen flame ionisation detector was used. Eluates were collected for characterisation by introducing a 1:1 post-column splitter and passing the vapour through a heated Teflon tube (1/8-in o.d.) into traps cooled in liquid air.

Teflon columns (3/16-in o.d., length 2 ft. and 4 ft.) were used with liquid phase loadings of 5, 10 or 15% Apiezon L on "Universal B" (60–85 mesh) support. The substrate materials were obtained from Phase Separations Ltd., the "Universal B" support being reported as a diatomaceous material silanized in a manner covered by industrial patents. All columns were pre-conditioned for 24 h at 220° and nitrogen carrier-gas flow rates were measured by a soap film flowmeter. The nitrogen used was of B.O.C. white-spot grade.

RESULTS AND DISCUSSION

Thermal analysis

Thermograms of Pb(HPM)$_2$ were recorded at various heating rates; a typical TGA trace is shown in Fig. 1a. The trace indicates negligible thermal decomposition over the sublimation range 180°–300°, less than 3% of the sample remaining unsublimed. Thermograms recorded for Pb(TPM)$_2$ and Pb(PPM)$_2$ showed very similar characteristics but lower volatilities. This evidence of thermal stability and extent of volatilisation may be used to predict favourable gas chromatographic column conditions and indicate maximum source temperature for mass spectrometry.

The derivative thermogram (DTG) of Pb(HPM)$_2$ shown in Fig. 1b indicates a small degree of decomposition (< 3%) in the region 280°–300° of the same order as indicated subsequently by gas chromatography. This behaviour is confirmed by

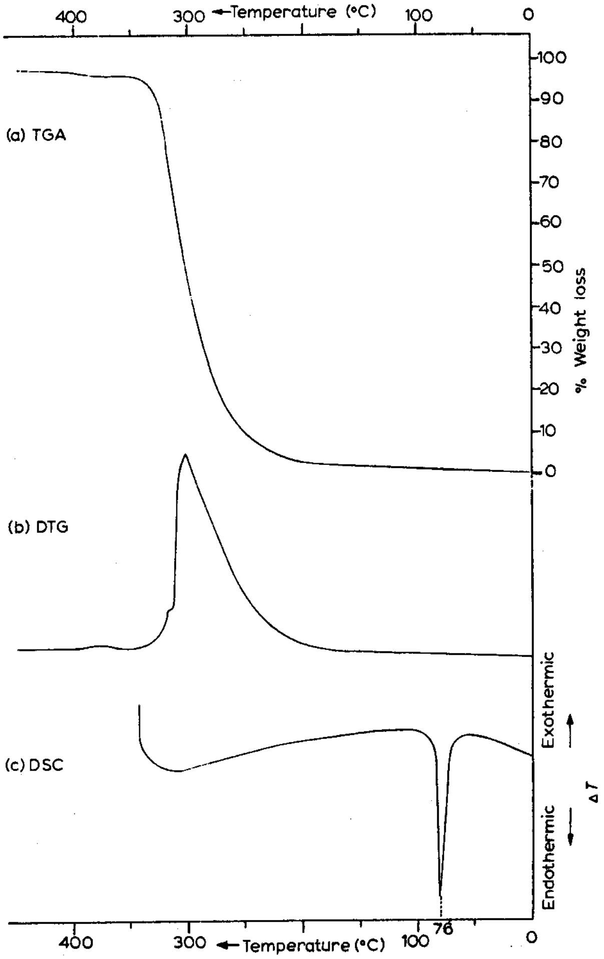

Fig. 1. Thermal analysis of Pb(HPM)$_2$. (a) Thermogravimetric analysis, (b) derivative thermogram, (c) differential scanning calorimetry. Heating rate 32° min^{-1}.

differential scanning calorimetry (DSC) (Fig. 1c), the trace indicating a sharp melting point (76°) and the onset of considerable exothermic thermal decomposition above 310°. Since $Pb(HPM)_2$ proved the most volatile of the chelates, mass spectral and gas chromatographic studies were made primarily on this compound.

Mass spectrometry

The mass spectrum of each chelate was recorded and used as a means of identification and to choose the optimal peak for the integrated ion-current measurements. These spectra were later used for direct comparison with the mass spectra of eluates from the gas chromatographic columns. The mass spectrum of $Pb(HPM)_2$ is shown in Fig. 2. Each lead chelate has a characteristic mass spectrum, but similar basic features occur. The first major peak in the spectrum of each chelate is caused by the molecular ion, although polymeric peaks of low intensity are also present above this peak in every spectrum. The next major fragment of mass number below the molecular ion in each spectrum is caused by the loss of a tertiary butyl group from the molecular ion. In no case is there evidence for a peak of high intensity caused by the loss of a trifluoromethyl group from the molecular ion, as reported previously[12]. The highest intensity peak in the spectrum of each chelate attributable to a chelate fragment was found to be the peak caused by loss of one ligand from the molecular ion.

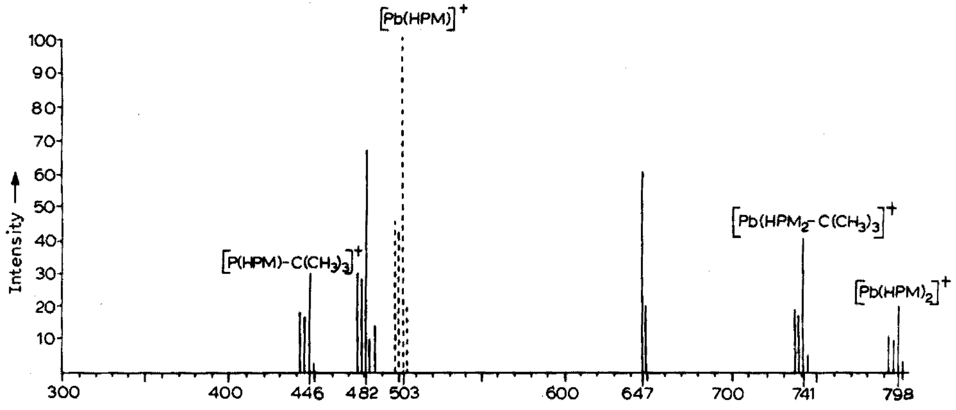

Fig. 2. Mass spectrum of $Pb(HPM)_2$ at 250°. (– – – –) Half actual peak intensity.

Integrated ion-current technique

The application of the integrated ion-current technique to the determination of submicrogram quantities of various metal chelates has been reported previously[12–16]. In the present study, the technique was applied to $Pb(HPM)_2$ only. The peak (*m/e* 503) caused by the loss of a ligand fragment from the molecular ion was chosen for the measurements and heptacosafluorotri-*n*-butylamine was used as the reference compound. Quantitative measurements were made for acetone solutions of the chelate at various concentrations ($3\cdot10^{-8}$g–$5\cdot10^{-7}$ g of $Pb(HPM)_2$). Aliquots of these solutions were introduced directly into the mass spectrometer source and the integrated ion-current curves were recorded and measured. The narrow well-defined shape of the ion-current curve (Fig. 3) indicates high thermal stability. A straight-line calibration graph was obtained, relating the peak area under the ion-current curves to the size of the lead chelate sample (Fig. 3). With the instrument operating at its highest sensitivity, the limit of detection for the lead chelate corresponded to *ca.* 10^{-14} g of lead. Although the integrated ion-current studies were made for solutions of the pure chelate in acetone, the straightforward preparation of $Pb(HPM)_2$ by direct reaction of the ligand with aqueous solutions of lead(II) and its ready extraction into organic solvents, should allow analytical procedures to be developed in accordance with the investigator's demands.

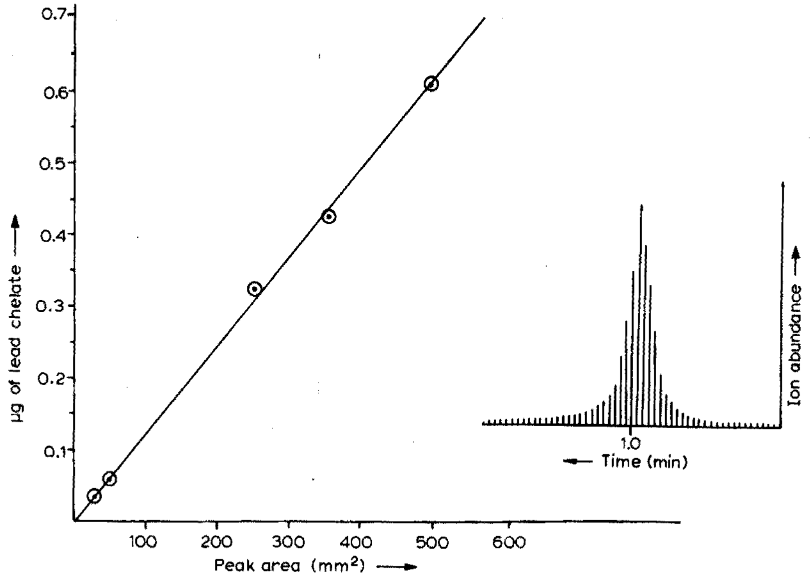

Fig. 3. Calibration graph for $Pb(HPM)_2$. $Pb(HPM)_2$ sample size *vs.* corresponding area of the integrated ion-current curve on the $Pb(HPM)^+$ peak at 250°.
Inset: Typical integrated ion-current curve for $Pb(HPM)_2$ on the $Pb(HPM)^+$ peak at 250°.

Gas chromatography

A Teflon column packed with 15% Apiezon L on "Universal B" was used to investigate the gas chromatographic behaviour of the lead complexes. The nitrogen flow rate was maintained at 60 ml min^{-1} and the injection port temperature was maintained 20° above that of the column. Portions (1 μl) of a 50% (w/v) solution of $Pb(HPM)_2$ in acetone (*ca.* 500 μg of chelate) were injected to establish the optimal column temperature for this chelate; $Pb(TPM)_2$ and $Pb(PPM)_2$ were then chromatographed at this temperature. For each chelate it was found that several samples were needed to condition the column before a consistent elution pattern was obtained.

The shape of the eluted peak was found to be strongly temperature-dependent. At a column temperature of 160°, broad peaks were obtained with a high degree of asymmetry and extensive tailing. Peak shape improved with the increase in temperature, 210° proving optimal. Chromatograms of the three chelates are reproduced in Fig. 4. Higher column temperatures and/or increased carrier gas flow caused overlapping of solvent and chelate peaks. Retention data and chromatographic parameters are given in Table II. Elution characteristics were not improved by using longer columns or different liquid-phase loading (5 or 10%), all of which increased peak tailing.

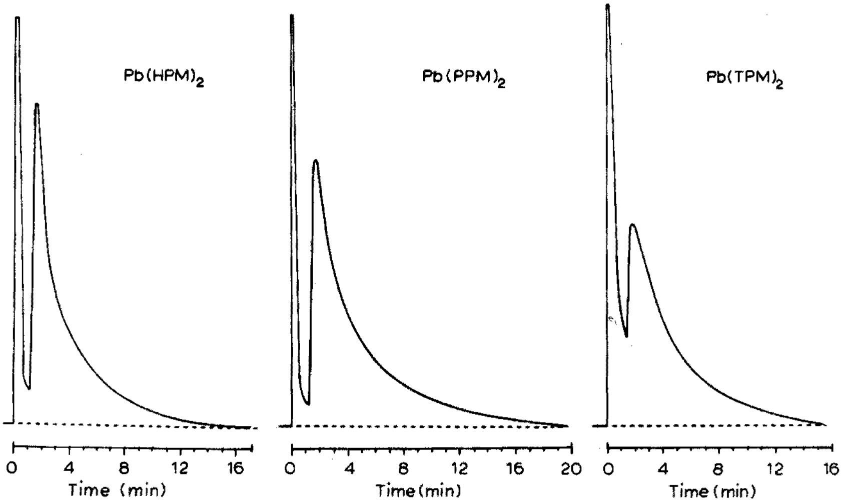

Fig. 4. Chromatograms of lead perfluoroalkanoylpivalylmethanates. 2-ft. Teflon column (3/16-in o.d.) filled with 15% Apiezon L on "Universal B" (60–85 mesh). Column temperature 210°. Nitrogen flow rate 60 ml min^{-1}.

TABLE II

GAS CHROMATOGRAPHIC DATA FOR LEAD PERFLUOROALKANOYLPIVALYLMETHANATES

(Injection temperature 230°; column temperature 210°; gas flow rate 60 ml min^{-1})

Chelate	*Retention time (sec)*	*Solution concentration in acetone (%)*	*Attenuation setting*
Pb(TPM)$_2$	110	10	$20 \cdot 10^2$
Pb(PPM)$_2$	100	50	$1 \cdot 10^4$
Pb(HPM)$_2$	96	50	$1 \cdot 10^4$

Eluted material corresponding to the peaks recorded for each chelate was collected and examined to establish that the response was not caused by decomposition products. Gas chromatographic, mass spectral and microanalytical examination showed the lead chelates to be eluted unchanged as the major peak in each chromatogram but small quantities (< 2%) of decomposition products were eluted with the solvent. In the case of Pb(HPM)$_2$, these were shown by gas chromatography to be pinacolone, HPM and an unidentified compound having a somewhat longer retention time than HPM which was also present in HPM stored for some weeks in the dark at 20°.

The relatively large quantities of the lead chelates which had to be injected to give reproducible elution indicated very strong adsorption. Accordingly, a study to determine lower elution limits was carried out. A 4-ft. column with 15% loading of

Apiezon L was used at a temperature of 200°, the injection port being held at 230°; carrier gas flow rate was 60 ml min^{-1} and 1-μl injections of chelate solutions of varying concentrations were made. It was found that no response could be obtained for sample sizes of less than 50 μg of $Pb(HPM)_2$, 70 μg of $Pb(PPM)_2$ and 100 μg of $Pb(TPM)_2$. In addition, diminution of sample size progressively broadened the peaks and increased their retention times.

In view of this behaviour, other substrates including fluorinated and non-fluorinated silicone oils were assessed for the chelates but all proved less satisfactory than Apiezon L.

The information gained from gas chromatography and thermal analysis provides strong evidence that column adsorption rather than thermal decomposition is largely responsible for the unsatisfactory elution characteristics of the lead chelates. Such adsorption has been observed for β-diketonates by other workers[17,18], who indicate contributions from both stationary phase and support material. It seems that the chromatographically favourable characteristics of relatively high volatility and thermal stability of the lead complexes are counteracted by very strong surface interactions which make only qualitative gas chromatography feasible. While $Pb(HPM)_2$ appeared to show the greatest potential for quantitative elution, any extension to sample sizes below *ca.* 100 μg of chelate (*ca.* 25 μg Pb) necessitates column materials of a less active character, the investigation of which is being pursued.

Our thanks are due to the Science Research Council for a research studentship (I.J.T.) and to Mr. M. R. COTTRELL and to Perkin-Elmer Limited for assistance with the thermoanalytical measurements. We also thank Miss M. J. A. READE for recording the mass spectra.

SUMMARY

Preparative details for perfluoroalkanoylpivalylmethanes and their lead chelates are given. Thermal analysis, gas chromatography and mass spectral studies all indicate high thermal stability, but strong column interaction makes successful quantitative gas chromatography difficult. The integrated ion-current technique is applied to determine lead heptafluorobutanoylpivalylmethanate in the range 10^{-9}–10^{-7} g of lead, but a lower detection limit of *ca.* 10^{-14} g is indicated.

RÉSUMÉ

On décrit la préparation de perfluoralcoylpivalmethanes et de leurs chélates avec le plomb. Une étude est effectuée par analyse thermique, chromatographie gazeuse et spectroscopie de masse. On en déduit que la stabilité thermique est élevée, mais des interactions sur la colonne rendent la chromatographie gazeuse quantitative difficile. La technique à courant ionique intégré est appliquée au dosage de l'heptafluoralcoylpivalmethanate de plomb avec des teneurs en plomb de 10^{-9} à 10^{-7} g.

ZUSAMMENFASSUNG

Präparative Einzelheiten über Perfluoralkanoylpivalylmethane und deren

Blei-Chelate werden vorgelegt. Thermische Analyse, Gaschromatographie und Untersuchungen der Massenspektren zeigen eine hohe thermische Stabilität an; jedoch ist eine erfolgreiche quantitative Gaschromatographie wegen starker Kolonnenwechselwirkung schwierig. Das Verfahren des integrierten Ionenstroms wird angewendet, um Blei-heptafluorbutanoylpivalylmethanat im Bereich 10^{-9}–10^{-7} g Blei zu bestimmen; es sind jedoch Hinweise auf eine niedrigere Nachweisgrenze von *ca.* 10^{-14} g vorhanden.

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INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDE BY SOLVENT EXTRACTION AS TRIS(1,10-PHENANTHROLINE)IRON(II) THIOCYANATE*

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For the colorimetric determination of low concentrations of chloride, methods based on silver chromate and diphenylcarbazide, or silver phosphate and molybdate have been reported[1], but their sensitivity is as low as that of turbidimetry[2]. A small amount of chloride can also be estimated by its suppression of reaction of mercury(II) ions with diphenylcarbazide or diphenylcarbazone[1,3]. This method is sensitive but is effective only in a narrow concentration range under strictly controlled pH conditions. UTSUMI *et al.*[4,5] and TOMONARI[6] developed a method based on the colorimetric determination of a specific amount of thiocyanate ions liberated from slightly dissociated mercury(II) thiocyanate by substitution with chloride ions, using iron(III) alum as a color developer. In these conventional colorimetric methods, care is needed to avoid errors caused by the fading of the color intensity of iron(III) thiocyanate and mercury(II)-diphenylcarbazide or -diphenylcarbazone.

Recently, a new and consistent method for thiocyanate ions was suggested[7]; thiocyanate, as low as $2 \cdot 10^{-6}$ *M*, was extracted from aqueous solution into nitrobenzene as tris(1,10-phenanthroline)iron(II) thiocyanate and determined colorimetrically. In this method, the absorbance was very stable, and chloride, even if present in a large amount, was not extracted and did not interfere with the determination of thiocyanate. Accordingly, if this solvent extraction with tris(1,10-phenanthroline)-iron(II) is employed for the determination of chloride ions instead of using iron(III) as the color developer for thiocyanate released from mercury(II) thiocyanate, higher sensitivity together with higher color stability should be achieved. This consideration led to the present study, in which an indirect colorimetric method for the determination of a small amount of chloride has been established and successfully applied to analyses for chloride in fresh water.

EXPERIMENTAL

Apparatus

The spectrophotometric measurements were made with a Hitachi Model 139 with 10-mm cells. An Iwaki Model KM shaker with a time switch was used for extraction. The pH measurements were made with a Hitachi-Horiba H-5 pH meter.

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* The spectrophotometric determination of anions by solvent extraction with metal chelate cations. Part XI. Part X of this series: K. KOTSUJI, T. SAKURAI AND Y. YAMAMOTO, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, 86 (1965) 519.

Reagents

Standard chloride solution. A stock 10^{-1} *M* solution was prepared by dissolving 2.923 g of sodium chloride (dried at 450–500°) and diluting to 500 ml with water. Solutions of suitable concentrations were prepared by dilution.

Mercury(II) thiocyanate solution. A $1.0 \cdot 10^{-3}$ *M* solution was prepared by dissolving 0.158 g of mercury(II) thiocyanate[4] and diluting to 500 ml with water.

Tris(1,10-phenanthroline)iron(II) chelate solution. A $1.0 \cdot 10^{-2}$ *M* solution (pH 2.5) was prepared by dissolving 1.961 g of iron(II) ammonium sulphate hexahydrate and 2.973 g of 1,10-phenanthroline monohydrate in dilute sulphuric acid solution and diluting to 500 ml with water. Solutions of suitable concentrations were prepared by dilution.

Buffer solution. The phosphate buffer was 0.25 *M* in potassium dihydrogen phosphate and was adjusted to pH 2.5 with sulphuric acid.

Unless otherwise stated, all the chemicals were of reagent grade and the water used was passed through a monobed ion-exchange resin.

Recommended procedure

Pipette 5 ml of the phosphate buffer solution, 5 ml of the mercury(II) thiocyanate solution, 5 ml of standard chloride solution ($2.00 \cdot 10^{-4}$ *M*) and 5 ml of tris-(1,10-phenanthroline)iron(II) chelate solution ($6.0 \cdot 10^{-4}$ *M*) into a 100-ml separating funnel. Dilute the mixture to 25 ml with water and shake the solution for 2 min with 10 ml of nitrobenzene. After 30 min, separate the organic phase and dry it with about 1 g of anhydrous sodium sulphate. Measure the absorbance of the transparent extract at 516 nm using a reagent blank extract or nitrobenzene as a reference.

RESULTS AND DISCUSSION

Absorbance spectra

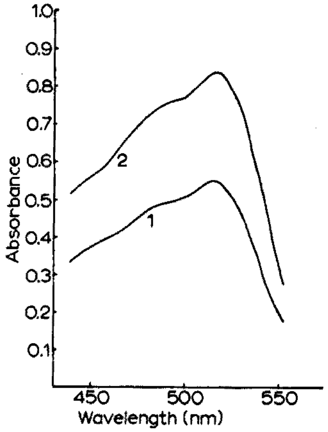
The absorbance spectra are shown in Fig. 1. They were measured for a nitrobenzene solution obtained by extraction from an aqueous solution which contained chloride and one which did not. It can be seen that the presence of chloride in aqueous solution leads to a marked increase in the absorbance and that both curves with an absorption maximum at 516 nm are identical with the spectrum of tris(1,10-phenanthroline)iron(II) thiocyanate salt dissolved in nitrobenzene[7]. The absorbances of the reagent blank extract (curve 1) are quite high, probably because of extraction of the thiocyanate ions derived from the slightly dissociated mercury(II) thiocyanate. If chloride is present in the aqueous phase, it reacts with mercury(II) thiocyanate to liberate thiocyanate ions; these as well as thiocyanate formed by dissociation of mercury(II) thiocyanate can then be extracted into nitrobenzene with the iron(II) chelate cations (curve 2).

Effect of pH

Although tris(1,10-phenanthroline)iron(II) thiocyanate showed a maximum degree of extraction within a pH range 5–10 when extracted from an aqueous solution which did not contain mercury(II) thiocyanate[7], further investigation was carried out, since pH strongly affects the substitution reaction between mercury(II) thiocyanate and chloride ions. When chloride was present in the aqueous solution, the absorbance of the extracts against the reagent blank was constant when the pH was held within the range 1.5–3.5. The pH was therefore adjusted to 2.5 with 5 ml of 0.25 M phosphate buffer solution in the final procedure. The concentration of the resulting solution was 0.05 M in phosphate. No apparent deleterious effect of the concentration of phosphate on the extraction was observed over the tested range of 0.04–0.10 M.

Effect of tris(1,10-phenanthroline)iron(II) chelate concentration

With other variables constant, different amounts of tris(1,10-phenanthroline)-iron(II) chelate ranging from 0.2 to $2.8 \cdot 10^{-4}$ M were added to an aqueous solution, and the extraction was done as described above. It was found that the chelate should be present in at least equimolar concentration to chloride ions to obtain a constant absorbance. The chelate concentration was usually kept at $1.2 \cdot 10^{-4}$ M. Larger concentrations did not affect the results.



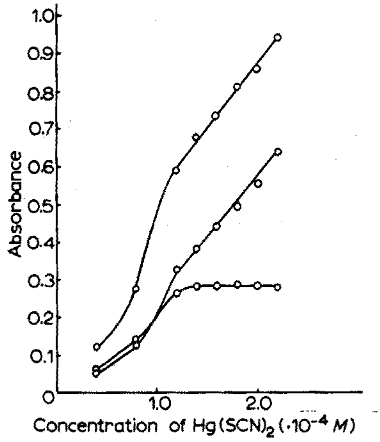


Fig. 1. Absorbance spectra against nitrobenzene as reference. Spectra of organic extracts from aqueous solutions containing $1.2 \cdot 10^{-4}$ M Fe(phen)$_3$, $2.0 \cdot 10^{-4}$ M Hg(SCN)$_2$, and 0.05 M phosphate buffer. (1) In absence of chloride; (2) in presence of $4.00 \cdot 10^{-5}$ M chloride. pH of the aqueous phase 2.5.

Fig. 2. Effect of Hg(SCN)$_2$ concentration. Chloride $4.00 \cdot 10^{-5}$ M, Fe(phen)$_3$ $1.2 \cdot 10^{-4}$ M, phosphate buffer 0.05 M, pH 2.5.

Effect of mercury(II) thiocyanate concentration

Increasing the concentration of mercury(II) thiocyanate increased the absorbance of the reagent blank because of dissociation of mercury(II) thiocyanate. However, this effect could be cancelled out by measuring the absorbance of an extract against the reagent blank as reference. A constant absorbance from $4.00 \cdot 10^{-5}$ M chloride solution was obtained, when the concentration of mercury(II) thiocyanate exceeded $1.4 \cdot 10^{-4}$ M (Fig. 2). Therefore a concentration of $2.0 \cdot 10^{-4}$ M was selected.

Effect of shaking time

The shaking time for the extraction was varied from 0.5 to 30 min, while the other variables were kept constant, but there was no improvement in extraction when the shaking time was prolonged more than 1 min; 2 min was therefore employed as the period for the extraction.

Calibration curve and precision

The standard procedure was established on the basis of the above results. A calibration curve was obtained by using varying amounts (1–7 ml) of a standard chloride solution ($2.00 \cdot 10^{-4}$ *M*). The calibration curve was linear for the tested concentration range of 0.8–$5.6 \cdot 10^{-5}$ *M* of chloride initially present in the aqueous phase. An estimate of the precision was obtained from the results of eight sample solutions, each $4.00 \cdot 10^{-5}$ *M* in chloride; these samples gave a mean absorbance of 0.283 with a standard deviation of 0.007 units (relative standard deviation 2.4%).

Color stability

The color intensity of extracts remained constant even after 12 h under normal laboratory conditions. This extraction system is little affected by temperature over the range 15–25°.

Effect of diverse ions

The influence of diverse ions on the extraction was examined under experimental conditions similar to those used for the calibration curve. Considerable amounts of sulphate, phosphate, sodium, potassium, and ammonium ions did not interfere. On the other hand, bromide, iodide, cyanide, sulphide, and thiosulphate ions reacted in the same way as chloride, and produced serious positive errors. Perchlorate and iodide ions as well as thiocyanate ions form ion pairs with tris(1,10-phenanthroline)iron(II) and were also extracted into nitrobenzene. Of the ions mentioned, sulphide, thiosulphate, cyanide, and thiocyanate ions can be destroyed by heating with hydrogen peroxide in alkaline medium, and nitrite can also be decomposed by boiling with sulphamic acid solution. Table I cites the limiting concentrations of various ions.

TABLE I

EFFECT OF DIVERSE IONS[a]

Ions	*Added as*	*Limit*[b] *(p.p.m.)*	*Ions*	*Added as*	*Limit*[b] *(p.p.m.)*
F^-	KF	290	Mg^{2+}	$MgSO_4$	60
Br^-	KBr	0.1	Ca^{2+}	$(CH_3COO)_2Ca$	40
I^-	KI	0.1	Al^{3+}	Potassium alum	65
CN^-	KCN	0.03	Cr^{3+}	$Cr_2(SO_4)_3$	50
ClO_4^-	$KClO_4$	0.03	Fe^{2+}	$Fe(NH_4)_2(SO_4)_2$	60
NO_3^-	$NaNO_3$	25	Fe^{3+}	Iron alum	50
NO_2^-	$NaNO_2$	0.1	Co^{2+}	$CoSO_4$	150
CO_3^{2-}	Na_2CO_3	260	Ni^{2+}	$NiSO_4$	50
SiO_3^{2-}	Na_2SiO_3	80	Cu^{2+}	$CuSO_4$	50
CH_3COO^-	CH_3COONa	320	Zn^{2+}	$ZnSO_4$	140
			Cd^{2+}	$CdSO_4$	90

[a] Cl^- taken: 1.34 p.p.m. ($4.00 \cdot 10^{-5}$ *M*).
[b] Permissible concentration within 3% error.

Analyses for chloride in fresh water

Table II shows analyses in which chloride in fresh water was determined by the proposed method and the mercury(II) thiocyanate–iron(III) method[5] for comparison. These samples were collected at a point 6 km from the mouth of each river, and therefore can be regarded as being virtually free from sea water. The two sets of results are in good agreement with each other. This proposed method has about a four-fold higher apparent sensitivity than the mercury(II) thiocyanate–iron(III) method. The interfering ions are not present in fresh waters in concentrations sufficient to cause serious errors.

TABLE II

ANALYSES FOR CHLORIDE IN FRESH WATER

Sample	*pH*	*Total hardness*[a]	*Cl^- found (p.p.m.)*	
			Fe(II)-phen	*Fe(III)*
Otagawa (Ota-river)	6.4_8	22.7	8.1_7	8.3_1
Nishikigawa (Nishiki-river)	6.6_5	27.8	5.0_8	5.5_4
Ozegawa (Oze-river)	6.5_0	15.8	4.3_0	4.5_8

[a] p.p.m. as $CaCO_3$.

SUMMARY

An indirect spectrophotometric method for the determination of small amounts of chloride in fresh waters is described. Chloride ions react with mercury(II) thiocyanate to liberate thiocyanate ions, which can be selectively extracted into nitrobenzene with tris(1,10-phenanthroline)iron(II) chelate cations. The red color (516 nm) of the organic phase measured against a reagent blank is proportional to the initial concentration of chloride ions in the aqueous phase. At least an equimolar amount of tris(1,10-phenanthroline)iron(II) chelate and a 3-fold amount of mercury(II) thiocyanate are needed; the optimal pH range is 1.5–3.5. Beer's law is obeyed over the concentration range of $0.8\text{–}5.6 \cdot 10^{-5}$ *M* of chloride. The color stability and the apparent sensitivity are better than those of the mercury(II) thiocyanate–iron(III) method. Large amounts of sulphate, phosphate, fluoride, carbonate, acetate, potassium, sodium, and ammonium ions had negligible or no effect; bromide, iodide, cyanide, sulphide, and thiocyanate interfere.

RÉSUMÉ

Une méthode spectrophotométrique indirecte est décrite pour le dosage de faibles quantités de chlorures dans les eaux. Les chlorures réagissent avec le thiocyanate de mercure(II); les ions thiocyanates libérés peuvent être extraits sélectivement dans le nitrobenzène au moyen de tris(1,10-phénanthroline)fer(II). L'intensité de la coloration rouge de la phase organique mesurée à 516 nm est proportionnelle à la phase concentration initiale des chlorures dans la phase aqueuse. La loi de Beer s'applique à des solutions 0.8 à $5.6 \cdot 10^{-5}$ *M* en chlorure. La stabilité de couleur et la sensibilité apparente sont meilleures que celles obtenues avec la méthode au thiocyanate de mercure(II)–fer(III). De grandes quantités de sulfate, phosphate, fluorure, carbonate, acétate, potassium, sodium et ammonium n'ont pratiquement pas d'influence. Par contre bromure, iodure, cyanure, sulfure et thiocyanate gênent.

ZUSAMMENFASSUNG

Es wird eine indirekte spektrophotometrische Methode für die Bestimmung kleiner Mengen Chlorid in Frischwasser beschrieben. Chloridionen setzen sich mit Quecksilber(II)-Thiocyanat zu freien Thiocyanationen um, die mit Tris(1,10-phenanthrolin)Eisen(II)-Chelatkationen durch Nitrobenzol selektiv extrahiert werden können. Die rote Färbung (516 nm) der organischen Phase wird gegen eine Reagenzienblindlösung gemessen; sie ist der anfänglichen Konzentration der Chloridionen in der wässrigen Phase proportional. Es werden mindestens eine äquimolare Menge Tris(1,10-phenanthrolin)Eisen(II)-Chelat und eine dreifache Menge Quecksilber(II)-Thiocyanat benötigt; der günstigste pH-Bereich ist 1.5–3.5. Das Beersche Gesetz ist im Konzentrationsbereich 0.8–$5.6 \cdot 10^{-5}$ *M* Chlorid erfüllt. Die Stabilität der Färbung und die scheinbare Empfindlichkeit sind besser als die der Quecksilber(II)-Thiocyanat–Eisen(III)-Methode. Grosse Mengen an Sulfat, Phosphat, Fluorid, Carbonat, Acetat, Kalium, Natrium und Ammoniumionen haben einen vernachlässigbaren oder keinen Einfluss, Bromid, Jodid, Cyanid, Sulfid und Thiocyanat stören.

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1-[(5-CHLORO-2-PYRIDYL)AZO]-2-NAPHTHOL AS A NEW EXTRACTION–PHOTOMETRIC REAGENT FOR METALS

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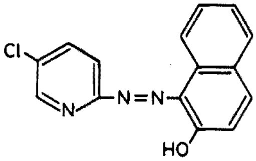
During the past ten years, the analytical application of 2-pyridylazo compounds has been studied extensively. Two representatives of this group, 1-(2-pyridylazo)-2-naphthol (β-PAN) and 4-(2-pyridylazo)resorcinol (PAR), have proved to be very versatile reagents for metals[1-3]. In a search for new sensitive and selective reagents, a thorough study of some of the azo compounds containing halogen-substituted pyridine or naphthol has been made. In a previous paper[4], the potentiality of the 1-[(5-bromo-2-pyridyl)azo]-2-naphthol (5-Br-β-PAN) as an extraction–photometric reagent for metals was discussed. In this paper, the possibilities of 1-[(5-chloro-2-pyridyl)azo]-2-naphthol (I, 5-Cl-β-PAN) as an analytical reagent are described.



(I)

EXPERIMENTAL

Reagents

5-Cl-β-PAN solution. A methanolic 10^{-3} *M* solution was prepared from the pure material (see below). The solution is stable for several months if stored in an amber bottle.

Buffer solution. Borax–boric acid–sodium acetate, boric acid–hydrochloric acid, sodium hydroxide–borax and sodium acetate–acetic acid mixtures were used for pH adjustment.

Potassium cyanide (10%), 0.1 *M* EDTA disodium salt and 10% sodium citrate, sodium tartrate and sodium fluoride solutions were used as masking reagents.

Organic solvents were purified by the usual methods. All the other reagents used, including metal standard solution, were made from high-purity materials or purified reagents, and all solutions were prepared with redistilled water.

Apparatus

Absorbance curves were measured with a Model EPS-3T Hitachi recording spectrophotometer with 1-cm cells; absorbances were measured with a Model 124 Hitachi spectrophotometer with 1-cm cells. A Hitachi M5 type pH meter was used.

Preparation of reagent

The reagent was prepared by coupling 2-naphthol with 5-chloro-2-pyridyldiazotate in ethanol with slow passage of carbon dioxide. The diazotate was prepared by adding a solution of iso-amylnitrite to a mixture of 5-chloro-2-aminopyridine and sodium amide under reflux.

Chlorination of 2-aminopyridine. The chlorination of 2-aminopyridine in 20% sulfuric acid at 25° is much more satisfactory than the chlorination in alcoholic solution as described by CHICHIBABIN. Chlorine was passed into a solution of 20 g of 2-aminopyridine in 20% sulfuric acid at 25°. After chlorination, the product was shaken with 100 ml of carbon tetrachloride, to extract highly chlorinated materials, and the residue was precipitated from solution in dilute hydrochloric acid. After treatment with charcoal, about 50% yield of white 2-amino-5-chloropyridine was obtained (yield, 50%; m.p. 137°).

Preparation of diazotate. Freshly prepared isoamyl nitrite (5.46 g) was added to a solution containing 6 g of 2-amino-5-chloropyridine and 2.4 g of sodium amide in 100 ml of absolute ethanol. The mixture was refluxed for 3 h and cooled, and the precipitated diazonium salt of 2-amino-5-chloropyridine was filtered and dried in air.

Coupling reaction. 2-Naphthol (5 g) was dissolved in 30 ml of ethanol and a solution of 5 g of diazonium salt in 70 ml of ethanol was added. This mixture was heated to 40–50° for 4 h in a stream of carbon dioxide. The mixture was let cool overnight, and the precipitated orange-red needles were filtered. If a little water was added to the filter, a further yield of crude dye could be obtained. Finally, the precipitate was dissolved into hot ethanol and recrystallized from aqueous 50% (v/v) ethanol (m.p. 158.2°). Analysis: calculated 63.5% C, 14.8% N, 3.8% H, 12.5% Cl; found 63.7% C, 14.9% N, 3.9% H, 12.7% Cl.

RESULTS AND DISCUSSION

Acid dissociation constant

The reagent is almost insoluble in water, but soluble in various organic solvents, including ethanol, acetone, dioxane, carbon tetrachloride, ether and chloroform as well as in strongly acidic or alkaline aqueous solution.

This compound shows acid–base indicator properties and is yellow in acidic

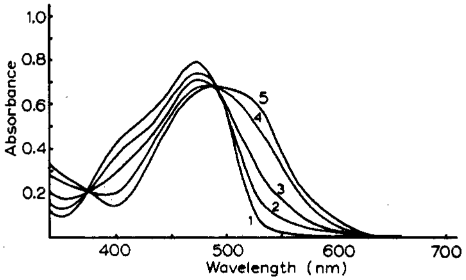


Fig. 1. Absorbance curves of 5-Cl-β-PAN in aqueous 40% (v/v) dioxane. $1.2 \cdot 10^{-4}$ *M*. $\mu = 0.2$ $NaClO_4$. pH: (1) 2.30, (2) 11.18, (3) 11.68, (4) 12.57, (5) 13.36.

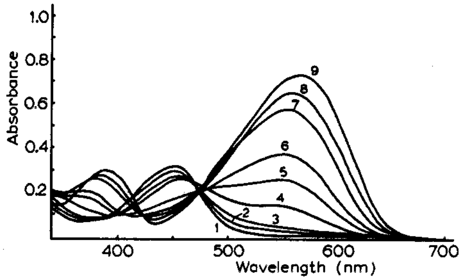


Fig. 2. Absorbance curves of 5-Cl-β-PAN in sulfuric acid. $4 \cdot 10^{-6}$ *M*. H_2SO_4 (95%) (ml/10 ml): (1) 5, (2) 5.5, (3) 6.0, (4) 6.5, (5) 7.0, (6) 7.5, (7) 8.0, (8) 9.0, (9) 9.5.

and neutral solution and red in strongly alkaline solution; in concentrated sulfuric acid, it is violet. Three species of 5-Cl-β-PAN, H_2L^+, HL and L^-, are involved in its acid–base behavior; in strong sulfuric acid solution, two additional protonated species, H_3L^{2+}, and H_4L^{3+}, probably occur, the extra proton being attached to the azo group. In sulfuric acid, the value of pK_a was obtained from the following equation

$$pK_a = H_0 + \log \frac{\varepsilon - \varepsilon_1}{\varepsilon_2 - \varepsilon}$$

where H_0 is the Hammett acidity function of the sulfuric acid solution[6,7], ε_1, ε_2 and ε are the molar absorptivities of a solution containing the two protonated species, and a mixture of the two species, respectively. The absorbance curves of 5-Cl-β-PAN in aqueous 40% (v/v) dioxane and in sulfuric acid solution are shown in Figs. 1 and 2. The wavelength of maximum absorbance and the molar absorptivity of each species, and the pK_a values obtained are listed in Tables I and II.

TABLE I

WAVELENGTHS OF MAXIMUM ABSORBANCE AND MOLAR ABSORPTIVITIES FOR THE 5-Cl-β-PAN IN SULFURIC ACID MEDIA

Reagents	H_4L^{3+} $-H_0 \sim 10.5^b$ λ_{max} (nm) ($\varepsilon \cdot 10^{-4}$)	H_3L^{2+} $-H_0 \sim 4^b$ λ_{max} (nm) ($\varepsilon \cdot 10^{-4}$)	H_2L^+ pH ~ 0 λ_{max} (nm) ($\varepsilon \cdot 10^{-4}$)	HL pH ~ 5 λ_{max} (nm) ($\varepsilon \cdot 10^{-4}$)	L^- pH ~ 14 λ_{max} (nm) ($\varepsilon \cdot 10^{-4}$)
β-PAN[a]	—	—	425 (16.2)	470 (17.2)	490 (13.2)
5-Cl-β-PAN	570 (45.0)	—	—	474 (19.7)	498 (17.1)
5-Br-β-PAN[a]	570 (24.1)	460 (19.4)	450 (18.8)	475 (19.6)	500 (16.6)

[a] In aqueous 50% (v/v) dioxane.
[b] $-H_0$, Hammett acidity function (in sulfuric acid).

TABLE II

DISSOCIATION CONSTANTS OF THE 5-Cl-β-PAN

Reagents	$pK_{H_2L^+}$	pK_{HL}	$pK_{H_3L^{2+}}$	$pK_{H_4L^{3+}}$
β-PAN[a]	1.8	12.3	—	—
5-Cl-β-PAN[b]	1.6	11.8	—	~ 7.5[c]
5-Br-β-PAN[a]	1.0	11.8	~ 3.9[c]	~ 7.6[c]

[a] In aqueous 50% (v/v) dioxane, $\mu = 0.1$.
[b] In aqueous 50% (v/v) dioxane, $\mu = 0.2$.
[c] Hammett acidity function (in sulfuric acid).

Chelate formation

The chelate compounds are easily prepared by adding a methanolic solution of 5-Cl-β-PAN to a solution of heavy metals. Generally, the solutions containing heavy metals showed a red colour under acidic, neutral or alkaline conditions, except

TABLE III

SOLUBILITY AND COLOUR OF METAL CHELATES IN VARIOUS SOLVENTS

(The reagent is yellow)

Metals	*Water*	*Chloroform*	*Benzene*	*Ether*
V^{5+}	Dark yellow green	Pale yellow green	—	—
Cr^{3+}	Pale orange	Pink	—	—
Mn^{2+}	Purple	Red	Reddish purple	Purple
Fe^{3+}	Red-brown	Reddish brown	Reddish purple	—
Co^{2+}	Red-purple	Red	Reddish purple	—
Co^{3+}	Green	Green	Green	Green
Ni^{2+}	Deep red-purple	Red	Reddish purple	Reddish purple
Cu^{2+}	Purple red	Bluish purple	Purple	Purple
Zn^{2+}	Purple red	Red	Purplish red	Purple
Y^{3+}	Red orange	Purplish pink	Reddish yellow	—[a]
Nb^{5+}	Pink	Pink	—	—
Pd^{2+}	Green	Green	Pale green	Pale green
Ag^{+}	Brown	Purplish pink	Pink	Pale pink
Cd^{2+}	Red	Red	Red	Red
Hg^{2+}	Red-purple	—[a]	—[a]	—[a]
Tl^{3+}	Red-purple	Reddish purple	Reddish purple	Pink
Pb^{2+}	Red-purple	—[a]	—[a]	—[a]
Bi^{3+}	Red-purple	—[a]	—[a]	—[a]
La^{3+}	Pink	Orange	—[a]	—[a]
Ce^{3+}	Red-purple	Pink	—[a]	—[a]
Th^{4+}	Orange	Orange	Reddish yellow	—[a]
UO_2^{2+}	Red	—	—	—

[a] Decomposed to the yellow colour of reagent.

for cobalt(III), palladium, vanadium(V), iron(III) and silver. The ions that gave a colour or precipitate with the reagent are listed in Table III. The tests were made by adding one drop of 10^{-3} *M* reagent solution in methanol to 1 ml of the metal ion solution (0.1 mg/ml). The following ions failed to give a detectable precipitate or coloration at room temperature: lithium, beryllium, boron, sodium, aluminum, potassium, germanium, arsenic, strontium, molybdenum, tin, barium, tungsten, thallium(I), tellurium and almost all common anions. The reaction of the following ions were very weak: calcium, magnesium, titanium, zirconium, hafnium, thorium and antimony.

Reactivity in the presence of masking reagent

An attempt was made to use common masking reagents, such as EDTA, cyanide or citrate, in order to improve the selectivity of the reagent. Suitable amounts of neutral or slightly acidic metal ion solution were mixed with 5 ml of the masking reagent and 1 ml of methanolic 10^{-3} *M* reagent solution, and the pH was adjusted to the optimal value before the mixture was stirred for a few minutes.

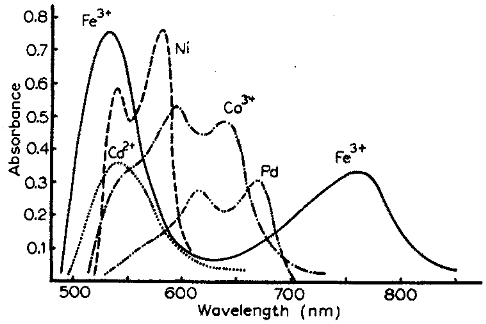
EDTA prevented all the metals mentioned in Table III from reacting with reagent, except uranium and bismuth. Cyanide prevented the reaction of metals except manganese, lead, bismuth, rare earths and vanadium. Citrate prevented the reaction of zinc, lead, vanadium, chromium, manganese, yttrium, silver, cadmium, lanthanum and uranium.

Solvent extraction

The highly coloured chelate formed with many heavy metals under various conditions could be used for the detection of certain metals. These colored chelates were soluble in various organic solvents (Table III). Colorimetric determinations could be made by extraction with an organic solvent, or directly in an aqueous solution by adding dioxane, or by adding gum arabic to prevent turbidity. For comparison, the absorbance curves of the metal chelates in chloroform are shown in Fig. 3. Most 5-Cl-β-PAN chelates have absorption maxima lying between 530 nm and 580 nm, but some chelates absorb at longer wavelength.

Effect of pH

A series of solutions containing a definite amount of the required metal and 1 ml of 10^{-3} *M* reagent solution was prepared. Figure 4 shows the influence of hydrogen ion concentration on the extraction of some metals with chloroform from aqueous solution. Although above pH 11, some metal chelates were formed in aqueous solution, the extractability was decreased, probably because hydroxy species were formed. The results clearly show that chelate formation and extractability are strongly dependent on the acidity of the reaction medium.



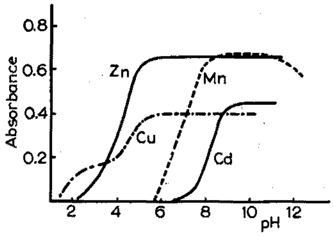


Fig. 3. Absorbance curves of metal–5-Cl-β-PAN complexes in chloroform against a reagent blank. 1-cm cells. (Fe) 1 p.p.m., (Ni) 0.3 p.p.m., (Co) 1 p.p.m., (Pd) 4 p.p.m.

Fig. 4. pH dependence of chloroform extraction of metal complexes.

TABLE IV

APPARENT MOLAR ABSORPTIVITY OF SOME METAL–5-Cl-β-PAN COMPLEXES

Metals	λ_{max} *(nm)*	*Molar absorptivity l mole⁻¹ cm⁻¹* $\varepsilon\cdot 10^{-4}$	β-*PAN*	
			λ_{max}	$\varepsilon\cdot 10^{-4}$
Mn(II)	566	7.2	562	(4.8)
Fe(III)	530	4.2	775	(1.6)
	765	1.9		
Co(II)	540	2.1		—
Ni(II)	580	7–8	570	(5.0)
Cu(II)	567	5.8	564	(4.4)
Zn(II)	569	7.1	550	(5.6)
Pd(II)	670	0.77	678	(1.9)
Cd(II)	560	7.0	555	(4.9)

Beer's law and sensitivity

The absorbances of the metal chelates in organic solvents or aqueous solution were found to be linearly related to the concentration of the metals. From Beer's law, the apparent molar absorptivity for each metal was calculated. In Table IV, these values are summarized, together with the wavelength of maximum absorbance of the different complexes in comparison with these of β-PAN.

Stripping into aqueous solution

The selectivity of extraction and determination of metals could be increased by back-washing or back-extraction. Potassium cyanide (0.2%) allowed back-extraction of thallium(III), copper, iron, zinc, cadmium, niobium and vanadium(V). Acetate buffer pH 4 allowed back-extraction of iron, manganese, silver, chromium(III) and rare earths.

Effect of temperature

Chelate formation generally proceeded instantaneously at room temperature but for platinum metals and nickel, the reaction was accelerated by warming on a water bath.

Nature of complex

The empirical formulae of the coloured complexes were determined by the continuous variation and mole ratio method. A typical example for the continuous variations method is shown in Fig. 5. Generally these complexes contain two molecules of reagent to one metal. The nature of each complex will be mentioned in a later paper. The composition of some metal complexes can depend on the ratio of the reactants, and on the nature and acidity of the solvent.

As an example, the copper(II) complex was investigated in detail. The absorbance curves of the purple copper(II) complex in chloroform, extracted from aqueous solution of pH 3.4 showed only one absorbance maximum at 570 nm. The mole ratio method clearly indicated the formula $CuLX$ ($X = Cl$). The absorbance curves of the reddish purple copper(II) complex extracted by chloroform from

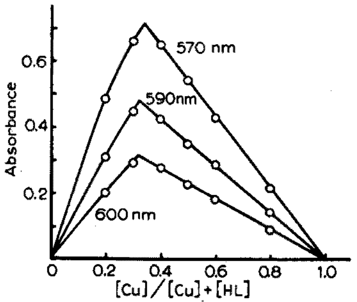


Fig. 5. Composition of the coloured copper complex at different wavelengths. pH 8.0, aqueous 50% (v/v) dioxane.

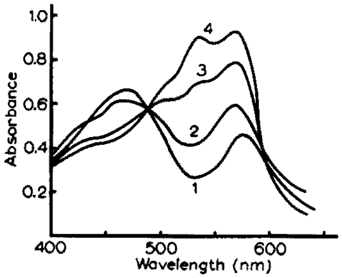


Fig. 6. Absorbance curves of copper(II)–5-Cl-β-PAN complexes in chloroform, extracted from aqueous solutions of different pH. pH: (1) 1.0, (2) 3.4, (3) 8.0, (4) 10.0. [Cu]:[HL] = 1:2.

aqueous solution of pH 10 were different from those obtained at pH 3.4. In this case, two absorbance maxima, at 535 and 567 nm, were clearly shown, and the mole ratio method clearly indicated the formula CuL_2. The value for the molar absorptivity of the 1:2 complex was nearly twice that of the 1:1 complex. The absorbance curves of the copper(II) complexes extracted by chloroform from aqueous solution of various pH value and at a constant molar ratio 1:2 for Cu : 5-Cl-β-PAN, are shown in Fig. 6. These plots unequivocally show that the copper(II) complex formed depends on the pH of the reaction medium; generally, the MLX type complexes are rather soluble in water, whereas the ML_2 type complexes are almost insoluble. The complex formation of copper(II) with 5-Cl-β-PAN in various solvents is summarized in Table V.

Finally, as a typical example, the infrared spectra of the reagent and its copper chelate are shown in Fig. 7. The results obtained suggest the coordination of the heterocyclic nitrogen and azo group. It appears that 5-Cl-β-PAN acts as a tridentate ligand, forming two stable five-membered chelate rings by means of the *o*-hydroxyl group, the heterocyclic nitrogen and the azo group, and that the commonest chelates are of the type ML and ML_2.

TABLE V

COMPOSITION OF Cu(II)–5-Cl-β-PAN CHELATES

In H_2O
CuLCl at $[Cu] / [L] \geqq 1$, needle crystal, independent with pH.
CuL_2 at $[Cu] / [L] \leqq 0.5$, amorphous crystal, pH > 7.

In aqueous 50% (v/v) dioxane
CuLX[a] λ_{max} 570 nm, $<$ pH 4.
CuL_2 λ_{max} 536 nm, $>$ pH 7 at $[Cu] \ll [L]$.
565 nm

In $CHCl_3$
CuLX[a] λ_{max} 570 nm, $<$ pH 4.
CuL_2 λ_{max} 535 nm, $>$ pH 6.
567 nm

[a] X = monovalent anions.

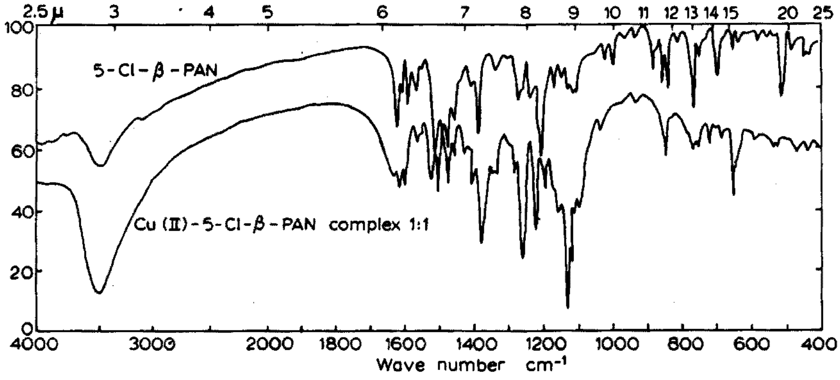


Fig. 7. The infrared spectrum of 5-Cl-β-PAN and its copper chelate. KBr tablet. Cu:5-Cl-β-PAN = 1:1 species.

CONCLUSION

As an extraction and spectrophotometric reagent, 1-[(5-chloro-2-pyridyl)-azo]-2-naphthol seems to be promising, because of the high molar absorptivity and reasonable stability of its complexes. Although the bathochromic shifts produced on chelation are no greater than those with the analogous bromine compound, the selectivity is improved. In particular, the reactivities of tri- and tetravalent metal ions are decreased appreciably by the introduction of chlorine into the pyridine ring.

SUMMARY

The heterocyclic azo compound, 1-[(5-chloro-2-pyridyl)azo]-2-naphthol (5-Cl-β-PAN), forms various coloured metal chelates, which can be extracted with different organic solvents. Chelate stability is greatly affected by pH. The molar absorptivities are usually considerably greater than those of the β-PAN chelate. Although the bathochromic shifts produced on chelation are no greater than those with 5-Br-β-PAN, the selectivity is increased. The reactivity of tri- and tetravalent metal ions is decreased appreciably by introduction of the chlorine. A correct choice of pH, solvent and masking reagent allows 5-Cl-β-PAN to be made reasonably selective.

RÉSUMÉ

Le composé azo-hétérocyclique 1-[(5-chloro-2-pyridyl)azo]-2-naphtol (5-Cl-β-PAN) forme divers chélates métalliques colorés pouvant être extraits dans différents solvants organiques. La stabilité de ces chélates est très influencée par le pH. Les coefficients d'extinction molaires sont généralement becaucoup plus élevés que ceux des chélates β-PAN. La réactivité des ions métalliques tri- et tétravalents diminue sensiblement par introduction du chlore. Un choix correct du pH, du solvant et de l'agent masquant permet d'obtenir une bonne sélectivité avec le 5-Cl-β-PAN.

ZUSAMMENFASSUNG

Die heterocyclische Azoverbindung 1-[(5-Chlor-2-pyridyl)azo]-2-naphthol (5-Cl-β-PAN) bildet gefärbte Metallchelate, die mit verschiedenen organischen Lösungsmitteln extrahiert werden können. Die Chelatstabilität wird durch den pH-Wert stark beeinflusst. Die Extinktionskoeffizienten sind für gewöhnlich erheblich grösser als die des β-PAN-Chelates. Obgleich die bathochromen Verschiebungen, die durch die Chelatbildung bewirkt werden, nicht grösser sind als die mit 5-Br-β-PAN, nimmt die Selektivität zu. Die Reaktionsfähigkeit der drei- und vierwertigen Metallionen nimmt durch Einführung des Chlors ab. Durch eine sorgfältige Wahl des pH-Wertes, des Lösungsmittels und des Maskierungsmittels wird 5-Cl-β-PAN ziemlich selektiv.

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COLUMN REVERSED-PHASE PARTITION CHROMATOGRAPHY FOR THE ISOLATION OF SOME RADIONUCLIDES FROM BIOLOGICAL MATERIALS*

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As is well known, *reversed-phase partition chromatography* or *extraction chromatography* is the separation technique in which an organic non-polar extractant is retained on an inert support (paper, cellulose powder, kieselguhr, organic microporous polymers, etc.), while a polar mobile phase is used as the eluting agent[1-3]. Column reversed-phase partition chromatography has been successfully employed for the isolation of very small quantities of radionuclides in the urines of nuclear workers. For instance, a column of Kel-F (polytrifluorochloroethylene) supporting tri-*n*-butylphosphate (TBP) has been used for the determination of enriched uranium[4], and tri-*n*-octylphosphine oxide (TOPO) in cyclohexane has been supported on the same polymer for the determination of natural thorium[5], while a Kel-F–tri-*n*-octylamine (TNOA) column has been employed for the determination of plutonium[6].

This paper describes some new applications of column reversed-phase partition chromatography, and of the batchwise separation process with supported extractants to the resolution of practical analytical problems in the radiation protection field, *e.g.* the determination of natural thorium, enriched uranium and strontium-90 in urine, and the isolation of iodine from synthetic diets.

Microthene-710 (microporous polyethylene) was chosen as the inert support, consideration being given to its low cost, its ready availability, its stability to powerful chemical reagents as well as its adsorption properties, behaviour in column packing, exchange rate, etc.

Tri-*n*-octylphosphine oxide (TOPO) was chosen for the extraction of uranium[7,8] and thorium[5,7,8], di(2-ethylhexyl)orthophosphoric acid (HDEHP) for the extraction of yttrium[9-11], and benzene for the retention of iodine.

EXPERIMENTAL

Apparatus

A Spectrascope Model 400 (Laben, Milan) 400-channel analyzer was used with a 3×3 in NaI (Tl) crystal, and an Olivetti Tekne 3 typewriter. Other equipment included an automatic superscaler Model DCS 4 15 A V (Selo, Milan) with a 2-in

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α-probe; a low-background β-detector Model CBL/2 (ASPN, Gazzada Schianno, Varese) with two anticoincidence plastic scintillators; a laboratory lyophilizer (C. Erba, Milan); a low-temperature asher, Model LTA/600 (Tracerlab, U.S.A.) with five 4×9×1 cm boats; a Unicam Model SP 600 spectrophotometer; and a Radiometer Model 22 pH meter.

Chromatographic columns (10 and 25 mm i.d.) were used with a G-2 fritted glass disc or some Teflon wool in the bottom.

Reagents

The following reagents were employed: Microthene-710 (microporous polyethylene), 50–100 mesh (Columbia Organic Chemicals, S.C., U.S.A.); tri-*n*-octylphosphine oxide (TOPO), $(C_8H_{17})_3PO$, (Eastman Organic Chemicals, U.S.A.); di-(2-ethylhexyl)orthophosphoric acid (HDEHP), $CH_3(CH_2)_3$–$CH(C_2H_5)$–$CH_2O)_2POOH$, (K.K. Laboratories, Hollywood, Calif., U.S.A.); arsenazo III, $C_{22}H_{16}As_2N_4Na_2O_{14}S_2$, (B.D.H., Great Britain).

The tracers ^{90}Sr, ^{90}Y and ^{131}I were supplied by the Radiochemical Centre of Amersham (Great Britain). Uranyl nitrate hexahydrate, thorium nitrate tetrahydrate and other reagents were of analytical grade (C. Erba, Milan).

Preparation of the Microthene–extractant slurry

Add a certain volume of the extractant (0.5 *M* TOPO in cyclohexane, 1.5 *M* HDEHP in toluene, or benzene) with slow stirring, to a similar weight of Microthene-710 (50–100 mesh). Pre-equilibrate the slurries obtained with the solutions appropriate for the extraction (4 *M* nitric acid, 0.3 *M* nitric acid or 1 *M* sulphuric acid, respectively). Prepare the columns by transferring the slurries into chromatographic columns and pressing lightly with some Teflon wool.

Mineralization and preparation of the biological samples

Urines. For the determination of enriched uranium and natural thorium, mix 500 ml of urine with 10 ml of 120-vol. hydrogen peroxide and 100 ml of concentrated nitric acid; boil for 60 min; the sample volume is then reduced to about 400 ml.

For the determination of strontium-90 through the isolation of yttrium-90, heat gently 500 ml of urine with 10 ml of 120-vol. hydrogen peroxide and 25 ml of concentrated nitric acid until the sample is clarified. Adjust the pH to 0.5 with dilute nitric acid or ammonia solution.

Foodstuffs. For the determination of natural iodine in foods, lyophilize 1 g of the wet sample and transfer the residue (100–150 mg) to a low-temperature asher in which oxygen ionized by radiofrequency is used[12,13]. When the radiofrequency power was kept at 90 W and the oxygen flow at 70 ml min^{-1} the temperature did not exceed 150°. Then dissolve the mineralized sample (5–10 mg) in 10 ml of 1 *M* sulphuric acid and oxidize iodide to iodine with some sodium nitrite.

Determination of natural thorium in urine with a Microthene–TOPO column

Percolate the mineralized urine (4 *M* in nitric acid) through a column consisting of 2 g of Microthene supporting 2 ml of 0.5 *M* TOPO in cyclohexane, at a flow-rate of 5 ml min^{-1}; wash with 50 ml of 4 *M* nitric acid at 5 ml min^{-1}, and elute thorium into a 100-ml beaker with 40 ml of 0.3 *M* sulphuric acid at a flow-rate of 1 ml min^{-1} (Fig. 1, elution diagram A). Evaporate the solution to dryness and add 4.5 ml of 8 *M* hydrochloric acid and 1 ml of arsenazo III solution (0.05% in 8 *M* hydrochloric acid). Measure the absorbance against a blank in 4-cm cells at a wavelength of 665 nm[14].

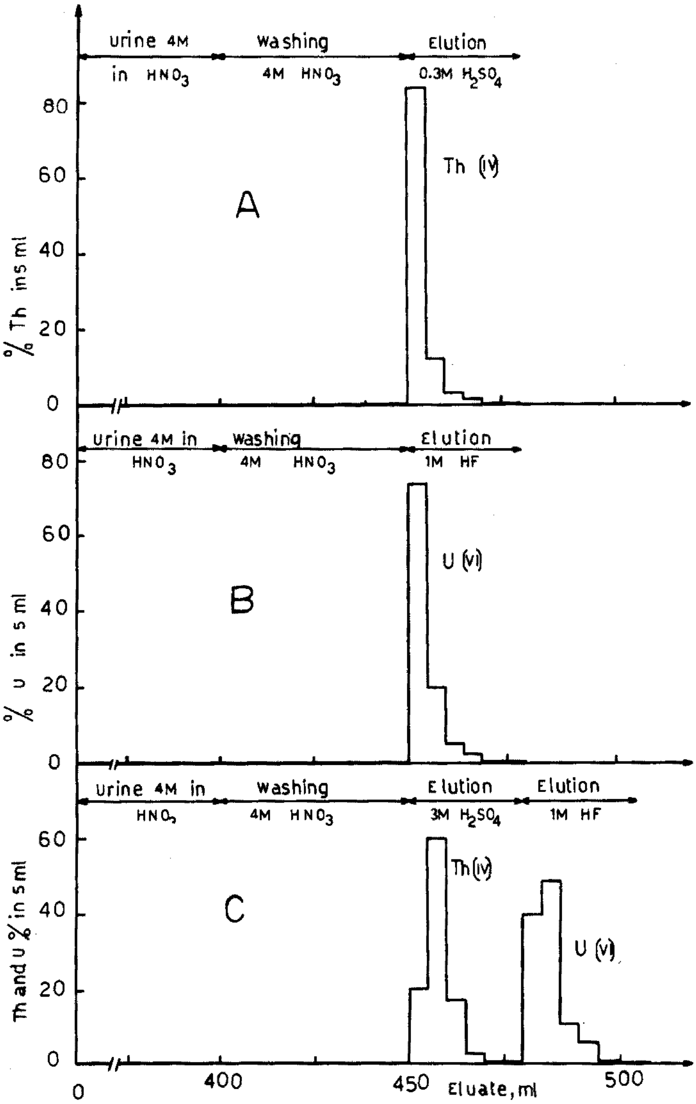

Fig. 1. Column (i.d. 10 mm; h = 50 mm) made of 2 g of Microthene supporting 2 ml of 0.5 *M* TOPO in cyclohexane. Flow-rate: 5 ml min^{-1} for urine percolation and washing and 1 ml min^{-1} for elution. (A) Elution diagram for thorium, (B) elution diagram for uranium, (C) elution diagram for the simultaneous determination of thorium and uranium.

On the basis of 10 analyses, the final yield was found to be 98.2±6.7% with a sensitivity limit of about 0.2 μg l^{-1} of urine. The time required for one analysis was about 5 h.

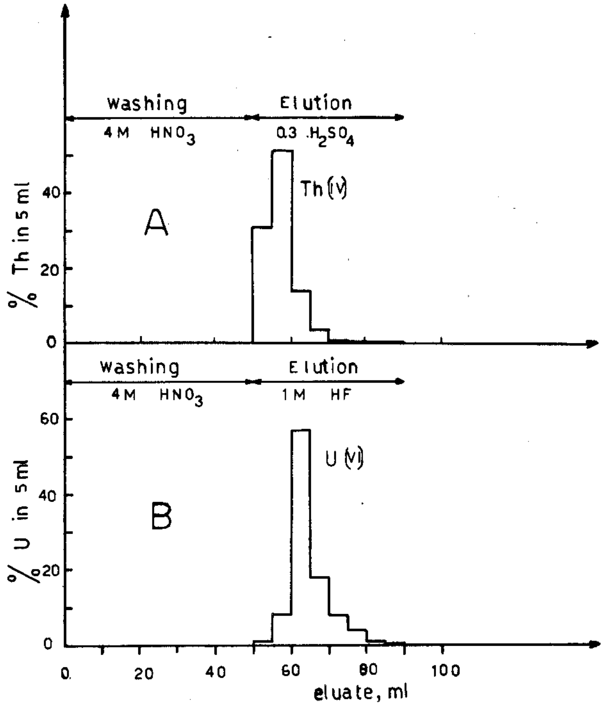

Fig. 2. Elution of thorium (A) and uranium (B) after a batchwise separation process with 2.0 g of Microthene supporting 2.0 ml of 0.5 *M* TOPO in cyclohexane. Flow-rate: 5 ml min^{-1} for washing and 1 ml min^{-1} for the elution. Column, 10 mm i.d.

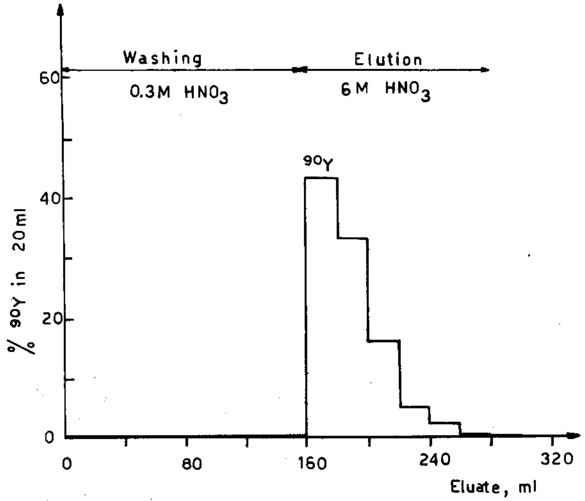

Fig. 3. Yttrium elution after a batchwise separation process with 5.0 g of Microthene supporting 5.0 ml of 1.5 *M* HDEHP in toluene. Flow-rate: 15 ml min^{-1} for washing and 5.0 ml min^{-1} for elution. Column, 25 mm i.d.

Determination of enriched uranium in urine with a Microthene–TOPO column

Carry out the initial steps of the analysis as described above. Use a chromatographic column with some Teflon wool at the bottom. Elute the uranium with 40 ml of 1 M hydrofluoric acid at a flow-rate of 1 ml min^{-1} (Fig. 1, elution diagram B). Evaporate the solution to dryness in a platinum vessel, transfer to a 2-in watch glass with some 8 M nitric acid and count for 60 min on a 2-in ZnS(Ag) α-probe, which had a counting efficiency of 38% for natural uranium and an α-background of 0.05–0.1 counts min^{-1}.

On the basis of 10 analyses, the final yield was found to be $75.6 \pm 3\%$, with a sensitivity limit of 1 d.p.m. l^{-1} of urine. The time required for one analysis was about 6 h.

Simultaneous determination of natural thorium and enriched uranium in urine with a Microthene–TOPO column

If 40 ml of 3 M sulphuric acid is used for the elution of thorium[15], it is possible to retain uranium(VI) on the Microthene–TOPO column, as shown in elution diagram C (Fig. 1); uranium can then be eluted with 40 ml of 1 M hydrofluoric acid. The final determinations of natural thorium and enriched uranium are done by colorimetry and α-counting as outlined above. This type of analysis is recommended when the urine sample must be analyzed for both the contaminants.

Determination of natural thorium and enriched uranium in urine by a batchwise separation process with Microthene–TOPO

Batchwise separation processes can be successfully employed by stirring the mineralized urine with the Microthene–extractant slurry; when this procedure gives a good extraction yield, it is to be preferred to the column method because of its greater simplicity and speed, especially for routine urine analyses.

For the extraction step of thorium and uranium, stir 500 ml of the wet mineralized urine for 20 min with 2 g of Microthene supporting 2 ml of 0.5 M TOPO in cyclohexane. Then transfer the slurry to a 10-mm chromatographic column; after washing with 50 ml of 4 M nitric acid, elute thorium with 40 ml of 0.3 M sulphuric acid (Fig. 2, elution diagram A), and uranium with 40 ml of 1 M hydrofluoric acid (Fig. 2, elution diagram B). Determine thorium and uranium as indicated for the column process.

On the basis of ten experiments the final yield was found to be $95.2 + 4\%$ for thorium, and $80.1 \pm 5\%$ for enriched uranium. The time required for one analysis was 4 h for natural thorium and 5 h for enriched uranium, but 8–10 analyses could be carried out simultaneously.

Determination of strontium-90 in urine by batchwise separation of yttrium-90 with Microthene–HDEHP

This method is based on the batch extraction of yttrium-90 (in equilibrium with strontium-90) from 500 ml of urine with Microthene supporting HDEHP. After the addition of 5 mg of stable strontium and yttrium, clarify the urine sample as indicated previously, and adjust the pH to 0.5. Add a slurry consisting of 5 g Microthene and 5 ml of 1.5 M HDEHP in toluene to the sample and stir on a magnetic stirrer for 20 min. Rapidly transfer the slurry to a 25-mm chromatographic column and wash with 100 ml of 0.3 *M* nitric acid at a flow-rate of 10–15 ml min^{-1}; elute yttrium with 100 ml of 6 *M* nitric acid at a flow-rate of 5 ml min^{-1} (Fig. 3).

Evaporate the solution to 10 ml and add 20 ml of 8% (w/v) ammonium oxalate solution; adjust the pH to 1.5 by adding dilute ammonia solution, and filter the yttrium oxalate precipitate through a 25-mm sintered glass radiochemical filtering system; wash the oxalate three times with methanol and count directly in a low-background β-detector. The counting efficiency was 30% for yttrium-90 with a background of 1.4 counts min^{-1}.

By following the yttrium-90 decay for 7–8 days and by extrapolating the curve to zero time (corresponding to the batch extraction process), the strontium-90 activity can be calculated more accurately.

On the basis of ten analyses, the final yield was found to be 91.7 ± 2.9%, with a sensitivity limit of about 5 pCi l^{-1} of urine. The time required for one analysis was about 4 h, and as many as eight analyses could be done simultaneously within 6 h.

Chromatographic isolation of natural iodine from synthetic foods with a Microthene–benzene column

Mineralize a 100–150 mg lyophilized sample for 3 h at a low temperature in the special asher, as outlined previously. Transfer the white residue (5–10 mg) to a cooled separatory funnel connected with a cooled (5°) column consisting of 2 g of Microthene supporting 2 ml of benzene. Add 10 ml of 1 *M* sulphuric acid gradually and oxidize iodide to iodine with 1 ml of aqueous 30% (w/v) sodium nitrite. Pass the solution through the column at 1 ml min^{-1}; after washing with 20 ml of water, elute iodine by reduction to iodide with 20 ml of 0.1 *M* ascorbic acid.

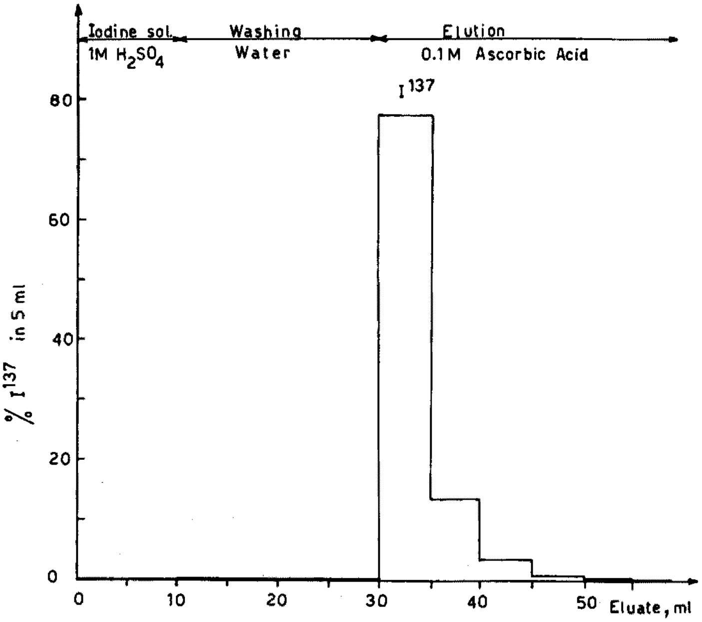

Fig. 4. Elution diagram of iodine with a Microthene–benzene column (2 g/2 ml). Flow-rate: 1 ml min^{-1}; column, 10 mm i.d.

By this method, the iodine recovery was found to be about 90%. Figure 4 shows the elution diagram obtained by spiking the iodine with ^{131}I and following the radionuclide by γ-spectrometry; by the same counting technique, the mean yield for the mineralization process (80%) and the final recovery of the inorganic iodine (72%) were calculated.

DISCUSSION AND CONCLUSIONS

As regards the radiotoxicological determinations, the "action level" is the daily urinary excretion when the body burden corresponds to the "maximum permissible body burden" (MPBB); the "reference level", which is generally one-tenth of the action level, is the value which an acceptable analytical method has to detect with a good precision.

For natural thorium a colorimetric method was preferred to radiometric counting because of the very low specific activity of thorium-232; the combination of the Microthene–TOPO chromatographic technique with the arsenazo III colorimetric method ($\varepsilon = 130{,}000$) gives a sensitivity limit of 0.2 μg l^{-1} of urine, which is sufficient to detect the reported reference level of 1 μg l^{-1} of urine[16]; the final chemical yield is good and the method is simple and rapid.

The reported reference level for enriched uranium is 25 α d.p.m. l^{-1} of urine[16]. In this regard, the outlined method gives a very good sensitivity limit (1 d.p.m. l^{-1}), but the final recovery is not very satisfactory because of some losses during the evaporation of hydrofluoric solution and during the transference step from the platinum vessel to the watch glass; moreover, some selfabsorption effect may cause a low α-counting efficiency. In any case, the rapidity and simplicity of the chromatographic technique, especially for the batchwise extraction process, justifies the suggested method for routine analyses.

The reference level for strontium-90 in the urine is reported[16] to be 200 pCi l^{-1}; in this respect, the outlined batch-extraction method for yttrium-90 gives a very good sensitivity limit (5 pCi l^{-1}) and a satisfactory final recovery.

With regard to the isolation of iodine from foodstuffs, the outlined mineralization technique, based on the combination of lyophilization and low-temperature oxidation process, seems to be of a certain interest. The iodine losses are controlled to a reasonable amount and the Microthene–benzene column works very well to retain iodine selectively. This chromatographic technique is to be preferred to a liquid–liquid extraction process when activation analysis ($^{127}I(n,\gamma)^{128}I$) is used[17,18], because of its greater rapidity and safety.

SUMMARY

Reversed-phase partition chromatography is a very useful tool for selective isolation of radionuclides from biological materials. Some new applications of this technique to the resolution of practical problems in radiation protection are reported. Natural thorium and enriched uranium can be determined separately and together in urine by means of a column of Microthene-710 supporting a solution of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane; batchwise extraction processes with Microthene supporting TOPO are also successful. Strontium-90 is determined in urine by a batch extraction of yttrium-90 with a slurry of Microthene supporting the liquid cation exchanger di-(2-ethylhexyl)phosphoric acid. Only a wet mineralization of the urines is required and the analyses are simple, rapid and sufficiently accurate. A method for the isolation of iodine from foodstuffs with a Microthene–benzene column is also described.

RÉSUMÉ

La chromatographie de partage à phase renversée, sur colonne est très utile pour une séparation sélective de radionuclides dans des milieux biologiques. Quelques nouvelles applications sont décrites. Le thorium naturel et l'uranium enrichi peuvent être dosés séparément ou ensemble dans l'urine au moyen d'une colonne de Microthène-710 supportant une solution de tri-*n*-octylphosphineoxyde dans le cyclohexane. On donne également une méthode de dosage du strontium-90. Ces procédés ne nécessitent qu'une minéralisation par voie humide des urines; les analyses sont simples, rapides et suffisamment précises. On décrit également une méthode de séparation de l'iode d'avec des aliments.

ZUSAMMENFASSUNG

Die Verteilungschromatographie mit umgekehrten Phasen ist ein sehr gebräuchliches Hilfsmittel für die selektive Abtrennung von Radionukliden von biologischen Materialien. Über einige neue Anwendungen dieser Methode auf die Lösung praktischer Probleme im Strahlenschutz wird berichtet. Natürliches Thorium und angereichertes Uran in Urin können getrennt oder zusammen bestimmt werden mit Hilfe einer Kolonne von Microthene-710, auf dem eine Lösung von Tri-*n*-octylphosphinoxid (TOPO) in Cyclohexan aufgetragen ist; absatzweise Extraktionsprozesse mit mit TOPO beladenem Microthene sind ebenfalls geeignet. Strontium-90 in Urin wird bestimmt durch eine absatzweise Extraktion des Yttriums-90 mit einem Brei von Microthene, das mit dem flüssigen Kationenaustauscher Di-(2-äthylhexyl)-phosphorsäure beladen ist. Es ist nur eine nasse Veraschung des Urins erforderlich, und die Analysen sind einfach, schnell und genügend genau. Eine Methode für die Isolierung von Jod aus Nahrungsmitteln mit einer Microthene–Benzol-Kolonne wird ebenfalls beschrieben.

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EXTRACTION DE L'ACIDE SILICOMOLYBDIQUE PAR LE NITRATE DE TRIISOOCTYLAMINE EN MILIEU DICHLORO-1,2-ETHANE

NATURE DES ÉQUILIBRES AND APPLICATION ANALYTIQUE

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Au cours d'un précédent travail concernant l'extraction du molybdène par une amine à longue chaine[1], le dichloro-1,2-éthane a été préféré au toluène par suite de sa plus grande polarité: on évite ainsi la formation d'agrégats ioniques. En outre, ce solvant est aisément purifiable et maniable, très peu miscible à l'eau, et surtout non toxique.

Nous avons donc repris le même solvant et la même amine, le nitrate de triisooctylamine, pour tenter d'améliorer le dosage de l'acide silicomolybdique en présence de molybdène. Par extraction, on sépare très bien ces deux composés, et le dosage spectrophotométrique direct dans l'u.v. de l'acide silicomolybdique devient très sensible puisqu'on n'est plus gêné par la superposition du spectre du molybdène. On obtient même une meilleure sensibilité qu'avec la méthode classique de réduction de l'acide en dérivés bleus, sans en avoir les nombreux inconvénients[2].

Rappelons qu'il existe deux isomères, appelés α et β par STRICKLAND[3], de l'ion silicomolybdate $SiMo_{12}O_{40}^{4-}$. Leurs propriétés sont légèrement différentes, comme l'a montré MASSART[4]. En particulier, le pK de l'acide βH^{3-} est environ 2.5 tandis que l'acide αH^{3-} serait plus fort. Une revue générale de leurs propriétés a été faite par MALAPRADE[5], puis par SOUCHAY[6].

Nous avons préféré n'étudier que l'isomère α bien que son coefficient d'absorption soit égal à la moitié de celui de β. Du point de vue analytique, ce facteur 2 nous semble largement compensé par l'inconvénient d'avoir à préparer l'isomère β dépourvu de α, puisque β est instable dans l'eau et se transforme lentement en α.

PARTIE EXPÉRIMENTALE

Technique d'extraction, préparation et dosage des solutions de triisooctylamine et de molybdate ont été décrits dans un précédent mémoire[1]. Le silicomolybdate d'ammonium a été obtenu à partir de l'acide α préparé selon la méthode de MASSART[4], en précipitant en fin d'opération le silicomolybdate par addition de nitrate d'ammonium en excès. L'analyse chimique et l'analyse thermogravimétrique[7] confirment la formule: $SiO_4(MoO_3)_{12}(NH_4)_4 \cdot 5H_2O$.

Le composé contenait en outre des traces de molybdène sous forme chimique non déterminée, dans la proportion de $2.7 \cdot 10^{-3}$ atomes gramme de molybdène par mole de silicomolybdate. Tous les résultats ont été corrigés en conséquence.

Dosage du silicomolybdate

Dans le dichloro-1,2-éthane, le dosage spectrophotométrique direct est possible à toute longueur d'onde comprise entre 300 et 400 nm. Dans l'eau et en l'absence de molybdate, le silicomolybdate est décomposé en molybdate par chauffage au bain-marie en milieu soude 10^{-1} *M*. Le molybdate est titré par la méthode habituelle.

Dosage des mélanges aqueux molybdène–silicomolybdate

Lorsque molybdène et silicomolybdate sont présents simultanément dans la phase aqueuse, la méthode de dosage par décomposition en milieu basique conduit à déterminer le molybdène total provenant du molybdène libre et des ions silicomolybdate.

On détermine le molybdène libre initialement présent dans la solution en se plaçant en milieu acide sulfurique concentré. Dans ces conditions, le silicomolybdate n'est pas décomposé et seul, le molybdène libre est dosé par la méthode habituelle (réduction de Mo(VI) par les ions fer(II) et formation du complexe thiocyané rouge de Mo(V)). La solution doit être maintenue froide, pour éviter la réduction par fer(II) des ions nitrate servant à maintenir la force ionique au cours des extractions. Le silicomolybdate est obtenu par différence.

ÉQUILIBRE D'EXTRACTION

En milieu acide (pH < 2), l'acide silicomolybdique α est présent dans l'eau sous l'une des formes α^{4-}, αH^{3-}, αH_2^{2-} etc., que nous symboliserons par α. On ignore aussi quelle est l'espèce extraite par le nitrate de triisooctylamine en milieu dichloro-1,2-éthane neutre. En opérant en présence d'un excès d'hétéropolyacide, on vérifie que pour toute acidité de la phase aqueuse comprise entre 10^{-2} *M* et 4 *M*, et en présence de nitrate de lithium 1 *M*, le silicomolybdate est extrait quantitativement dans le solvant neutre par quatre cations R_3NH^+. C'est donc la forme α^{4-} qui prédomine en phase organique. L'équilibre d'extraction peut être représenté ainsi:

$$\alpha_{aq}+4(R_3NHNO_3)_s \rightleftharpoons [\alpha(R_3NH)_4]_s+4(NO_3^-)_{aq}+qH_{aq}^+$$

avec $0 \leqq q \leqq 4$.

Le p*K* de dissociation des paires d'ions volumineux est généralement compris entre 3 et 4 dans le dichloroéthane[8]. En milieu dilué, il faut donc envisager une éventuelle dissociation de $\alpha(R_3NH)_4$ qui peut porter sur 1, 2, 3 ou 4 cations R_3NH^+ successivement. Pour simplifier, nous admettrons, comme cela sera justifié par la suite, qu'une espèce prédomine $[\alpha(R_3NH)_{4-n}]^{n-}$ avec $0 < n < 4$. Comme R_3NHNO_3 n'est pratiquement pas dissocié aux concentrations que nous avons utilisées[1], en raison sans doute de la très grande différence de taille entre l'anion et le cation, l'équilibre d'extraction est alors le suivant:

$$\alpha_{aq}+4(R_3NHNO_3)_s \rightleftharpoons [\alpha(R_3NH)_{4-n}]_s^{n-}+n(R_3NH^+)_s+4(NO_3^-)_{aq}+qH_{aq}^+$$

$$K = \frac{a_{\alpha(R_3NH)_{4-n}^{n-}} \cdot a^n_{R_3NH^+} \cdot a^4_{NO_3^-} \cdot a^q_{H^+}}{a_\alpha \cdot a^4_{R_3NHNO_3}}$$

La constante *K* est définie en fonction des activités. En phase organique où les espèces sont en concentration inférieure à 10^{-2} M, on peut admettre que les coefficients d'activité sont égaux à l'unité et assimiler activité et concentration. Ce n'est plus vrai pour les espèces en phase aqueuse, puisque la concentration en électrolyte est importante, et dans une partie de nos expériences, variable (10^{-1} à 4 M). Si l'on dispose de valeurs numériques dans le cas des ions nitrate, on ignore la valeur des coefficients d'activité des ions α^{4-} et αH^{3-}. Il est vraisemblable, compte tenu du nombre des charges négatives, qu'ils sont très inférieurs à l'unité, et très variables avec la force ionique[9]. Les seules constantes que nous ayons pu déterminer sont donc des constantes apparentes valables à force ionique donnée.

DÉTERMINATION DE n ET D'UNE CONSTANTE APPARENTE K'

Pour déterminer n, nous avons maintenu constants le pH et la force ionique de la phase aqueuse dans les conditions suivantes: $LiNO_3 = 0.9$ M, $HNO_3 = 0.1$ M. La concentration en ions nitrate varie légèrement du fait du transfert d'une certaine quantité de ces ions de la phase organique (R_3NHNO_3) vers la phase aqueuse. Ces variations sont cependant suffisamment faibles (10% au maximum) pour que l'on puisse supposer constants les coefficients d'activité. On définit une constante apparente K', valable à pH constant:

$$K' = \frac{C_{\alpha(R_3NH)^{n-}_{4-n}} \cdot C^{n}_{R_3NH^+} \cdot C^{4}_{NO_3^-}}{C_\alpha \cdot C^{4}_{R_3NHNO_3}}$$

Puisque le nitrate d'amine R_3NHNO_3 n'est pas dissocié en ions dans les conditions de concentrations utilisées[1], nous avons:

$$C_{R_3NH^+} = nC_{\alpha(R_3NH)^{n-}_{4-n}}$$

$$K' = \frac{n^n \cdot C^{n+1}_{\alpha(R_3NH)^{n-}_{4-n}} \cdot C^{4}_{NO_3^-}}{C_\alpha \cdot C^{4}_{R_3NHNO_3}}$$

Si, comme nous l'avons supposé, le silicomolybdate existe sous une forme prédominante en phase organique, la courbe:

$$\log \frac{C_\alpha \cdot C_{R_3NHNO_3}}{C^{4}_{NO_3^-}} = \mathrm{f}\left[\log C_{\alpha(R_3NH)^{n-}_{4-n}}\right]$$

doit être une droite de pente $n+1$. Si plusieurs espèces coexistent, la courbe n'est plus une droite.

Les résultats des extractions faites à concentration variable en acide silicomolybdique et nitrate d'amine sont réunis dans le Tableau I. La courbe précédemment définie est une droite de pente $n+1 = 2.06 \pm 0.1$. Ceci indique que le silicomolybdate existe sous une forme prédominante dans les conditions de concentration utilisées, l'anion $[\alpha(R_3NH)_3]^-$.

L'équilibre d'extraction est donc:

$$\alpha_{aq} + 4(R_3NHNO_3)_s \rightleftharpoons [\alpha(R_3NH)_3]_s^- + (R_3NH)_s^+ + 4(NO_3^-)_{aq} + qH^+$$

TABLEAU I

EXTRACTION DE L'ACIDE SILICOMOLYBDIQUE (α) PAR LE NITRATE DE TRIISOOCTYLAMINE (R_3NHNO_3) EN MILIEU DICHLORO-1,2-ÉTHANE (S)

(Conditions initiales: $HNO_3 = 10^{-1}$ *M*, $LiNO_3 = 0.90$ *M*.
Concentrations à l'équilibre en mole litre^{-1}. K' en mole litre^{-1})

α_S	α_{aq}	$(R_3NHNO_3)_S$	$(NO_3^-)_{aq}$	$(H^+)_{aq}$	pK'
$2.84 \cdot 10^{-2}$	$1.95 \cdot 10^{-5}$	$1.13 \cdot 10^{-2}$	1.113	0.10	-9.59
$1.42 \cdot 10^{-2}$	$3.55 \cdot 10^{-5}$	$5.72 \cdot 10^{-3}$	1.057	0.10	-9.81
$7.05 \cdot 10^{-3}$	$5.30 \cdot 10^{-5}$	$3.00 \cdot 10^{-3}$	1.028	0.10	-10.11
$3.47 \cdot 10^{-3}$	$7.88 \cdot 10^{-5}$	$1.72 \cdot 10^{-3}$	1.014	0.10	-10.26
$1.67 \cdot 10^{-3}$	$1.013 \cdot 10^{-4}$	$1.12 \cdot 10^{-3}$	1.007	0.10	-10.25
$7.83 \cdot 10^{-4}$	$1.040 \cdot 10^{-4}$	$7.70 \cdot 10^{-4}$	1.003	0.10	-10.23
$3.59 \cdot 10^{-4}$	$8.60 \cdot 10^{-5}$	$5.40 \cdot 10^{-4}$	1.00	0.10	-10.24
$1.56 \cdot 10^{-4}$	$6.65 \cdot 10^{-5}$	$3.51 \cdot 10^{-4}$	1.00	0.10	-10.38
$6.0 \cdot 10^{-5}$	$5.15 \cdot 10^{-5}$	$2.48 \cdot 10^{-4}$	1.00	0.10	-10.27

Nous lui associons la constante apparente K' à pH constant:

$$K' = \frac{C_{\alpha(R_3NH)_3^-} \cdot C_{R_3NH^+} \cdot C^4_{NO_3^-}}{C_\alpha \cdot C^4_{R_3HNO_3}}$$

p$K' = -10.2 \pm 0.15$ au seuil de confiance 95%.

Influence des ions nitrate

Les résultats précédents ont été obtenus en maintenant constante la force ionique de la phase aqueuse. Nous avons recherché le domaine de validité de la constante apparente K' lorsque la concentration en ions nitrate, et par conséquent la force ionique varient, la concentration en protons gardant évidemment la même valeur.

Les résultats des déterminations analytiques sont résumés dans le Tableau II. Lorsque la concentration en ions nitrate est inférieure à 1 *M*, on observe une certaine décomposition de l'acide silicomolybdique en molybdate; en-dessous de 0.4 *M*, la détermination de l'acide silicomolybdique restant en phase aqueuse devient impossible.

On constate que lorsque la force ionique du milieu diminue, pK' garde approxi-

TABLEAU II

INFLUENCE DES IONS NITRATE (MÉLANGES $HNO_3 + LiNO_3$) SUR L'EXTRACTION DE L'ACIDE SILICOMOLYBDIQUE (α) PAR LE NITRATE DE TRIISOOCTYLAMINE (R_3NHNO_3) EN MILIEU DICHLORO-1,2-ÉTHANE (S)

(Concentrations à l'équilibre en mole litre^{-1}. K' en mole litre^{-1})

NO_3^-	α_S	α_{aq}	R_3NHNO_3	H^+	pK'
0.403	$7.94 \cdot 10^{-4}$	$\# \cdot 10^{-7}$	$1.29 \cdot 10^{-3}$	0.10	$\# -10.8$
0.603	$7.93 \cdot 10^{-4}$	$1.3 \cdot 10^{-6}$	$1.29 \cdot 10^{-3}$	0.10	-10.36
0.803	$7.92 \cdot 10^{-4}$	$4.7 \cdot 10^{-6}$	$1.29 \cdot 10^{-3}$	0.10	-10.30
1.00	$7.90 \cdot 10^{-4}$	$9.7 \cdot 10^{-6}$	$1.30 \cdot 10^{-3}$	0.10	-10.35
2.00	$7.84 \cdot 10^{-4}$	$1.6 \cdot 10^{-5}$	$1.32 \cdot 10^{-3}$	0.10	-11.30
3.00	$7.75 \cdot 10^{-4}$	$2.5 \cdot 10^{-5}$	$1.36 \cdot 10^{-3}$	0.10	-11.75
4.00	$7.66 \cdot 10^{-4}$	$3.4 \cdot 10^{-5}$	$1.39 \cdot 10^{-3}$	0.10	-12.07

mativement la même valeur. Cela peut s'expliquer par le fait que les coefficients d'activité passent généralement par un minimum, et par conséquent varient peu, dans la zone de concentration en électrolyte 10^{-1} M–1 M[9,10]. La constante apparente K' que nous avons définie, est donc valable à des fins analytiques dans ce domaine de force ionique.

En revanche, lorsque la concentration en électrolyte devient supérieure à 1 M, les variations des coefficients d'activité ne sont plus négligeables. Il est donc nécessaire de déterminer expérimentalement la constante K' dans chaque milieu.

Influence de l'acidité

Les essais précédents, effectués à acidité constante, ne permettent pas de savoir si l'isomère α est sous forme acide ou non dans l'eau. Afin de faire varier le pH dans un large domaine tout en maintenant constante la force ionique, les extractions ont été menées en présence d'électrolytes en concentration beaucoup plus élevée, 4 M, fixée à l'aide des mélanges $LiNO_3 + HNO_3$ tels que $C_{NO_3^-} = 4$ M. Les résultats sont indiqués dans le Tableau III.

TABLEAU III

INFLUENCE DE L'ACIDITÉ SUR L'EXTRACTION DE L'ACIDE SILICOMOLYBDIQUE (α) PAR LE NITRATE DE TRIISOOCTYLAMINE (R_3NHNO_3)

(Concentration en NO_3^- ($LiNO_3 + HNO_3$) = 4 M. Concentrations à l'équilibre en mole litre^{-1}. K'' en mole litre^{-1})

H^+	α_s	α_{aq}	$(R_3NHNO_3)_s$	$(NO_3^-)_{aq}$	pK''_{app}
0.010	$7.48 \cdot 10^{-4}$	$5.25 \cdot 10^{-5}$	$1.07 \cdot 10^{-3}$	4.0	−12.32
0.050	$7.39 \cdot 10^{-4}$	$6.15 \cdot 10^{-5}$	$1.12 \cdot 10^{-3}$	4.0	−12.16
0.10	$7.31 \cdot 10^{-4}$	$6.85 \cdot 10^{-5}$	$1.16 \cdot 10^{-3}$	4.0	−12.04
0.20	$7.21 \cdot 10^{-4}$	$7.90 \cdot 10^{-5}$	$1.20 \cdot 10^{-3}$	4.0	−11.91
0.50	$6.97 \cdot 10^{-4}$	$1.03 \cdot 10^{-4}$	$1.29 \cdot 10^{-3}$	4.0	−11.64
1.0	$6.66 \cdot 10^{-4}$	$1.34 \cdot 10^{-4}$	$1.42 \cdot 10^{-3}$	4.0	−11.32
2.0	$6.07 \cdot 10^{-4}$	$1.93 \cdot 10^{-4}$	$1.65 \cdot 10^{-3}$	4.0	−10.82
3.0	$5.63 \cdot 10^{-4}$	$2.37 \cdot 10^{-4}$	$1.83 \cdot 10^{-3}$	4.0	−10.48
4.0	$4.96 \cdot 10^{-4}$	$3.04 \cdot 10^{-4}$	$2.10 \cdot 10^{-3}$	4.0	−10.03

La constante apparente K'', définie comme K' mais valable dans un milieu de force ionique différente, dépend du pH de la phase aqueuse (Fig. 1). La relation liant K'' au pH n'est pas simple. Qualitativement, les phénomènes s'expliquent par la fixation de un, puis éventuellement de deux protons vraisemblablement, entrainant une diminution du coefficient de partage lorsque le pH diminue, puisque l'espèce extraite est α^{4-}.

$$\alpha^{4-} + H^+ \rightleftharpoons \alpha H^{3-}$$

$$\alpha H^{3-} + H^+ \rightleftharpoons \alpha H_2^{2-}$$

Pratiquement, l'acidité de la phase aqueuse doit être comprise entre 10^{-2} M et 10^{-1} M si l'on veut conserver un grand coefficient de partage tout en évitant la décomposition de l'isomère α en molybdate qui se produit en milieu faiblement acide.

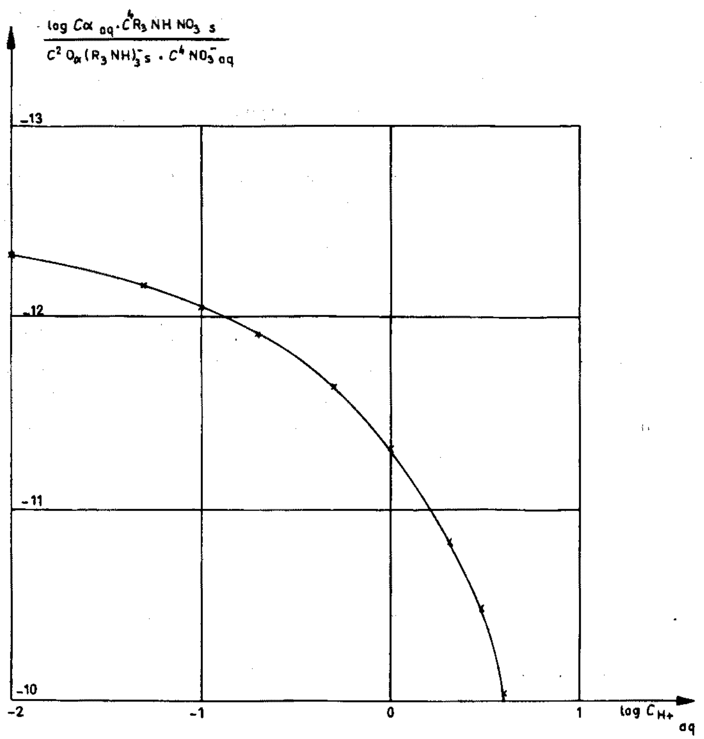

Fig. 1. Influence de l'acidité du milieu aqueux sur l'extraction de l'ion silicomolybdate.

APPLICATION ANALYTIQUE

De bonnes conditions de dosage de la silice peuvent être déduites des résultats précédents. Dissoute dans l'eau sous forme de silicate, la silice est transformée en silicomolybdate, en milieu acide, en présence d'un excès de molybdate. L'extraction par le nitrate de triisooctylamine de l'acide silicomolybdique permet une séparation très sélective de l'excès de molybdate, et plus généralement de toutes les espèces cationiques, à condition que la phase aqueuse soit suffisamment acide. A pH $=0.5$, le coefficient de partage du silicomolybdate est supérieur à 100, celui du molybdate inférieur à $5 \cdot 10^{-3}$.

Après extraction, le silicomolybdate est dosé directement par spectrophotométrie dans le dichloroéthane, à 300 nm ($\varepsilon = 28000$ l cm^{-1} mole^{-1}). Dans l'eau, en présence de l'excès de molybdène, on peut se placer au mieux à 350 nm ($\varepsilon = 7000$ l cm^{-1} mole^{-1}), la solution de référence contenant exactement la même concentration de molybdène.

Dans ces conditions, la limite de sensibilité de la méthode est environ $2 \cdot 10^{-6}$ atomes gramme de silicium par litre (Tableau IV).

Mode opératoire proposé

Introduire la prise d'essai dans une fiole de 50 ml (environ 10^{-5} moles de SiO_3^{2-} contenues dans 10 ml). Y ajouter 10 ml de molybdate de sodium $5 \cdot 10^{-2}$ *M*, et

TABLEAU IV

DOSAGE SPECTROPHOTOMÉTRIQUE DU SILICIUM

(Concentrations en atomes gramme de silicium par litre)

λ (nm)	*Concentration théorique*	*Concentration trouvée*
435	$2.23 \cdot 10^{-3}$	$2.23 \cdot 10^{-3}$
	$1.11 \cdot 10^{-3}$	$1.10 \cdot 10^{-3}$
400	$5.56 \cdot 10^{-4}$	$5.55 \cdot 10^{-4}$
	$2.50 \cdot 10^{-4}$	$2.48 \cdot 10^{-4}$
350	$4.45 \cdot 10^{-5}$	$4.40 \cdot 10^{-5}$
	$2.98 \cdot 10^{-5}$	$2.90 \cdot 10^{-5}$
300	$8.90 \cdot 10^{-6}$	$8.80 \cdot 10^{-6}$
	$5.57 \cdot 10^{-6}$	$5.40 \cdot 10^{-6}$
	$3.57 \cdot 10^{-6}$	$3.10 \cdot 10^{-6}$

15 ml de nitrate de lithium 2 *M*. Ajuster par de l'acide nitrique à pH 2.9. Agiter 20 minutes en chauffant légèrement (on obtient le silicomolybdate α seul).

Extraire par 15 ml de solution de nitrate de triisooctylamine 10^{-2} *M* dans le dichloro-1,2-éthane. Pour la mesure spectrophotométrique, la longueur d'onde choisie varie de 435 à 300 nm selon la teneur en silicium de la prise d'essai.

CONCLUSION

L'équilibre d'extraction de l'acide silicomolybdique α par le nitrate de triisooctylamine suppose la dissociation du composé extrait dans le dichloro-1,2-éthane en ions R_3NH^+ et $\alpha(R_3NH)_3^-$. Si l'extraction est effectuée en milieu suffisamment acide, on obtient une séparation très efficace de l'excès de molybdène nécessaire pour former le complexe silicomolybdique à partir de silice. Le dosage spectrophotométrique de l'hétéropolyacide directement dans le dichloroéthane est dans ces conditions simple et sensible.

L'un des auteurs (R.K.) remercie M. le Professeur CHARLOT de l'avoir acueilli dans son laboratoire et aidé de ses conseils, ainsi que la Direction des Etudes et Techniques Nouvelles de la Société Gaz de France de l'avoir autorisé à effectuer ce travail au Laboratoire de Chimie Analytique de l'E.S.P.C.I.

RÉSUMÉ

L'acide silicomolybdique α en solution aqueuse est extrait par le nitrate de triisooctylamine R_3NHNO_3 en milieu dichloro-1,2-éthane (S) selon un équilibre qui fait intervenir la dissociation en ions de l'espèce extraite dans la phase organique:

$$\alpha_{aq} + 4(R_3NHNO_3)_S \rightleftharpoons [\alpha(R_3NH)_3]_S^- + (R_3NH)_S^+ + 4(NO_3^-)_{aq} + xH^+$$

Par extraction, α est séparé de l'excès de molybdène nécessaire pour former quantitativement α à partir de silice et de molybdate. Une méthode de dosage spectrophotométrique direct est donnée.

SUMMARY

α-Molybdosilicic acid (α) in aqueous solution is extracted by triisooctylamine nitrate (R_3NHNO_3) in dichloro-1,2-ethane (S) according to an equilibrium which involves the dissociation of the extracted species in the organic phase:

$$\alpha_{aq}+4(R_3NHNO_3)_S \rightleftharpoons [\alpha(R_3NH)_3]_S^- + (R_3NH)_S^+ + 4(NO_3^-)_{aq} + xH^+$$

Extraction allows separation of α from the excess of molybdenum necessary for its quantitative formation from silicate and molybdate. The direct spectrophotometric determination of the heteropolyacid in the organic phase is simple and sensitive ($\varepsilon = 28000$ l cm^{-1} mole^{-1} at 300 nm).

ZUSAMMENFASSUNG

α-Molybdatokieselsäure (α) in wässriger Lösung wird durch Triisooctylaminnitrat (R_3NHNO_3) in 1,2-Dichloräthan (S) entsprechend einem Gleichgewicht extrahiert, in dem die Dissoziation der extrahierten Spezies in der organischen Phase enthalten ist:

$$\alpha_{aq}+4(R_3NHNO_3)_S \rightleftharpoons [\alpha(R_3NH)_3]_S^- + (R_3NH)_S^+ + 4(NO_3^-)_{aq} + xH^+$$

Die Extraktion erlaubt die Trennung von α vom Molybdän-Überschuss, der für die quantitative Bildung von α aus Silicat und Molybdat notwendig ist. Die direkte spektrophotometrische Bestimmung der Heteropolysäure in der organischen Phase ist einfach und empfindlich ($\varepsilon = 28000$ l cm^{-1} mol^{-1} bei 300 nm).

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COMPLEXES FORMED IN THE CHLOROFORM EXTRACTION OF COBALT(II) WITH OXINE

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Several works have been published on the extractive photometric determination of cobalt with oxine[1-3]. However, these methods of determination are not always successful because of large variations of the absorbance readings[2]; moreover, the optimal pH range for complete extraction (pH 7.3–8.2[3]) seems too narrow for such a wide pH range for complete precipitation of a well defined cobalt(II) oxinate (pH 4.3–14.5[4]). A theoretical study on the solvent extraction of cobalt(II) with oxine has been published[5], but no answer has been given on such questions. Moreover, there is another important question whether cobalt is extracted in the cobalt(II) or cobalt(III) states.

In the present work, cobalt was extracted with oxine solutions in chloroform in the cobalt(II) state and the compositions of the extractable complexes were determined from the distribution data.

EXPERIMENTAL

Materials and apparatus

All the reagents and chemicals were of G.R. grade. Chloroform containing 0.5% (v/v) ethanol was used. Aqueous solutions of cobalt(II) were prepared by dissolving cobalt(II) chloride hexahydrate in 0.01 *M* perchloric acid.

A ^{60}Co radiotracer was used in all the extraction experiments. The radiochemical purity was verified to be adequate for this work, by measurements of the distribution ratios of cobalt by γ-countings at various energy levels.

The apparatus used included a Hitachi 124 automatic recording spectrophotometer and 1-cm glass cells for absorbance spectra measurements, a Bausch-Lomb Spectronic 20 Colorimeter and the accessory 0.5-in. test tubes for absorbance measurements, a Kobe AN-10 γ-ray spectrometer equipped with a well-type NaI(Tl) crystal for counting measurements, and a Horiba Model P pH meter with a glass and 3.33 *M* calomel electrode pair for pH measurements. The concentration of hydrogen ion was calculated as $-\log[H^+] = \text{pH}$ for convenience.

Distribution measurements of cobalt(II)

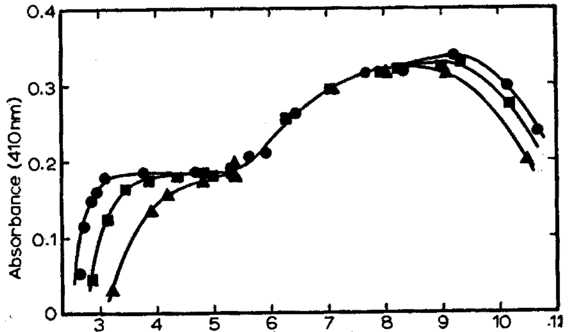
A solution of oxine in chloroform (5 ml of 0.05–0.2 *M*) and an equal volume of an aqueous solution containing cobalt(II) ion at a constant ionic strength (0.1) were equilibrated by shaking in a glass cylindrical tube for 3 min, an adequate time for the attainment of equilibrium. The pH of the aqueous phase was adjusted by addition of perchloric acid and sodium hydroxide. Small amounts (< 0.002 *M*) of acetate or borate were added to buffer the aqueous phase. Such amounts of these salts were found not to alter the distribution ratio of cobalt within experimental error. The ionic strength was kept constant by addition of sodium perchlorate. The mixtures were centrifuged for 2 min. After the phase separation, equal volumes (1 ml) of both phases were pipetted out and counted separately. The residual aqueous and organic phases were removed for pH and absorbance measurements, respectively.

The experiments were all carried out in a temperature controlled room at 20°.

RESULTS AND DISCUSSION

Absorbance spectra of cobalt oxine complexes

The absorbance at 410 nm of cobalt extracted into the organic phase is given as a function of pH in Fig. 1 (the absorbance by excess oxine is negligible at 410 nm). For 0.2 *M* oxine, starting at pH 2.5 the absorbance increases and then reaches a constant value in the pH range 3.2–5.5. From pH 5.5 the absorbance increases again, takes a maximum value at pH 9.3, and then decreases. Despite the difference in the absorbance, cobalt is almost completely extracted in the pH range 3.2–9.5 for 0.2 *M* oxine (Fig. 3; $\log D_{\mathrm{Co}} > 1$). Similar results are obtained for 0.1 and 0.05 *M* oxine (Fig. 1).



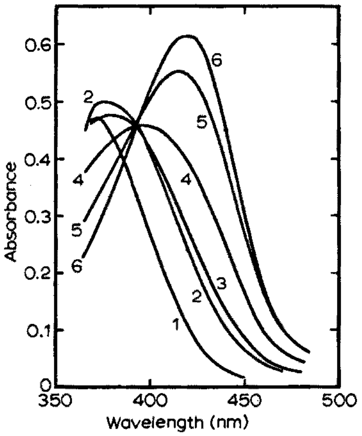


Fig. 1. Absorbance (410 nm) of cobalt(II) oxine complexes in organic extracts as a function of pH. Initial concentration of Co(II) in aqueous phase, $7.20 \cdot 10^{-5}$ *M*. Initial concentration of HOx in organic phase: (●) 0.2 *M*, (■) 0.1 *M*, (▲) 0.05 *M*.

Fig. 2. Absorbance spectra of cobalt extracted with oxine solutions in chloroform. Initial concentration of Co(II) in aqueous phase, $7.20 \cdot 10^{-5}$ *M*. Initial concentration of HOx in organic phase and final pH of aqueous phase: (1) 0.05 *M*, 4.5; (2) 0.025 *M*, 8.0; (3) 0.01 *M*, 8.0; (4) 0.005 *M*, 8.0; (5) 0.0025 *M*, 8.0; (6) 0.01 *M*, 8.0, in the presence of 0.8 *M* H_2O_2. Spectra identical with those of (1) and (2) were obtained for higher concentrations of oxine solutions in chloroform at both pH's. References, reagent blanks.

The absorbance spectra of cobalt oxine complexes in organic extracts are given in Fig. 2. Cobalt was verified to be quantitatively extracted by radioactivity measurement. Curve 1 in Fig. 2 shows a spectrum of cobalt extracted with a 0.05 *M* oxine solution in chloroform at pH 4.5. It was not essentially altered by changing the concentration of oxine in the organic phase or by addition of hydrogen peroxide (0.8 *M*) or ascorbic acid (0.02 *M*) to the aqueous phase before extraction. Curve 2 was obtained with a 0.025 *M* oxine solution at pH 8, and again not influenced by increasing concentration of oxine or by addition of ascorbic acid on preparation. Curves 1 and 2 could be interchanged by shaking the organic extracts with aqueous solutions for 1 min at pH 8 and 4.5, respectively. These results indicate that spectra 1 and 2 are those of cobalt(II) complexes.

The absorbance spectrum of cobalt in the organic extract at pH 8 is changed by decreasing concentration of oxine in the organic phase (curves 2–5, Fig. 2). These four absorbance spectra show an isosbestic point at 393 nm, above which the absorbance increases remarkably with decreasing concentration of oxine. Curve 6 in Fig. 2 shows the spectrum of cobalt extracted with 0.01 *M* oxine solution at pH 8 in the presence of 0.8 *M* hydrogen peroxide in the aqueous phase; this spectrum has a maximum at 420 nm, and was not changed by prolonged shaking, indicating that curve 6 corresponds to the cobalt(III) complex.

These results lead to the following conclusions. Cobalt can be extracted either in the cobalt(II) or cobalt(III) states. There are two extractable cobalt(II) complexes, the spectra of which are shown by curves 1 and 2 in Fig. 2. Changes in the spectra as shown by curves 2–5 are due to oxidation of cobalt(II) to cobalt(III).

Thus, cobalt is much more easily oxidized on extraction from an aqueous alkaline solution than from an acidic one. However, oxidation of the cobalt(II) complexes can be readily avoided if the extraction is carried out with >0.05 *M* oxine solutions in the absence of any strong oxidizing agents such as hydrogen peroxide. It is of interest to find that a large excess of oxine prevents the oxidation of the cobalt(II) complex.

Back-extraction behavior of cobalt oxine complexes

The oxidation states of extractable cobalt oxine complexes were verified by back-extraction of the complexes from the organic extracts with aqueous EDTA solutions at pH 4–5 and 7–9. The results of the experiments at initial concentrations of $7.20 \cdot 10^{-5}$ *M* cobalt with 0.1 *M* oxine are given in Table I.

Cobalt, which was verified to be in the cobalt(II) state by its spectra, was almost completely back-extracted with the acidic EDTA solution (Table I), but only slightly back-extracted with alkaline EDTA solution. In the latter case, the cobalt oxine complex retained the spectrum of curve 2 in Fig. 2. Thus, the back-extractability is mainly dependent on the pH of the aqueous EDTA solution.

In Table I are also given the results of the back-extraction when the initial extracts were prepared in the presence of 0.8 *M* hydrogen peroxide in the aqueous phase. Cobalt extracted from acidic aqueous solutions in the presence of hydrogen peroxide was easily back-extracted with the acidic EDTA solution, but not with the alkaline EDTA solution (Table I); the cobalt remaining in the organic phase again gave the spectrum corresponding to curve 2 in Fig. 2. Thus, the presence of hydrogen peroxide has little effect on extraction of cobalt(II) in the acidic region, but an important effect in the alkaline region.

TABLE I

BACK-EXTRACTION OF COBALT OXINE COMPLEXES WITH 0.001 *M* EDTA

(Initial concentration of Co(II) in aqueous phase, $7.20 \cdot 10^{-5}$ *M*; initial concentration of oxine in organic phase, 0.1 *M*)

Extraction			*Back-extraction with EDTA*			
Exp. no.	*pH*[a]	*Spectrum*[b]	*pH*[c]	*Shaking time*[d]	*Spectrum*[b]	*% Back-extracted*
Organic extracts prepared in absence of H_2O_2						
1	4.00	1	4.28	30		99.46
2	4.00	1	4.28	60		99.35
3	4.02	1	7.52	30	2	5.07
4	4.02	1	7.52	60	2	8.05
5	8.20	2	8.00	30	2	4.31
6	8.20	2	8.00	60	2	7.69
7	8.56	2	5.09	30		90.63
8	8.56	2	5.09	60		90.50
Organic extracts prepared in presence of 0.8 M H_2O_2						
9	4.05	1	4.93	30		98.90
10	4.05	1	4.93	60		98.81
11	4.05	1	7.30	30	2	6.22
12	4.05	1	7.30	60	2	13.50
13	7.63	6	5.03	30	6	8.40
14	7.63	6	5.03	60	6	8.33
15	7.63	6	7.29	30	6	1.22
16	7.63	6	7.29	60	6	1.81

[a] pH of aqueous phase after extraction.
[b] Type of spectrum of cobalt in the organic phase. Numbers correspond to those of curves in Fig. 2.
[c] pH of aqueous phase after back-extraction.
[d] Shaking time (sec) for back-extraction.

TABLE II

BACK-EXTRACTION OF COBALT OXINE COMPLEXES WITH 0.001 *M* EDTA

(Shaking time for back-extraction, 60 sec; initial concentration of cobalt(II), $2.0 \cdot 10^{-7}$ *M*; initial concentration of HOx, 0.1 *M*)

Exp. no.	*pH*[a]	*pH*[b]	*% Back-extracted*
1	4.14	4.10	90.5
2	4.32	4.39	84.5
3	4.59	4.89	87.3
4	8.39	4.55	0.17

[a] pH of aqueous phase after extraction.
[b] pH of aqueous phase after back-extraction.

Cobalt extracted from alkaline aqueous solutions in the presence of hydrogen peroxide gives the spectrum of the cobalt(III) complex. This complex is not back-extracted with acidic or alkaline EDTA solutions (Table I); the small amount of cobalt that is extracted is due to the existence of cobalt(II) complex in the initial organic extract, for complete oxidation is not always possible especially in the acidic region.

Thus, the oxidation states of the extractable cobalt oxine complexes can be established by treatment of the organic extracts with EDTA solution: cobalt(II) complexes are back-extracted at pH 4–5, and cobalt(III) complexes are not.

As the oxidation states at tracer concentrations ($2.0 \cdot 10^{-7}$ *M*) of extractable cobalt oxine complexes could not be determined spectrophotometrically, they were determined only from the back-extractability. Such data are shown in Table II. Cobalt extracted from acidic solutions was readily back-extracted with the acidic EDTA solution, indicating that the complex in the organic extract was mainly in the cobalt(II) state. The back-extraction efficiency for cobalt(II) complexes with the acidic EDTA solution was somewhat smaller for $2.0 \cdot 10^{-7}$ *M* cobalt (Table I) than for $7.20 \cdot 10^{-5}$ *M* cobalt (Table II), indicating that the oxidized fraction of extractable cobalt was larger in the former case than in the latter. Cobalt extracted from alkaline solutions showed the typical back-extraction behavior of the cobalt(III) complex.

Distribution of cobalt(II)

The distribution ratio of cobalt(II), D_{Co}, is shown as a function of pH in Fig. 3.

In the case of $7.20 \cdot 10^{-5}$ *M* cobalt, the $\mathrm{pH}_{1/2}$ values were 2.72, 3.10 (not shown in Fig. 3), and 3.55 for 0.2, 0.1 and 0.05 *M* oxine, respectively. The distribution ratio decreased with increasing pH above 5.5, suggesting that an anionic cobalt(II) oxine complex is formed. The $\mathrm{pH}_{1/2}$ values for 0.1 and 0.01 *M* oxine were given by STARÝ to be 3.21 and 5.08[5], respectively. For 0.1 *M* oxine the $\mathrm{pH}_{1/2}$ value determined by STARÝ is somewhat larger than that determined in the present work.

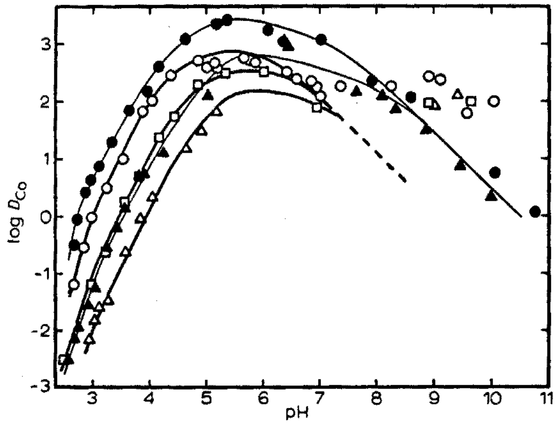


Fig. 3. Distribution curve of cobalt (II). Initial concentration of cobalt: solid symbols, $7.20 \cdot 10^{-5}$ *M*; open symbols, $2.0 \cdot 10^{-7}$ *M*. Initial concentration of HOx: (○, ●) 0.2 *M*; (□, ■) 0.1 *M*, (△, ▲) 0.05 *M*.

The enhancement of the distribution ratio by addition of oxine is remarkable in the acidic region, but it becomes smaller above pH 5–6 and is negligible above pH 8.

In the case of $2.0 \cdot 10^{-7}$ *M* cobalt, the $\mathrm{pH}_{1/2}$ values were 3.02, 3.47 and 3.87 for 0.2, 0.1, and 0.05 *M* oxine, respectively, which are larger than those in the case of $7.20 \cdot 10^{-5}$ *M* cobalt. The distribution ratio does not decrease in the alkaline region for $2.0 \cdot 10^{-7}$ *M* cobalt, because of oxidation of cobalt(II) to cobalt(III) complex on extraction as shown by Table II. However, the effect of oxidation seems to be practically negligible as far as pH 7, for the distribution curves for $2.0 \cdot 10^{-7}$ *M* cobalt are practically parallel to those for $7.20 \cdot 10^{-5}$ *M*.

The increase in the distribution ratio for increase in the initial concentration of cobalt from $2.0 \cdot 10^{-7}$ to $7.20 \cdot 10^{-5}$ *M* indicates that the extractable cobalt(II) complexes are polymerizing in the latter case. Preliminary experiments showed that in the alkaline region $\Delta \log D_{Co}/\Delta \log [Co]_i$ for initial concentrations of cobalt, $[Co]_i$, of $7.20 \cdot 10^{-6}$ *M* and $7.20 \cdot 10^{-5}$ *M*, was close to 1, suggesting the existence of an extractable dimerized cobalt(II) complex.

Comparison of Figs. 1 and 3 indicates that the absorbance of cobalt(II) complexes in the organic phase remains a lower constant value in the low pH range (*e.g.* pH 3.2–5.5 for 0.2 *M* oxine) where the distribution ratio of cobalt increases with increasing pH, while it increases where the distribution ratio decreases (pH 5.5–9.5).

It can be seen from Fig. 3 that $\Delta \log D_{Co}/\Delta \log [HOx]_i$ is close to 3 at pH 3 for either concentration of cobalt, where $[HOx]_i$ is the initial concentration of oxine in the organic phase. This suggests that cobalt(II) cannot be extracted as a simple oxine chelate such as $CoOx_2$, and the predominant complex in the organic phase is more likely to be $CoOx_2HOx$.

Since the distribution ratio was practically independent of the concentration of cobalt below $7.20 \cdot 10^{-6}$ *M* within experimental error, it was assumed that only mononuclear complexes exist in the distribution system for $2.0 \cdot 10^{-7}$ *M* cobalt. The species present in the aqueous phase are Co^{2+}, $CoOx^+$, $CoOx_2$, and $CoOx_3^-$. The stability constants of these cobalt(II) oxine complexes are defined as:

$$\beta_1 = \frac{[CoOx^+]}{[Co^{2+}]\,[Ox^-]},\ K_1 = \frac{[CoOx^+]}{[Co^{2+}]\,[Ox^-]} \tag{1}$$

$$\beta_2 = \frac{[CoOx_2]}{[Co^{2+}]\,[Ox^-]^2},\ K_2 = \frac{[CoOx_2]}{[CoOx^+]\,[Ox^-]} \tag{2}$$

$$\beta_3 = \frac{[CoOx_3^-]}{[Co^{2+}]\,[Ox^-]^3},\ K_3 = \frac{[CoOx_3^-]}{[CoOx_2]\,[Ox^-]} \tag{3}$$

The extraction process of cobalt(II) was assumed to be as follows. When the neutral cobalt(II) oxine complex, $CoOx_2$, is formed in the aqueous phase, the chloroform takes it up, and the complex combines with oxine in the organic phase to form a complex, $CoOx_2HOx$.

The stability constant of the complex, $CoOx_2HOx$, in the organic phase is defined as:

$$K = \frac{[CoOx_2HOx]_o}{[CoOx_2]_o\,[HOx]_o} \tag{4}$$

where the subscript "o" denotes the organic phase.

The distribution coefficient of $CoOx_2$, $D_{Co}{}^0$, is defined as:

$$D_{Co}{}^0 = \frac{[CoOx_2]_o}{[CoOx_2]} \tag{5}$$

The distribution ratio of cobalt(II) is then given by:

$$D_{\mathrm{Co}} = \frac{[\mathrm{CoOx_2HOx}]_o}{[\mathrm{Co^{2+}}]+[\mathrm{CoOx^+}]+[\mathrm{CoOx_2}]+[\mathrm{CoOx_3^-}]} \tag{6}$$

In eqn.(6) it is assumed that the complex in the organic phase has the composition of $\mathrm{CoOx_2HOx}$ in both the alkaline and acidic regions, though the absorbance spectra studies showed that the complexes are not the same. The difference in the spectra may be due to differences in the extent of polymerization of the complex in the organic phase; if this is the case, the difference in spectra can be ignored for $2.0 \cdot 10^{-7}$ *M* cobalt.

Substitution of the appropriate equilibrium expressions in eqn.(6) gives:

$$D_{\mathrm{Co}} = \frac{D_{\mathrm{Co}}{}^0 K\beta_2[\mathrm{Ox^-}]^2\,[\mathrm{HOx}]_o}{1+\beta_1[\mathrm{Ox^-}]+\beta_2[\mathrm{Ox^-}]^2+\beta_3[\mathrm{Ox^-}]^3} \tag{7}$$

or

$$\log D_{\mathrm{Co}} - \log[\mathrm{HOx}]_o = \log D_{\mathrm{Co}}{}^0\,K\beta_2 - 2\mathrm{pOx} - \log(1+\beta_1[\mathrm{Ox^-}]+\beta_2[\mathrm{Ox^-}]^2+\beta_3[\mathrm{Ox^-}]^3) \tag{8}$$

According to eqn. (8) a plot of $\log D_{\mathrm{Co}} - \log[\mathrm{HOx}]_o$ against pOx should give a single curve independent of the initial concentration of oxine. The validity of eqn. (8) in the description of the extraction of cobalt(II) with oxine may be seen from Fig. 4, for which pOx was calculated as in the previous work[6] and $\log[\mathrm{HOx}]_o$ was calculated by eqn. (9).

$$\log[\mathrm{HOx}]_o = \log[\mathrm{HOx}]_i - \log\left(1+\frac{[\mathrm{H^+}]}{K_{\mathrm{I}}D_{\mathrm{R}}{}^0}+\frac{1}{D_{\mathrm{R}}{}^0}+\frac{K_{\mathrm{II}}}{D_{\mathrm{R}}{}^0[\mathrm{H^+}]}\right) \tag{9}$$

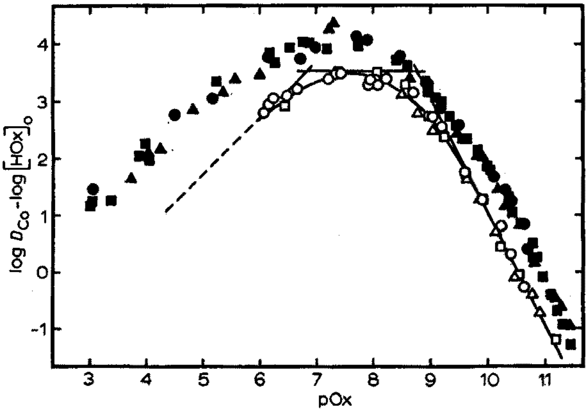


Fig. 4. A plot of $\log D_{\mathrm{Co}} - \log[\mathrm{HOx}]_o$ *vs.* pOx. For symbols, see Fig. 3. Normalized curves in the position of best fit. The straight lines are the asymptotes.

where K_{I} and K_{II} are the acid dissociation constants of oxinium ion and oxine, respectively, and $D_{\mathrm{R}}{}^0$ the distribution coefficient of oxine. The value $\mathrm{p}K_{\mathrm{I}} = 5.14$, $\mathrm{p}K_{\mathrm{II}} = 9.74$, and $\log D_{\mathrm{R}}{}^0 = 2.64$ were used for the calculation[6].

The experimental points for three concentrations of oxine fall on a single curve above pOx 6, but those below pOx 6 cannot be treated similarly, for the extracted cobalt is mainly present as the cobalt(III) complex. In the lower pH range or the higher pOx range where Co^{2+} predominates in the aqueous phase, eqn. (8) may be simplified to:

$$\log D_{Co} - \log[HOx]_o = \log D_{Co}{}^0 K\beta_2 - 2pOx \tag{10}$$

Thus, a plot of $\log D_{Co} - \log[HOx]_o$ against pOx should give a straight line with limiting slope -2 as shown in Fig. 4. The plot in Fig. 4 can also be explained by eqn. (8) through the whole pOx region studied.

For reference the experimental points for $7.20 \cdot 10^{-5}$ *M* cobalt are also plotted in Fig. 4. They seem also to fall on another single curve. The difference in the plots for two concentrations of cobalt is larger in the low pOx range than in the high pOx range, suggesting that polymerization or dimerization of the extractable cobalt(II) oxine complexes is more prominent in the alkaline than in the acidic region.

From Fig. 4 the values of the equilibrium constants of complex formation and extraction were determined by a curve fitting method[7] assuming that the distribution ratio of cobalt(II) is represented by eqn. (8). In the higher pOx range of the maximum of $\log D_{Co} - \log[HOx]_o$, the experimental points were compared to the normalized curves:

$$Y = \log(1 + pv + v^2), \quad X = \log v \tag{11}$$

where p is a parameter and v is an auxiliary variable:

$$p = \frac{\beta_1}{\sqrt{\beta_2}}, \quad v = \frac{1}{\sqrt{\beta_2}[Ox^-]} \tag{12}$$

In the lower pOx range the experimental points were compared to the normalized curve:

$$Y = \log(1 + u), \quad X = \log u \tag{13}$$

where u is an auxiliary variable:

$$u = \frac{\beta_3 [Ox^-]}{\beta_2} \tag{14}$$

The normalized curves, $Y(X)$, and the asymptotes for $2.0 \cdot 10^{-7}$ *M* cobalt are given in Fig. 4. The curve for $p = 2$ fits the experimental data in the higher pOx region. From the position of the normalized curves at the best fit, the following equilibrium constants were determined

$\log\beta_1 = 9.06$, $\log K_1 = 9.06$

$\log\beta_2 = 17.52$, $\log K_2 = 8.46$

$\log\beta_3 = 24.35$, $\log K_3 = 6.83$

$\log D_{Co}{}^0 K = 3.53$

The first and second stepwise stability constants determined in the present work may be compared with those given by ALBERT[8] ($\log K_1 = 9.1$ and $\log K_2 = 8.1$ at ionic strength of 0.01 at 20°) and JOHNSTONE AND FREISER[9] ($\log K_1 = 10.55$ and $\log K_2 = 9.11$ in 50% (v/v) aqueous dioxane).

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SUMMARY

Absorption spectra of cobalt–oxine complexes extracted into chloroform indicate that two cobalt(II) and one cobalt(III) complexes can be extracted depending on pH and the initial concentrations of oxine in the organic phase or cobalt(II) ion in the aqueous phase. The oxidation state of cobalt in the complexes was determined by treatment of organic extracts with an 0.001 *M* EDTA solution at pH 4–5; cobalt(II) complexes were back-extracted, and the cobalt(III) complex was not. The equilibrium distribution ratios of cobalt(II) between aqueous perchlorate solutions and oxine solutions in chloroform were determined at 20°. A plot of $\log D_{Co} - \log[HOx]_o$ *vs.* pOx gave a single curve for different concentrations of oxine; it was concluded that cobalt(II) is extracted as $CoOx_2HOx$.

RÉSUMÉ

Des spectres d'absorption des complexes cobalt–oxine extraits dans le chloroforme indiquent que deux complexes de cobalt(II) et un de cobalt(III) peuvent être extraits, suivant le pH et les concentrations initiales de l'oxine dans la phase organique ou du cobalt(II) dans la phase aqueuse. Les degrés d'oxydation du cobalt dans ces complexes peuvent également être déterminés en traitant les extraits organiques par une solution d'EDTA 0.001 *M* à pH 4–5: les complexes du cobalt(II) sont extraits en retour contrairement à celui du cobalt(III). On a déterminé les constantes d'équilibre du cobalt(II) entre solutions aqueuses de perchlorate et solutions d'oxine dans le chloroform.

ZUSAMMENFASSUNG

Die Absorptionsspektren von mit Chloroform extrahierten Kobalt–Oxin-Komplexen zeigen, dass je nach pH-Wert und Anfangskonzentration des Oxins in der organischen Phase oder der Kobalt(II)-Ionen in der wässrigen Phase zwei Kobalt(II)-Komplexe und ein Kobalt(III)-Komplex extrahiert werden können. Die Oxidationsstufe des Kobalts in den Komplexen wurde durch Behandlung der organischen Extrakte mit 0.001 *M* EDTA-Lösung bei pH 4–5 ermittelt; im Gegensatz zum Kobalt(III)-Komplex wurden die Kobalt(II)-Komplexe zurückextrahiert. Die Gleichgewichtsverteilungsverhältnisse von Kobalt(II) zwischen wässrigen Perchlorat-Lösungen und Oxin-Lösungen in Chloroform wurden bei 20° ermittelt. Eine Auftragung von $\log D_{Co} - \log[HOx]_o$ gegen pOx ergab eine einfache Kurve für verschiedene Oxinkonzentrationen; es wird angenommen, dass Kobalt(II) als $CoOx_2HOx$ extrahiert wird.

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THE STABILITY CONSTANTS OF SOME METAL CHELATES OF TRIETHYLENETETRAMINEHEXAACETIC ACID (TTHA)

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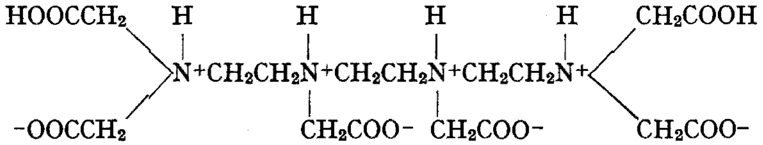
Triethylenetetraminehexaacetic acid, TTHA, was introduced by Frost[1] and has been used for analytical purposes by many authors, particularly by Pribil (see references listed in ref. 20). It has the following structure:



The compound has ten coordinating centers and forms binuclear complexes with several metal ions. The acid can also be expected to form protonated metal complexes. It forms particularly stable complexes with metal ions of high charge (3+ and 4+) and high coordination number.

Stability constants of various metal–TTHA complexes have been reported by a number of authors[2–11], who based their calculations predominantly on pH measurements. As protons are liberated when metal ions replace hydrogen ions in the ligand, the concentration of the ligand not bound to metal ions can be determined from the change in pH. The method is appropriate in cases where a metal ion coordinates with one or several ligand molecules and was successfully used by Bjerrum as early as in 1941 for the determination of the stepwise stability constants of metal ammine complexes[12].

If polynuclear complexes are formed, methods based on the measurement of the free metal ion concentration are very useful. The free metal ion concentration can be determined potentiometrically—with metal electrodes or redox systems—or polarographically. Modern ion-specific electrodes seem suitable for the determination of the stability constants of polynuclear complexes. This pM method is also very useful when very stable metal complexes are formed, *i.e.* when the protons in the ligand are so completely replaced by the metal ion that the pH titration curve resembles the neutralization curve of a strong acid; in such cases pH measurements cannot yield accurate values of stability constants.

EXPERIMENTAL

Schmid and Reilley[13,14] introduced the mercury electrode which permits simple and rapid determination of stability constants of 1:1 complexes. Several applications of this method have been reported in the literature[15,16]. In this work, potentials were measured with a J-type mercury electrode. The Nernst equation for the mercury electrode at 25° can be written as follows:

$$E_{\mathrm{Hg}} = E^0_{\mathrm{Hg}} + 29.6 \log [\mathrm{Hg}^{2+}] \qquad (1)$$

The E's denote potentials and $[\mathrm{Hg}^{2+}]$ the molar concentration of the mercury(II) ion. The potentials were measured against a saturated calomel electrode ($E_{\mathrm{cal}} = 244.1$ mV). $E^0_{\mathrm{Hg}} = E^0_{\mathrm{cell}} + E_{\mathrm{cal}}$ was found experimentally to be 838 mV at various pH values and in the presence of varying amounts of mercury(II) nitrate. E_{cell} is the measured EMF of the cell. The reduction of mercury(II) at the metallic mercury electrode was taken into account in the calculation of E^0_{Hg} by applying a correction determined by the equilibrium $[\mathrm{Hg}_2^{2+}]/[\mathrm{Hg}^{2+}] = 85$.

At pH values above 3.5, the formation of hydroxo complexes of mercury(II) begins to predominate over the reduction to mercury(I). At these pH values the measurements with the mercury electrode were usually made after standing periods of 24 h.

STRAFELDA[17] titrated iron(III), copper(II) and thallium(III) ions complexi-metrically by measuring redox potentials with a platinum electrode. The present author used the redox system Fe(III)/Fe(II) in the determination of stability constants. The potential of the redox system is defined by

$$E = E^0 + 59.2 \log \frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}]} \qquad (2)$$

In sufficiently acid solutions (pH $< ca.$ 3) no complexation of iron(II) occurs, *i.e.* $[\mathrm{Fe}^{2+}]$ is known. E^0 was found experimentally to be 751 mV. A saturated calomel electrode was used as reference electrode.

The potentiometric pH titrations were made with a Metrohm Potentiograph E 336 pH meter and a combined glass–calomel electrode of the type Radiometer EA 120 X. The pH meter was calibrated with three buffer solutions. The solutions titrated usually contained metal and ligand in the molar ratio of 1:1 or 2:1 although a few titrations were performed in the presence of a greater excess of metal ions.

All measurements were made at 25° in an inert atmosphere (N_2). The ionic strength was adjusted to 0.1 by adding potassium nitrate. When activities were converted into concentrations, a modified form of Kjelland's table was used[18]. The value $10^{-14.00}$ (at 25°) was used for the ionic product of water.

The following logarithmic step stability constants for acid forms of TTHA reported by BOHIGIAN AND MARTELL[2] were used: 10.19, 9.40, 6.16, 4.16, 2.95, 2.42.

SYMBOLS AND CONCEPTS USED IN THE CALCULATIONS

The equilibrium constants of different mono- and binuclear chelates are defined by the following expressions (M = metal; L = ligand):

$$\mathrm{M} + \mathrm{L} = \mathrm{ML} \qquad K_{\mathrm{ML}} = \frac{[\mathrm{ML}]}{[\mathrm{M}]\,[\mathrm{L}]} \qquad (3)$$

$$\mathrm{ML} + \mathrm{H} = \mathrm{MHL} \qquad K^{\mathrm{H}}_{\mathrm{MHL}} = \frac{[\mathrm{MHL}]}{[\mathrm{ML}]\,[\mathrm{H}]} \qquad (4)$$

$$\mathrm{MHL+H=MH_2L} \qquad K^{\mathrm{H}}_{\mathrm{MH_2L}} = \frac{[\mathrm{MH_2L}]}{[\mathrm{MHL}]\,[\mathrm{H}]} \tag{5}$$

$$\mathrm{ML+M=M_2L} \qquad K^{\mathrm{M}}_{\mathrm{M_2L}} = \frac{[\mathrm{M_2L}]}{[\mathrm{ML}]\,[\mathrm{M}]} \tag{6}$$

$$\mathrm{2M+L=M_2L} \qquad \beta_{\mathrm{M_2L}} = \frac{[\mathrm{M_2L}]}{[\mathrm{M}]^2\,[\mathrm{L}]} \tag{7}$$

$$\mathrm{M_2L+H=M_2HL} \qquad K^{\mathrm{H}}_{\mathrm{M_2HL}} = \frac{[\mathrm{M_2HL}]}{[\mathrm{M_2L}]\,[\mathrm{H}]} \tag{8}$$

$$\mathrm{M_2HL+H=M_2H_2L} \qquad K^{\mathrm{H}}_{\mathrm{M_2H_2L}} = \frac{[\mathrm{M_2H_2L}]}{[\mathrm{M_2HL}]\,[\mathrm{H}]} \tag{9}$$

$$\mathrm{M_2L+2OH=M_2(OH)_2L} \qquad K^{\mathrm{2OH}}_{\mathrm{M_2(OH)_2L}} = \frac{[\mathrm{M_2(OH)_2L}]}{[\mathrm{M_2L}]\,[\mathrm{OH}]^2} \tag{10}$$

The upper index appended to a constant indicates the released species (component). Ionic charges are omitted for the sake of simplicity.

The alpha coefficients and the conditional constants have their usual meanings as defined by RINGBOM[19]. The primed symbol of a species thus denotes the sum of the concentrations of the species and all of its side reaction products. For the side reactions of a ligand with protons, we have the expression

$$[\mathrm{L'}]=[\mathrm{L}]+[\mathrm{HL}]+[\mathrm{H_2L}]+\ldots+[\mathrm{H}_n\mathrm{L}] \tag{11}$$

The coefficient $\alpha_{\mathrm{L(H)}}$ is defined by the equation

$$\alpha_{\mathrm{L(H)}} = \frac{[\mathrm{L'}]}{[\mathrm{L}]} \tag{12}$$

or

$$\alpha_{\mathrm{L(H)}} = 1 + \sum_{n=1}^{n} [\mathrm{H}]^n \beta_n \tag{13}$$

where the β symbols denote the cumulative stability constants of the proton complexes of the ligand. Similar expressions are valid for other α-coefficients.

The conditional constant is defined by the expression

$$K^{\mathrm{M',L'}}_{\mathrm{(ML)'}} = \frac{[\mathrm{(ML)'}]}{[\mathrm{M'}]\,[\mathrm{L'}]} \tag{14}$$

or

$$K^{\mathrm{M',L'}}_{\mathrm{(ML)'}} = \frac{\alpha_{\mathrm{ML}}}{\alpha_{\mathrm{M}}\,\alpha_{\mathrm{L}}} K_{\mathrm{ML}} \tag{15}$$

The latter expression gives the relationship between the stability constant and the conditional constant. The subscript and the superscripts appended to a constant are primed if the species in question is involved in one or more side reactions.

Also the following symbols are used:

C_L = total concentration of ligand,
C_M = total concentration of metal ion,
T_{OH} = total concentration of added base,
$T_H = 6C_L - T_{OH}$ = total concentration of free or bound hydrogen ions.

DETERMINATION OF STABILITY CONSTANTS BY pM MEASUREMENTS

The determination of stability constants for 1:1 complexes is relatively simple. When polynuclear complexes are also formed, the evaluation is more complicated. The results are more reliable when several methods are combined.

When a ligand forms binuclear as well as mononuclear complexes, the following equation is approximately valid for 1:1 metal–ligand mixtures:

$$[M]^2 = \frac{1}{K^M_{ML}\, K^M_{M_2L}} = \frac{1}{\beta_{M_2L}} \tag{16}$$

This equation is analogous to the well-known pH equation for the titration of a dibasic acid to the first equivalence point. Necessary conditions for its validity (*cf.* ref. 18, p. 167) are that

$$\alpha_{M(ML)} \gg \alpha_{M(OH,A)}$$

which implies that $\alpha_{M(ML)} \gg 1$. A is some interfering ligand present.

The constant β_{M_2L} can be calculated by substituting potentiometrically measured [M] values in eqn. (16). However, when side reactions of L and M_2L with H (or OH) also occur, the appropriate conditional constants must be used and eqn. (16) is transformed into

$$\beta_{(M_2L)'} = \beta_{M_2L} - \alpha_{M_2L(H)} = \frac{\alpha_{L(H)}}{[M]^2} \tag{17}$$

When the acidity constants of the ligand are known, $\alpha_{L(H)}$ can be easily calculated by means of eqn. (13). Consequently, the cumulative constant, $\beta_{(M_2L)'}$, can be computed from eqn. (17). If the obtained values vary with pH, the formation of acid (or basic) binuclear complexes is probable, *i.e.* $\alpha_{M_2L(H)}$ exceeds unity. Estimates of the values of the constants $K_{M_2H_mL}$ can be obtained from the shift of $\beta_{(M_2L)'}$ with pH, but a more exact evaluation can be based on values from a 2:1 pH curve, *i.e.* the curve obtained when a solution containing metal and ligand in the molar ratio of 2:1 is neutralized (p. 481).

Values of β_{Hg_2L} were evaluated from data recorded with a mercury electrode and values of β_{Fe_2L} from data recorded using the Fe(III)/Fe(II) system.

For the evaluation of K_{ML} for mercury(II) and iron(III), the free metal ion concentration is determined in the presence of an excess of ligand. K_{ML} is calculated from the equation

$$K_{ML} = \frac{[(ML)']\,\alpha_{L(H)}}{[L']\cdot[M]\cdot\alpha_{ML(H)}} \tag{18}$$

by taking

$$[(ML)'] = C_M$$

$$[L'] = C_L - C_M$$

K_{MH_mL}, and hence $\alpha_{ML(H)}$, was determined from the 1:1 pH titration curve (p. 481).

When β_{M_2L} and K_{ML} are known, $K^{M}_{M_2L}$ is immediately obtained. $K^{Fe}_{Fe_2L}$ can be determined from potentiometric data recorded with the redox system Fe(III)/Fe(II) for solutions containing iron(III) and ligand in the molar ratio of 2:1.

The mercury electrode and the redox electrode Fe(III)/Fe(II) can also be used to determine stability constants of complexes of other metals. In these determinations the molar ratios $C_{Hg(II)}:C_{TTHA}$ and $C_{Fe(III)}:C_{TTHA}$ are set equal to 1:1. In the presence of another metal ion N, the coefficient $\alpha_{L(H)}$ in eqn. (17) is replaced by $\alpha_{L(N)}$. This is permissible if the experiments are not done at a very low pH, where $\alpha_{L(H)}$ predominates. Under these conditions the following equation is valid (M = Hg(II) or Fe(III)):

$$\beta_{(M_2L)'} = \alpha_{L(N)}/[M]^2 \tag{19}$$

where

$$\alpha_{L(N)} = 1 + [N]K_{(NL)'} + [N]^2\beta_{(N_2L)'} \tag{20}$$

Usually the excess of N was so great that the free metal ion concentration [N] could be replaced by C_N in eqn. (20). If N forms stable binuclear complexes with the ligand, the second term in the above equation predominates.

It follows that $K_{(NL)'}$ and $\beta_{(N_2L)'}$ can be calculated.

In some cases iterative calculations were made for a more accurate evaluation of the concentration of free N ions, $K_{(NL)'}$ or $\beta_{(N_2L)'}$ and a few more equations were introduced.

TABLE I

THE DETERMINATION OF β_{Hg_2L} FROM DATA OBTAINED WITH A MERCURY ELECTRODE (EQNS. (16) AND (17))

($C_{Hg(II)} = C_{TTHA} = 9.60 \cdot 10^{-4}$ *M*. pH was adjusted with NaOH. The stability constants $K^{H}_{Hg_2HL} = 10^{3.6}$ and $K^{H}_{Hg_2H_2L} = 10^{2.7}$ were used)

pH	E_{cell}	*pHg*$^{2+}$	*log* $\alpha_{L(H)}$	*log* $\beta_{(Hg_2L)'}$	*log* β_{Hg_2L}
2.50	296.0	10.00	20.70	40.70	39.18
2.93	276.0	10.72	18.75	40.19	39.31
3.32	256.0	11.42	16.75	39.60	39.22
3.60	243.0	11.76	15.70	39.22	38.87
3.97	227.0	12.38	14.30	39.06	38.89
Logarithm of arithmetic mean					39.13

Table I presents data from experiments for the determination of $\beta^{H}_{Hg_2L}$. In the determination of the cumulative constant with the mercury electrode, a pH dependence was observed; the value of the constant increased at low pH values (Table I, fifth column) owing to the formation of acid binuclear complexes of the type M_2H_mL. From 2:1 pH titration data presented later (p. 481), the constants $K^{H}_{Hg_2HL} = 10^{3.6}$ and $K^{H}_{Hg_2H_2L} = 10^{2.7}$ were determined. Several determinations at various pH values yielded the average value $\beta_{Hg_2L} = 10^{39.1}$.

TABLE II

THE DETERMINATION OF K_{HgL} FROM DATA OBTAINED WITH A MERCURY ELECTRODE

(The stability constants $K^{H}_{HgHL} = 10^{6.3}$ and $K^{H}_{HgH_2L} = 10^{3.6}$ were used in the calculation of K_{HgL})

pH	$-\log C_{Hg(II)}$	$-\log (C_L - C_{Hg(II)})$	E_{cell}	pHg^{2+}	$\log \alpha_{L(H)}$	$\log \alpha_{HgL(H)}$	$\log K_{HgL}$
3.05	3.02	3.62	237.0	12.06	18.02	3.95	26.73
3.52	3.02	3.62	196.0	13.44	16.00	3.15	26.89
3.98	3.02	3.62	168.0	14.39	14.08	2.50	26.57
4.53	3.02	3.62	137.0	15.43	12.32	1.82	26.53
5.04	3.02	3.62	101.0	16.64	10.70	1.24	26.70
2.50	3.02	3.32	267.0	10.97	20.70	4.99	26.98
3.00	4.05	4.96	239.0	11.95	18.25	4.05	27.06
3.02	4.05	4.49	220.0	12.63	18.16	4.07	27.16
3.73	4.05	4.48	178.0	14.05	15.10	2.82	26.76
3.73	4.05	4.66	186.0	13.78	15.10	2.82	26.67
3.73	4.05	4.96	197.5	13.40	15.10	2.82	26.59
4.10	4.05	4.69	167.5	14.40	13.90	2.31	26.63
Logarithm of arithmetic mean							26.82

TABLE III

THE DETERMINATION OF β_{Co_2L} FROM DATA OBTAINED WITH A MERCURY ELECTRODE (EQN. (19))

($C_{Hg(II)} = C_{TTHA} = 5.00 \cdot 10^{-4}$ *M*. $C_{Co(II)} = 2.42 \cdot 10^{-3}$ *M*. The stability constants $K^{H}_{Co_2HL} = 10^{3.0}$ and $K^{H}_{Co_2H_2L} = 10^{2.6}$ were used in the calculations)

pH	E_{cell}	pHg^{2+}	$\log \alpha_{L(Co)}$	$\log \beta_{(Co_2L)'}$	$\log \beta_{Co_2L}$
2.42	353.0	8.17	24.41	29.87	28.77
2.61	354.5	8.10	24.26	29.70	28.87
2.83	354.0	8.11	23.95	29.39	28.78
3.06	356.5	8.04	23.81	29.25	28.85
3.48	358.5	7.95	23.61	29.05	28.87
3.85	358.5	7.95	23.41	28.81	28.75
3.98	359.5	7.92	23.42	28.86	28.80
4.90	361.5	7.85	23.42	28.86	28.85
Logarithm of arithmetic mean					28.82

The determination of K_{HgL}, which is based on eqn. (18), is presented in Table II. In spite of greatly varying experimental conditions, the constancy is satisfactory.

The stability constants of several metal complexes were evaluated by means of eqn. (19) from data determined with the mercury electrode. These measurements were made in the presence of an excess of the metal ion in question. For the transition metals copper(II), cobalt(II), nickel(II), lead(II) and zinc(II), a clear dependence of β_{M_2L} on pH was found, *i.e.* acid binuclear complexes were formed. Therefore, the determined constants for these metal ions have to be corrected by a factor $\alpha_{M_2L(H)}$. If the measurements are made above pH 4, the influence of $\alpha_{M_2L(H)}$ is only slight and β_{M_2L} is obtained directly. As an example, the determination of β_{Co_2L} at various pH values is shown in Table III.

The determination of equilibrium constants utilizing the redox system Fe(III)/Fe(II) follows the principle outlined for the mercury electrode. The stability constants determined by the two methods are given later in Table VI.

DETERMINATION OF STABILITY CONSTANTS BY pH MEASUREMENTS

Potentiometric pH titration data for solutions containing metal ion and ligand in varying ratios were used to determine several stability constants. The equilibrium constants of the magnesium(II) chelates of TTHA were calculated from such pH data. This was also the case for manganese(II), which, however, forms more stable complexes with TTHA than the alkaline earth metals. Stability constants for protonated and hydroxo metal complexes were calculated from 1:1 and 2:1 pH curves. The step stability constants for copper(II), cobalt(II) and nickel(II) and some other metals can be determined from 1:1 pH curves in the pH range 4–7. This presumes that β_{M_2L} is known in each case.

The pH titration curves must be interpreted with caution. For instance, the 1:1 pH curves for copper(II), cobalt(II) and nickel(II) show a marked buffer region when $a=2$–5. This can be interpreted to suggest the formation of stable protonated mononuclear complexes. Another interpretation, which turned out to be correct, was that binuclear complexes predominate in acid solutions when the ratio of metal ion to ligand is 1:1. Ligands released from the chelate are able to bind protons. As an example pH curves for the ligand alone and for the 1:1 and 2:1 copper(II)–TTHA systems are given in Fig. 1.

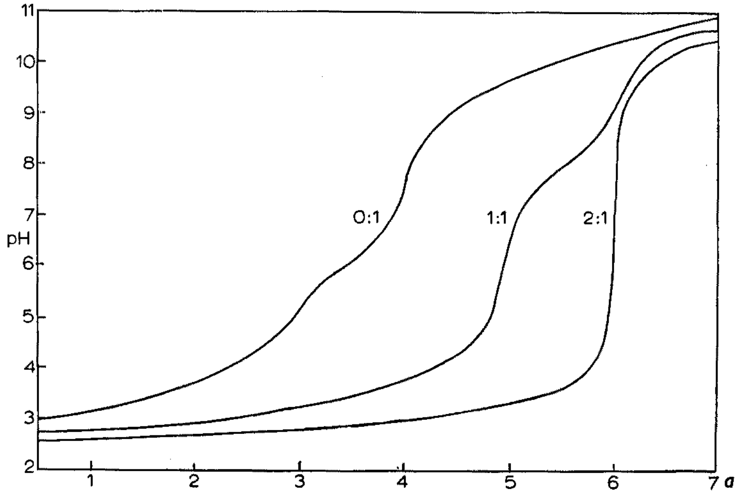


Fig. 1. Potentiometric pH titration curves for a $1.00 \cdot 10^{-3}$ *M* TTHA solution and for $1.00 \cdot 10^{-3}$ *M* TTHA solutions containing copper(II) in 1:1 and 2:1 molar ratios of metal to ligand (0.1 *M* KNO_3, 25°). a= moles of NaOH added per mole of TTHA.

Determination of stability constants of protonated and hydroxo metal–TTHA complexes

K^{H}_{MHL} can easily be calculated from 1:1 pH curves in which exist very marked buffer regions between 5 and 6 moles of added base. The calculation of $K^{H}_{MH_2L}$ for several transition metal complexes from similar data is more difficult, because binuclear complexes predominate also in 1:1 metal–TTHA systems of low pH.

The formation of protonated binuclear complexes by several transition metals leads to a buffer region on the 2:1 pH curve. If these complexes are not considered in the calculation of equilibrium constants from 2:1 pH curves, considerable errors will arise.

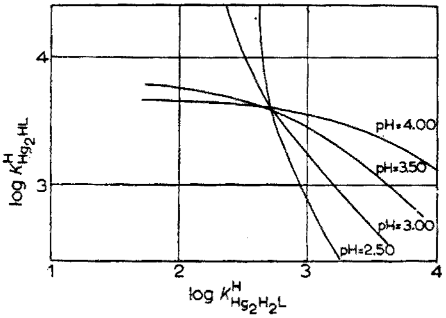


Fig. 2. Graphical determination of $K^{H}_{Hg_2HL}$ and $K^{H}_{Hg_2H_2L}$ using data from titrations of solutions containing metal and ligand in the molar ratio of 2:1.

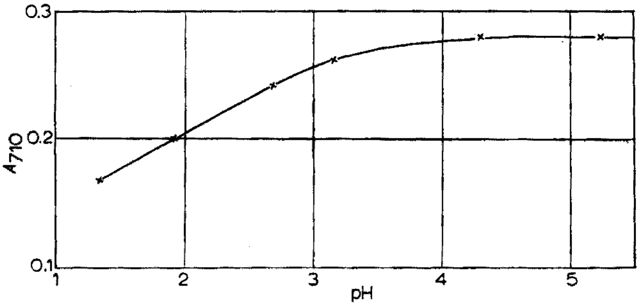


Fig. 3. The absorbance of the 2:1 copper(II)–TTHA system at 710 nm as a function of pH. $C_L = 2.00 \cdot 10^{-3}$ M.

Figure 2 illustrates the graphical determination of $K^{H}_{Hg_2HL}$ and $K^{H}_{Hg_2H_2L}$. By assuming different values for $K^{H}_{M_2HL}$, corresponding values for $K^{H}_{M_2H_2L}$ can be calculated from the equations.

$$T_H = [H] + [M_2HL] + 2[M_2H_2L] \tag{21}$$

$$C_L = [M_2L] + [M_2HL] + [M_2H_2L] \tag{22}$$

When the constants are calculated at several points on the 2:1 pH curve, the intersection point of the resulting curves gives the values of the equilibrium constants. For mercury(II), the values $K^{H}_{Hg_2HL} = 10^{3.6}$ and $K^{H}_{Hg_2H_2L} = 10^{2.7}$ were found.

The existence of protonated binuclear complexes of copper(II) could be verified by spectrophotometry. The absorbance of the binuclear chelates of copper(II) at 710 nm is plotted as a function of pH in Fig. 3. The absorbance is constant at pH values above 4, but begins to decrease at pH values below 4. This clearly indicates that protonated binuclear complexes are formed. The dissociation of the binuclear complex is of no significance at pH values above 2.

The existence of binuclear hydroxo complexes was established for the trivalent metals Fe(III) and Al(III). The equilibrium constants of these chelates can be calculated directly from 2:1 pH curves. Also Hg(II), Er(III) and Nd(III) seem to form binuclear hydroxo complexes, although the given values are somewhat uncertain. For the rare earths sufficient equilibrium data for the metal hydroxo complexes are not known.

Determination of the step stability constants (K^{M}_{ML} and $K^{M}_{M_2L}$) from 1:1 pH curves, when β_{M_2L} is known

When the value of β_{M_2L} for a metal complex has been determined from data obtained with the mercury electrode, with the redox system Fe(III)/Fe(II), or in some other way, the step stability constants can be evaluated from 1:1 pH curves. The following equilibrium was utilized

$$(n-2)\ H+2MHL=M_2L+H_nL$$

Calculations were made for several transition metals using data from the pH range 4–7. The concentrations [(ML)′], [M₂L] and [L′] were determined from 1:1 pH curves. Usually [M] is very low under the conditions in question, but if β_{M_2L} is known, values of [M] at various pH values can be calculated from eqn. (16) or (17).

The following equations are valid:

$$T_H=[H]+\bar{n}[L']+\bar{m}[(ML)'] \tag{23}$$

$$C_L=[L']+[(ML)']+[M_2L] \tag{24}$$

$\bar{n}$ and $\bar{m}$ *i.e.* the average ligand numbers, are defined as follows:

$$\bar{n} = \frac{[H]\beta_{HL}+2[H]^2\beta_{H_2L}+\ldots+6[H]^6\beta_{H_6L}}{1+[H]\beta_{HL}+[H]^2\beta_{H_2L}+\ldots+[H]^6\beta_{H_6L}} \tag{25}$$

$$\bar{m} = \frac{[H]\,K^{H}_{MHL}+2[H]^2K^{2H}_{MH_2L}}{1+[H]\,K^{H}_{MHL}+[H]^2K^{2H}_{MH_2L}} \tag{26}$$

If the pH is not very low and if the value of $K^{M}_{M_2L}$ is not very small, the concentration of free metal ion is very small in 1:1 metal–ligand systems; we have then the approximation $[M_2L]\approx[L']$. Equations (23) and (24) hence contain only two unknown quantities and can be solved.

When [(ML)′], [M₂L], [L′] and [M] are known, K^{M}_{ML} and $K^{M}_{M_2L}$ can be computed. The stepwise constants for Cu(II), Co(II), Ni(II), Pb(II), Zn(II) and Al(III) were cal-

TABLE IV

DETERMINATION OF THE STEPWISE STABILITY CONSTANTS K^{Cu}_{CuL} AND $K^{Cu}_{Cu_2L}$ FROM THE 1:1 pH CURVE

(β_{Cu_2L}, required to calculate pCu, was found to be $10^{32.6}$ from data recorded with the mercury electrode)

pH	*pCu*	C_L	$T_H-[H]$	$[L']=[Cu_2L]$	$[(CuL)']$	*log* K^{Cu}_{CuL}	*log* $K^{Cu}_{Cu_2L}$
4.50	10.09	$9.23\cdot10^{-4}$	$12.60\cdot10^{-4}$	$2.57\cdot10^{-4}$	$4.09\cdot10^{-4}$	19.21	13.39
5.00	10.88	$9.19\cdot10^{-4}$	$11.09\cdot10^{-4}$	$1.79\cdot10^{-4}$	$5.61\cdot10^{-4}$	19.21	13.39
5.50	11.62	$9.17\cdot10^{-4}$	$10.29\cdot10^{-4}$	$1.30\cdot10^{-4}$	$6.57\cdot10^{-4}$	19.23	13.37
6.00	12.31	$9.16\cdot10^{-4}$	$9.89\cdot10^{-4}$	$1.22\cdot10^{-4}$	$6.72\cdot10^{-4}$	19.23	13.37
Logarithm of arithmetic mean						19.22	13.38

TABLE V

DETERMINATION OF $K^{Mn}_{Mn_2L}$ FROM THE 2:1 pH CURVE

pH	C_L	T_H	$\bar{m}$	$[Mn] = [(MnL)']$	$[Mn_2L]$	$\log \alpha_{MnL(H)}$	$\log K^{Mn}_{Mn_2L}$
6.00	$9.42 \cdot 10^{-4}$	$3.16 \cdot 10^{-4}$	1.00	$3.15 \cdot 10^{-4}$	$6.27 \cdot 10^{-4}$	2.74	6.54
5.56	$9.44 \cdot 10^{-4}$	$4.66 \cdot 10^{-4}$	1.00	$4.63 \cdot 10^{-4}$	$4.81 \cdot 10^{-4}$	3.18	6.54
5.00	$9.49 \cdot 10^{-4}$	$6.96 \cdot 10^{-4}$	1.02	$6.71 \cdot 10^{-4}$	$2.77 \cdot 10^{-4}$	3.75	6.54
4.73	$9.51 \cdot 10^{-4}$	$8.20 \cdot 10^{-4}$	1.04	$7.67 \cdot 10^{-4}$	$1.83 \cdot 10^{-4}$	4.03	6.53
Logarithm of arithmetic mean							6.54

TABLE VI

LOGARITHMIC STABILITY CONSTANTS FOR METAL CHELATES OF TTHA AT 25° AND $\mu = 0.1$ (KNO_3)

Metal	*Log*								*Method*[a]
ion	K_{ML}	K^H_{MHL}	$K^H_{MH_2L}$	β_{M_2L}	$K^M_{M_2L}$	$K^H_{M_2HL}$	$K^H_{M_2H_2L}$	$K^{2OH}_{M_2(OH)_2L}$	
Al^{3+}				28.6					Hg
	19.7	5.85						15.9	gl
				28.9					Redox
Cd^{2+}	18.65								Hg
		8.32	3.2		8.2				gl
Co^{2+}				28.8					Hg
	17.1	8.12			11.7	3.0	2.6		gl
Cu^{2+}				32.6					Hg
	19.2	8.00			13.4	3.0	2.7		gl
Fe^{3+}	26.8			40.5	13.7				Redox
		7.60	2.75					21.0	gl
Hg^{2+}	26.8			39.1	12.3				Hg
		6.3	3.6			3.6	2.7	12.8	gl
Mg^{2+}	8.10	9.30		5.95					gl
	8.43								Hg
Mn^{2+}	14.65	8.74	3.45	6.54					gl
	14.30								Hg
La^{3+}		3.30		3.40					gl
	22.22								Hg
	22.30								Redox
Nd^{3+}		3.93		3.93				11.5	gl
	22.82								Hg
	22.82								Redox
Er^{3+}		4.50		3.73				13.0	gl
	23.19								Hg
	23.40								Redox
Ni^{2+}					32.4				Hg
	18.1	8.00		14.3		2.6	2.3		gl
Pb^{2+}					28.1				Hg
	17.1	8.20		11.0		3.0	2.6		gl
Th^{4+}	31.9								Redox
		3.05							gl
Zn^{2+}					28.7				Hg
	16.65	8.15		12.05		3.0	2.6		gl

[a] gl = measurement with the glass electrode.
Hg = measurement with the mercury electrode.
Redox = measurement with the Fe(III)/Fe(II) system.

culated according to these principles. The calculation of the stepwise stability constants for copper(II) from a 1:1 pH curve (Fig. 1) is shown in Table IV.

Determination of $K^{\mathrm{M}}_{\mathrm{M_2L}}$ from 2:1 pH curves

$K^{\mathrm{M}}_{\mathrm{M_2L}}$ was determined from 2:1 pH curves for La(III), Nd(III), Er(III), Mg(II), Mn(II) and Cd(II). These metal ions form relatively weak binuclear complexes with TTHA. The evaluations of $K_{\mathrm{M_2L}}$ were based on the approximate equation

$$T_{\mathrm{H}} = [\mathrm{H}] + \bar{m}[(\mathrm{ML})'] \qquad (27)$$

The binding of protons by the ligand was disregarded because its influence on the final results is negligible at the pH values in question. The existence of protonated binuclear complexes of these metal ions was not detected. As an example, the calculation of $K^{\mathrm{Mn}}_{\mathrm{Mn_2L}}$ is shown in Table V.

All the stability constants determined by different methods are summarized in Table VI.

DISCUSSION

The determination of the stability constants of metal chelates of TTHA proved to be rather complicated. The best results were obtained by combining different methods (the pH method and the pM method). The methods based on potentiometric measurement of free metal ion concentrations were especially useful in studies of the polynuclear complexes.

In some cases it was possible to determine the same equilibrium constant by different methods, which yielded results in good agreement. The pH and pHg methods gave values of $K^{\mathrm{M}}_{\mathrm{ML}}$ for magnesium(II) and manganese(II) chelates of TTHA that agreed within about 0.3 logarithmic units. The equilibrium constants for La(III), Nd(III), Er(III) and Al(III) were also evaluated from redox data. The values were slightly higher than the values based on measurements with the mercury electrode.

The existence of mixed binuclear chelates of type MNL where M and N represent different metal ion species could not be detected. Potentiometric titrations of mixtures of two metal ion species in varying proportions were performed with a mercury electrode, but no inflection points corresponding to the formation of mixed binuclear chelates were obtained.

While this work was in progress, stability constants for a number of metal chelates of TTHA were reported in the literature. In the following, the stability constants determined by different authors are compared with the constants determined in this work, and some comments are given.

Mercury(II)–TTHA chelates

SCHRÖDER[8] reported equilibrium constants for mercury(II) chelates of TTHA determined from pH data. He used dissociation constants for TTHA determined by GRIMES *et al.*[5]. For K_{HgL} he obtained the value $10^{25.27}$ which is lower than our value $10^{26.8}$. SCHRÖDER did not obtain any reproducible and reliable results with the mercury electrode. We found the mercury electrode very useful for the determination of the stability constants of mercury(II) chelates and also chelates of other metals.

The values of $K^{\mathrm{Hg}}_{\mathrm{Hg_2L}}$ differ. In this work the value $K^{\mathrm{Hg}}_{\mathrm{Hg_2L}} = 10^{12.3}$ was obtained with the mercury electrode, whereas SCHRÖDER who determined the constant from a 2:1 pH curve reports a value of $10^{8.4}$. The formation of protonated binuclear complexes, which complicates the determination of the value from pH data, was not taken into consideration. Because the coordination number of mercury(II) is 2 or 4, the formation of protonated binuclear complexes is probable. The formation of trinuclear mercury(II) chelates is also possible but their existence could not be proved.

Iron(III)-TTHA chelates

Stability constants for iron(III) chelates of TTHA were determined by SCHRÖDER[9]. For $K = [Fe_2(OH)_2L][H]^2/([FeL][Fe])$ he obtained $10^{2.9}$. He assumed that the main binuclear product was $Fe_2(OH)_2L$ for the mole ratio 2:1 in solutions containing less than 6 equivalents of added base and that Fe_2L does not exist in measurable quantities. In the present work the value $K^{2OH}_{Fe_2(OH)_2L} = 10^{21.0}$ was obtained. BOHIGIAN AND MARTELL[3] reported $10^{21.4}$ for the same constant. Consequently, Fe_2L predominates at pH values below 3. Also analytical experiments which will be reported in a later paper indicate that the value of the stability constant given by SCHRÖDER for the binuclear complex is too low. In this work, $K^{Fe}_{FeL} = 10^{26.8}$ and $K^{Fe}_{Fe_2L} = 10^{13.7}$ were obtained. SCHRÖDER gives the value $K^{Fe}_{FeL} = 10^{29.4}$. He also reports stability constants for mononuclear hydroxo complexes. However, potentiometric and photometric titration data do not point to the existence of such complexes.

Copper(II)-, nickel(II)- and cobalt(II)-TTHA chelates

The copper(II) chelates of TTHA have been investigated by several authors[2,4,6]. The following values of stability constants have been reported.

TABLE VII

LOGARITHMIC STABILITY CONSTANTS FOR COPPER(II) CHELATES OF TTHA

	Bohigian...	*Klausen...*	*This paper*
log K^{Cu}_{CuL}	20.3	15.4	19.1
log $K^{Cu}_{Cu_2L}$	7.3	9.1	13.5
log β_{Cu_2L}	27.6	24.5	32.6
log K^{H}_{CuHL}	7.96	8.0	8.0
log $K^{H}_{CuH_2L}$	4.05	—	—
log $K^{H}_{CuH_3L}$	2.86	—	—
log $K^{H}_{CuH_4L}$	2.04	—	—
log $K^{H}_{Cu_2HL}$	—	—	3.0
log $K^{H}_{Cu_2H_2L}$	—	—	2.7

The value for β_{Cu_2L} obtained by KLAUSEN and coworkers is apparently too low. It is 2–3 logarithmic units lower than the corresponding constant for DTPA, what is somewhat surprising from the coordination point of view. For the calculation of β_{Cu_2L}, KLAUSEN *et al.* used pH titration data for 1:1 and 1:2 metal–ligand mixtures in the pH range 4.0 to 5.0. β_{Cu_2L} cannot be calculated with any great accuracy because the concentration of free metal ion is very low ($[Cu] < 10^{-10}$ *M*) compared to the concentrations of the other species present under these conditions.

BOHIGIAN AND MARTELL[4] derived an expression for β_{M_2L} (*i.e.* $K^{L}_{M_2L}$), which indicates the presence of only M_2L, M and H_nL in 2:1 metal–ligand systems. They neglected the presence of mononuclear complexes. The assumption that $[M] = 2[H_nL]$ as well as their expression for β_{M_2L} are valid only at very low pH. Furthermore, the formation of protonated binuclear complexes complicates the calculation of β_{M_2L} for copper(II), cobalt(II) and nickel(II) from 2:1 metal–ligand systems at low pH.

In their calculation of 1:1 stability constants, BOHIGIAN AND MARTELL disregarded the formation of binuclear complexes. However, in solutions in which the molar ratio of copper(II) to ligand is 1:1, binuclear complexes predominate at pH values below *ca.* 4. Ligand ions which exert a buffer action are present. When they attempted to account for this buffer region, BOHIGIAN AND MARTELL proposed the existence of protonated mononuclear complexes containing up to four protons.

The above comments explain why some of the values of BOHIGIAN AND MARTELL given in Table VII do not agree well with the values reported in this paper.

BOHIGIAN AND MARTELL determined values of K_{ML} and β_{M_2L} for the nickel and cobalt complexes, which can be compared with the values determined in this work in Table VIII. Since BOHIGIAN AND MARTELL based their calculations on the

TABLE VIII

LOGARITHMIC STABILITY CONSTANTS FOR SOME NICKEL(II) AND COBALT(II) CHELATES OF TTHA

	Bohigian...	*This paper*
K_{NiL}	18.8	18.1
$K^{Ni}_{Ni_2L}$	10.7	14.3
β_{Ni_2L}	29.5	32.4
K_{CoL}	20.6	17.1
$K^{Co}_{Co_2L}$	7.4	11.7
β_{Co_2L}	28.0	28.8

TABLE IX

LOGARITHMIC STABILITY CONSTANTS FOR CADMIUM(II), LEAD(II) AND ZINC(II) CHELATES OF TTHA

	Lund...	*Soucek...*	*This paper*
K_{CdL}	17.6	19.8	18.65
$K^{Cd}_{Cd_2L}$	7.7		8.2
β_{Cd_2L}	25.3		26.85
K^{H}_{CdHL}	8.39		8.32
K_{PbL}	16.8	19.5	17.1
$K^{Pb}_{Pb_2L}$	11.3		11.0
β_{Pb_2L}	28.1		28.1
K^{H}_{PbHL}	8.29		8.20
$K^{H}_{Pb_2HL}$			3.0
$K^{H}_{Pb_2H_2L}$			2.6
K_{ZnL}	16.2	20.1	16.65
$K^{Zn}_{Zn_2L}$	11.7		12.05
β_{Zn_2L}	27.9		28.7
K^{H}_{ZnHL}	7.69		8.15
$K^{H}_{Zn_2HL}$			3.0
$K^{H}_{Zn_2H_2L}$			2.6

same assumptions as when they determined the constants for copper(II) complexes, good agreement can hardly be expected.

Cadmium(II)-, lead(II)- and zinc(II)-TTHA chelates

The stability constants shown in Table IX have been reported for TTHA complexes of cadmium, zinc and lead. LUND[8] calculated his stability constants from pH titration data using a digital computer. The constants computed by LUND are in fairly good agreement with our values. In a short communication, SOUCEK *et al.*[10] reported the stability constants K^{M}_{ML} for some transition metal complexes of TTHA. Apparently, their values are too high.

Magnesium(II)-, lanthanum(III)- and thorium(IV)-TTHA chelates

The stability constants shown in Table X have been reported for these chelates.

BOHIGIAN AND MARTELL[3] report that magnesium(II) and calcium(II) form trinuclear chelates with TTHA. For $K^{Mg}_{Mg_3L}$ they give a value of $10^{5.32}$, which is slightly lower than their value $K^{Mg}_{Mg_2L} = 10^{5.5}$. The present author titrated magnesium(II) to a bimetallic complex with TTHA. This would be impossible if the difference between the two stepwise stability constants were only 0.2 logarithmic units. The existence of trinuclear magnesium(II) chelates thus seems doubtful.

TABLE X

LOGARITHMIC STABILITY CONSTANTS FOR MAGNESIUM(II), LANTHANUM(III) AND THORIUM(IV) CHELATES OF TTHA

	Bohigian...	*Grimes...*	*This paper*
K_{MgL}	8.43	8.47	8.43
$K^{Mg}_{Mg_2L}$	5.5	5.94	5.95
β_{Mg_2L}	13.9	14.41	14.38
$K^{Mg}_{Mg_3L}$	5.32		
K_{MgHL}	9.31	9.35	9.30
K_{MgH_2L}	4.65	3.73	
K_{LaL}	23.1		22.22
K_{La_2L}	3.8		3.4
K_{LaHL}			3.3
K_{ThL}	$\gg 27$		31.9
K_{ThHL}			3.05

The values of the remaining stability constants given by different authors are in good agreement with our values.

The correctness of the values of the constants can be conveniently checked by visual, photometric and potentiometric titrations under various experimental conditions. A large number of such analyses have been performed. Part of the results have been reported elsewhere[20,21]. Good agreement with the expected results was obtained.

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SUMMARY

Stability constants for Al(III), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), La(III), Nd(III), Er(III), Mg(II), Mn(II), Ni(II), Pb(II), Th(IV) and Zn(II) complexes of triethylenetetraminehexaacetic acid (TTHA) have been evaluated from data obtained by pH and pM measurements. The pM method based on measurements with the mercury electrode and the redox system Fe(III)/Fe(II) proved to be very useful when binuclear complexes are formed.

RÉSUMÉ

On a examiné par mesures de pH et pM les constantes de stabilité des complexes de l'acide triéthylènetétraminohexacétique (TTH) avec Al(III), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), La(III), Nd(III), Er(III), Mg(II), Mn(II), Ni(II), Pb(II), Th(IV) et Zn(II). La méthode de pM, basée sur des mesures avec électrode de mercure et le système rédox Fe(III)/Fe(II), se montre très utile lorsque des complexes binucléaires sont formés.

ZUSAMMENFASSUNG

Die Stabilitätskonstanten der Komplexe von Al(III), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), La(III), Nd(III), Er(III), Mg(II), Mn(II), Ni(II), Pb(II), Th(IV) und Zn(II) mit Triäthylentetraminhexaessigsäure (TTHA) sind mit Hilfe von pH- und pM-Messungen ermittelt worden. Die pM-Methode, die auf Messungen mit der Quecksilberelektrode und dem Redoxsystem Fe(III)/Fe(II) beruht, erwies sich als sehr geeignet, wenn zweikernige Komplexe gebildet werden.

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COULOMETRIC PRODUCTION OF SULFHYDRYL REAGENTS

TITRATIONS OF LEAD(II) AND COPPER(II)

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Sulfhydryl compounds offer a wide range of application to analysis, for they have a strong affinity for certain metals and they possess reducing powers in the high pH range. However, their analytical applications are very limited because of their instability toward atmospheric oxidation, limited solubility in water and volatility. Constant-current coulometric generation has made available many unstable reagents[1,2], and has been successfully employed for the production of thioglycollic acid and monothioethylene glycol[3,4]. The generating reagents were the stable soluble mercury(II) complexes. The presence of groups other than the sulfhydryl one was found to limit the extension of the applicability of these reagents. On the basis of the good results previously obtained with other electrode systems[4–6], electrodes such as Ag/AgSPr and Ag/AgSPh, were studied for the production of 1-propanethiol and benzenethiol in the work described here.

EXPERIMENTAL

Materials

All chemicals were reagent-grade (Merck p.a. and Fluka). Twice-distilled water was used in the preparation of solutions. Nitrogen (99.99%), further purified[7], was used for the removal of oxygen.

Apparatus

For coulometric titrations H-shaped cells were used. The electrical apparatus consisted of a constant-current electronic generator (the stability of which is greater than 0.1%), a Leeds and Northrup model K3 potentiometer, a standard 1000-ohm Siemens Resistor, a Sefram Verispot Galvanometer, a Keithly Model 610 B Voltmeter, a 100-ohm Metrohm potentiometer, a photographic recording polarograph, a XY Hewlett Packard Model 2D-2M Recorder, and a Hewlett Packard Model 3300 A function generator in conjunction with an operational amplifier system.

For the production of the two sulfhydryl reagents, silver spiral electrodes with surfaces of about 10 cm^2 were employed. The counter electrode was made of platinum foil. The anodic and cathodic compartments were separated by a sintered glass disk. In the test of coulometric efficiency, the indicator electrodes were platinum wires covered with silver from a silver cyanide solution. In the titrations of lead and copper, the dropping mercury electrode was used for the determinations of the end-points.

Coulometric efficiency

The generating electrodes were prepared with a current of 2 mA for some hours by anodic deposition of a silver mercaptide layer from a methanolic solution containing 0.1 *M* sodium perchlorate and 0.1 *M* thiol. The electrodes were washed with methanol and then with twice-distilled water, and used immediately. The coulometric production of the sulfhydryl compounds was tested with electrolytically generated silver ions[8]. In the high pH range, the test solutions were also 1 *M* in ammonia to prevent interference from silver oxide formation. The end-points were detected by the biamperometric technique; this was possible because of the reversibility of the silver–silver ammine complex system. The potential difference between the indicator electrodes was 100 mV.

The efficiency of production of the layer of silver salt in the preparation of the working electrodes was also tested. The silver spiral was made the anode (current 2 mA) in a methanolic solution of thiol for an arbitrarily long time, and then, after washing, the reduction was carried out to exhaustion (current 2 mA) in 0.1 *M* sodium hydroxide–1 *M* ammonia solution. The sulfhydryl ions were then titrated as previously described.

Lead and copper titrations

Stock solutions of lead and copper were prepared by dissolving lead nitrate and copper nitrate in water, and were standardized by means of sodium oxalate[8] and EDTA[9] solutions, respectively. Small amounts of these stock solutions were introduced into the titration vessel. Titrations were started and the end-points were detected amperometrically[10].

In the first case the potential of the dropping mercury electrode was −850 mV *vs.* S.C.E., and the base electrolyte was 0.01 *M* sodium hydroxide; in the second case, the potential was −900 mV and the base electrolyte was 1 *M* ammonia–0.1 *M* sodium hydroxide.

In order to explain the nature of the titration reaction of copper(II) with the mercaptide, two different experiments were carried out. In the first, a platinum spiral and a silver mercaptide spiral were in turn cathodically polarized in a 0.01 *M* copper(II)–0.1 *M* sodium hydroxide–1 *M* ammonia solution (current 2 mA). Two platinum wire electrodes, with an interposed potential difference of about 100 mV revealed the presence of copper(I) complexes. The second experiment was a titration of copper(II) with a standard solution of 1-propanethiol which had been prepared by generating mercaptide ions in a known volume of 0.1 *M* sodium hydroxide–1 *M* ammonia solution. After each addition of standard solution, complete polarograms were traced.

RESULTS AND DISCUSSIONS

In Table I the results of the coulometric titrations of the electrically generated sulfhydryl compounds are reported. Figure 1 shows a titration curve of 1-propanethiol with silver ions. In the biamperometric titrations, indicator current was observed only after the end-point; this agrees with the irreversibility of the Ag/AgSR electrodes which was found in other experiments.

The constant but very high potentials (about −900 mV *vs.* S.C.E.) necessary

TABLE I

BIAMPEROMETRIC TITRATIONS OF ELECTROLYTICALLY GENERATED 1-PROPANETHIOL AND THIOPHENOL WITH SILVER IONS

(Volume in the cell = 80 ml. Base electrolyte 0.1 M NaOH, 1 M NH_3. i = 2 mA)

Coulombs for production of thiol	*Coulombs for production of Ag^+*	*Error (%)*
1-Propanethiol		
1.800	1.800	0.0
3.600	3.594	−0.2
10.800	10.836	+0.3
Thiophenol		
2.414	2.400	−0.6
4.800	4.800	0.0
10.800	10.779	−0.1

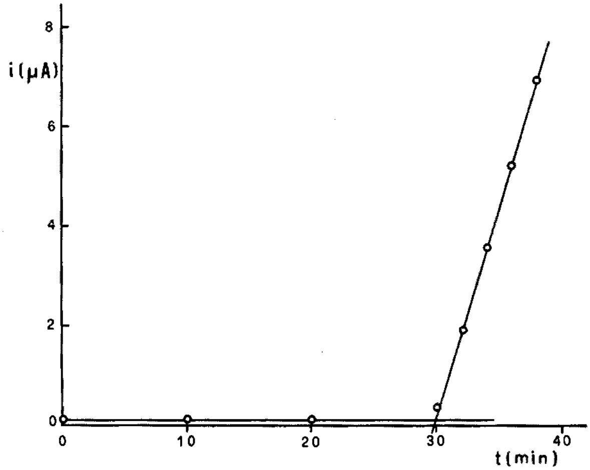

Fig. 1. Biamperometric titration of 1-propanethiol with silver ions. Base electrolyte 0.1 M NaOH–1 M NH_3.

for the reactions:

$$AgSPr + e^- \rightarrow Ag + PrS^-; \quad AgSPh + e^- \rightarrow Ag + PhS^-$$

to occur with a current of about 0.2 mA/cm², enforced a strict limit on the pH range in which the production of sulfhydryl group was the only reduction process. In fact, low results were found even at pH 9. The results of the titrations proved that sulfhydryl groups could be correctly produced by means of the cathodic reactions whether the silver compound used was the 1-propanethiol or thiophenol. In contrast, great differences were found in the preparation of the working electrodes. When a methanolic solution of 1-propanethiol was used, the equivalents of PrS^- found agreed with the coulombs used in the anodic preparation. Of course, the cathodic time was slightly longer than the anodic one to insure complete discharge of the silver mercaptide. In Table II the balances for the coulombs used in the anodic reaction for 1-propanethiol

TABLE II

BALANCES BETWEEN ANODIC COULOMBS AND COULOMBS OF PrS^- FOUND (i = 2 mA)

Coulombs (anodic time)	*Coulombs of RS^- found*	*Error (%)*
2.40	2.44	+1.7
4.20	4.18	−0.5
7.20	6.80	−5.5

TABLE III

AMPEROMETRIC TITRATIONS OF LEAD AND COPPER WITH ELECTROLYTICALLY GENERATED 1-PROPANETHIOL

(Volume in the cell = 80 ml. i = 2 mA)

Pb taken[a] *(μeq)*	*Pb found (μeq)*	*Error (%)*	*Cu taken*[b] *(μeq)*	*Cu found (μeq)*	*Error (%)*
109.80	109.24	−0.51	96.89	96.46	−0.44
27.45	27.49	+0.15	49.45	49.73	+0.58
27.45	27.57	+0.44	48.45	48.23	−0.46

[a] Base electrolyte, 10^{-2} M NaOH.
[b] Base electrolyte, 0.1 M NaOH–1 M NH_3.

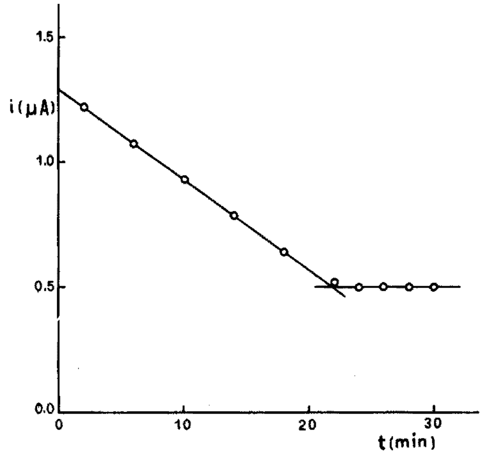

Fig. 2. Amperometric titration of lead(II) with electrolytically generated 1-propanethiol. Base electrolyte 0.01 M NaOH.

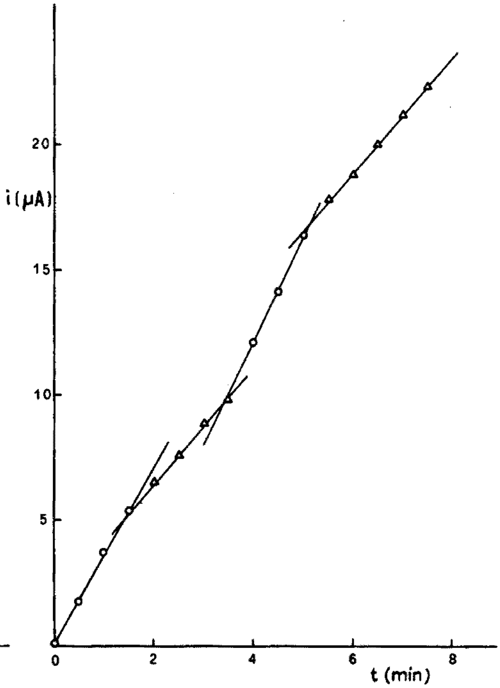

Fig. 3. Plot of biamperometric current against electrolysis time. Base electrolyte 0.01 M Cu(II)–0.1 M NaOH–1 M NH_3. Generating current 2 μA. (○) Platinum cathode, (△) Ag/AgSPr cathode.

are reported. In experiments with thiophenol only a very small fraction of the anodic coulombs was effective for the formation of the layer on the electrode.

Single-sweep voltammetry (200 mV/sec, platinum electrode) was used to check the oxidation of thiophenol to disulfide according to the equation:

$$2\text{Ph-SH} \rightarrow \text{PhSSPh} + 2\text{H}^+ + 2\,e^-$$

1-Propanethiol was oxidized under the experimental conditions used (methanolic 0.001 *M* thiol, 0.1 *M* sodium perchlorate solution) but at more positive potential. Perhaps the different behaviour of the two thiols can be ascribed to their different acidic strengths[11].

Table III shows the results of the titrations of lead and copper with electrolytically generated sulfhydryl groups, and Fig. 2 shows an example of the titration of lead.

Because many reactions are possible in the titration of copper with a sulfhydryl compound, attention was devoted to clarifying the mechanism of the reaction. According to the very low cathodic potential of the working electrode, ammino copper(II) complexes could be reduced to ammino copper(I) complexes and eventually to metallic copper. Furthermore, ammino copper(II) complexes could be reduced by the electrolytically generated mercaptide ions. Finally, copper(I) and copper(II)

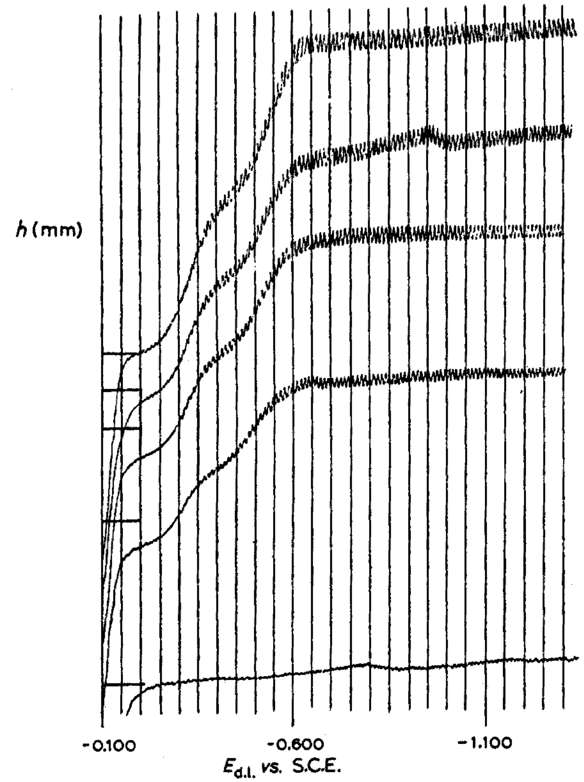

Fig. 4. Polarograms traced during the titration of copper(II) with standard 1-propanethiol. Base electrolyte 0.1 *M* NaOH–1 *M* NH_3.

mercaptides could precipitate. These different reactions have no consequence for a correct end-point because the same over-all stoichiometry is always exhibited. Experiments were made to check the existence of reduction near precipitation reactions. In Fig. 3, the biamperometric current is reported *versus* the electrolysis time for an experiment in which a platinum electrode and a silver mercaptide electrode were made cathodes in turn. The two different slopes suggest the occurrence of both reduction and precipitation when the silver mercaptide electrode was cathode. As mentioned above, the reduction could occur either at the electrode, which in this case is like an inert electrode, or by the action of the generated mercaptide ions. The occurrence of this reaction as well was proved by the titration of copper(II) with a standard solution of 1-propanethiol. Polarograms made during this titration showed anodic branches owing to the presence of ammino copper(I) complexes; Fig. 4 shows some of these polarograms recorded.

For every polarogram, the sum of twice the height of the first reduction curve plus the anodic curve corresponded to the total height of the reduction curves. Furthermore, if the initial concentration of copper(II) and the volume of the solution in the cell were known, it was possible to calculate the actual concentrations of copper-(II and I), and consequently to compare the equivalents of PrS^- introduced in the cell with those calculated from the modifications of the curves. Table IV shows the results obtained.

TABLE IV

RESULTS FROM POLAROGRAMS TRACED DURING THE TITRATION OF COPPER(II) WITH STANDARD 1-PROPANETHIOL SOLUTION ($4.97 \cdot 10^{-3}$ *M*)

(Volume in the cell = 46 ml. Base electrolyte 0.1 *M* NaOH–1 *M* NH_3. Galvanometer sensitivity $4.013 \cdot 10^{-2}$ μA/mm)

Volumes introduced (ml)	*0*	*2*	*4*	*5*
A.Height at −425 mV (mm)	39.5	28.5	19.0	14.0
B.Height at −200 mV (mm)	0.0	3.5	8.0	6.5
2A + B (mm)	79.0	60.5	46.0	34.5
Height at −1.150 mV (mm)	79.0	60.5	46.0	33.5
Cu(II) (moles/l · 10^4)	5.27	3.80	2.53	1.87
Cu(I) (moles/l · 10^5)	0.0	4.67	10.67	8.67
Amounts of PrS^- calculated (μeq)	0.0	9.76	17.85	24.98
Amounts of PrS^- introduced (μeq)	0.0	9.94	19.88	24.85

SUMMARY

The efficiency of generation of 1-propanethiol and thiophenol from the electrodes Ag/AgSR (R=Pr,Ph) was tested. Coulometric titrations of lead(II) and copper(II) with electrically generated sulfhydryl reagent are reported. The reaction between copper(II) and sulfhydryl ions was studied.

RÉSUMÉ

On a examiné le rendement coulométrique du propanethiol-1 et du thiophénol aux électrodes Ag/AgSR (R=Pr,Ph). Des titrages coulométriques du plomb(II) et du cuivre(II) sont décrits, utilisant le réactif sulfhydryle, coulométriquement produit. Une étude est effectuée sur la réaction cuivre(II) et ions sulfhydryles.

ZUSAMMENFASSUNG

Die Wirksamkeit der Erzeugung von 1-Propanthiol und Thiophenol an Ag/Ag-SR-Elektroden (R = Pr,Ph) wurde untersucht. Über coulometrische Titrationen von Blei(II) und Kupfer(II) mit elektrochemisch erzeugtem Sulfhydryl-Reagenz wird berichtet. Die Reaktion zwischen Kupfer(II) und Sulfhydryl-Ionen wurde untersucht.

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AUTOMATISATION DE L'ENTHALPIMETRIE A INJECTION

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(Reçu le 2 janvier, 1970)

Afin de répondre à un accroissement de demandes d'analyses ou en vue de diminuer le temps de réponse de ces dernières—en général trop long du point de vue du responsable de production—un laboratoire de contrôle aura tendance à rechercher des automatismes en vue de résoudre ses problèmes. En plus d'un gain de temps, l'automatisation des analyses présentera comme avantage d'améliorer la reproductibilité du mode opératoire. Le coût de l'analyse sera susceptible d'être abaissé. De plus il sera possible de multiplier le nombre des points de prélèvements analytiques au sein du procédé ce qui entraînera pour ce dernier une meilleure stabilité de marche d'où un meilleur rendement et une meilleure sécurité. Les données plus nombreuses mais numérisées pourront être traitées à l'aide d'un petit ordinateur—premier maillon d'un pilotage automatique du procédé.

Notre but a été de participer au développement de l'automatisation de l'enthalpimétrie à injection, méthode dérivée de l'analyse thermométrique. L'analyse thermométrique, basée sur une propriété très générale des processus chimiques, est applicable à toutes les réactions[1] aussi bien de neutralisation, de précipitation, de complexation, d'oxydo-réduction et même en milieu non aqueux[2]. Les premiers travaux utilisant la variation d'enthalpie pour déterminer la fin d'une réaction remontent aux années 1910–1920[3]. DUTOIT ET GROBET[4] ont développé par suite l'analyse thermométrique et l'ont appliqué à toute une variété de dosages. Cette technique devenue classique prit un nouvel essor grâce aux thermistances[5–7]. En 1964, WASILEWSKI *et al.*[8] introduisent l'enthalpimétrie à injection, méthode qui consiste à ajouter rapidement à la prise d'essai un excès de réactif et à suivre le dégagement calorifique consécutif. Comme développements récents, nous pouvons citer l'analyse rapide des argiles[9], la détermination de l'eau dans les solvants organiques ou les sels hydratés[10].

Du point de vue appareillage automatique d'analyse thermométrique, l'American Instrument Co. présente le "Titra-Thermo-Mat", appareil équipé de deux burettes à air comprimé mais dont les instructions séquentielles sont à commande manuelle. Dernièrement, MCLEAN ET PENKETH[11] ont associé un détecteur thermométrique à une chaine Autoanalyseur Technicon.

Dans un premier temps nous allons décrire l'appareil entièrement automatique à sortie analogique ou numérique que nous avons utilisé. Puis nous citerons quelques applications effectuées en laboratoire.

Le principe de la méthode que nous utilisons est d'ajouter à une quantité de réactif en excès, la prise d'échantillon de façon instantanée. La thermistance—capteur thermique—plongeant dans le milieu, transforme dans des conditions convenables le dégagement thermochimique en un signal électrique proportionnel à la concentration de l'élément à doser. La hauteur du pic enregistré est reliée ainsi de façon simple à la concentration cherchée.

APPAREILLAGE

L'ensemble utilisé est entièrement automatique et comporte trois parties (Fig. 1): un automate de prélèvement et de transfert, une cellule d'analyse, et un appareil de mesure. Ces différentes parties sont coordonnées à l'aide d'un programme d'analyse.

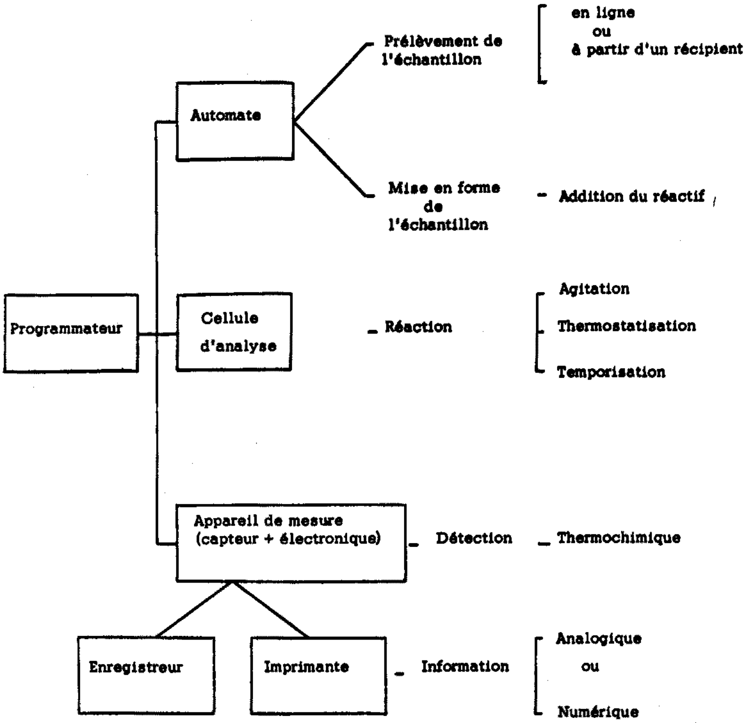

Fig. 1. Schéma de l'appareillage automatique.

Automate de prélèvement et de transfert

Cet automate (Fig. 2) est constitué de deux doseurs pneumatiques l'un relatif à l'échantillon, l'autre au réactif. Ils prélèvent et injectent dans la cellule d'analyse leur liquide respectif. Ils fonctionnent à l'air comprimé, 4 kg/cm^2, et sont commandés par des électrovannes. Chaque doseur comporte un double piston. Le premier piston—organe moteur—réagit aux deux arrivées d'air comprimé reliées à des électrovannes; le deuxième solidaire est en contact avec le liquide et fait office de pompe. Deux valves maintiennent l'intégrité de la prise d'essai, elle même réglable à l'aide d'une butée. Ces doseurs sont réalisés en matière plastique: plexiglas, téflon, polychlorure de vinyle. Les joints toriques d'étanchéité sont en viton. Les volumes prélevés varient de 1 à 100 ml et les erreurs sont de l'ordre de 1%.

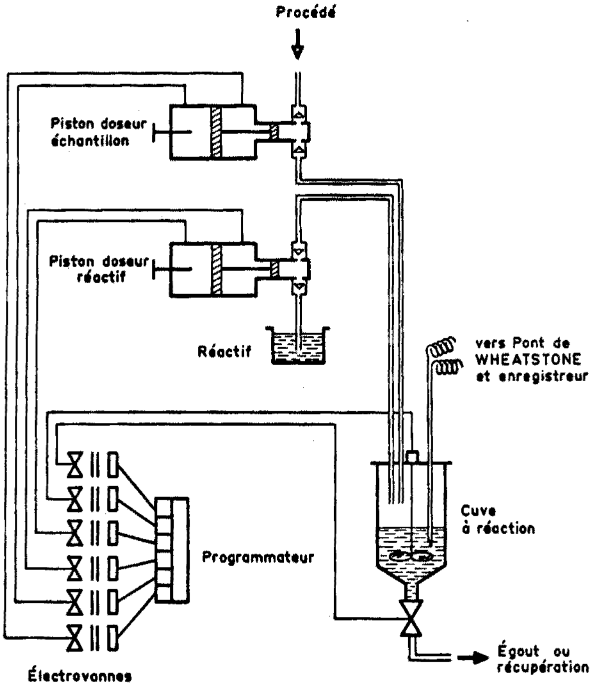

Fig. 2. Capteur thermochimique.

La prise d'essai peut être effectuée directement dans le procédé industriel. Pour des analyses de laboratoire, le système est utilisable à condition que la quantité de liquide à analyser permette le rinçage des canalisations, ce qui nécessite un volume de 5 ml.

Cellule d'analyse

La cellule d'analyse est en plexiglas. Elle est entourée d'une enveloppe remplie de billes en polystyrène. Elle comporte un agitateur actionné par une turbine à air comprimé, commandée par une électrovanne. Des orifices permettent l'arrivée de la prise d'échantillon, l'arrivée du réactif et le passage de la thermistance.

Dans le fond de la cuve est disposé un système de vidange dont l'ouverture ou la fermeture est commandée par électrovanne.

Appareil de mesure

L'appareil de mesure est constitué d'une thermistance, d'un pont de Wheatstone, d'un servomécanisme, et d'un enregistreur ou d'une imprimante.

Nous avons choisi d'utiliser les thermistances comme capteur thermique en raison de leur bonne sensibilité, de leur capacité calorifique négligeable et de leur réponse rapide. Nous avons employé dans notre montage une thermistance de la Radiotechnique du type E 205 CE/P 1 K.

La thermistance est montée dans une branche d'un pont de Wheatstone. Pour diminuer l'effet calorifique du courant à travers la thermistance, la tension d'alimentation du pont est limitée à 1.5 V ou moins.

L'appareil de mesure est rendu automatique à l'aide d'un servomécanisme de type nouveau (brevet C.E.A. n° PV 110 968). Ce servomécanisme rééquilibre le pont de Wheatstone en permanence.

Dans le cas d'une sortie analogique de la mesure nous utilisons un enregistreur galvanométrique de type courant. La numérisation du résultat est obtenue à partir du servomécanisme de rééquilibrage du pont. Un tiroir calcul permet après affichage du facteur analytique d'obtenir le résultat en concentration de l'élément cherché. Cette information pourrait d'ailleurs être acheminée vers un système d'acquisition de données.

Programmateur

Une fois les pistons doseurs réglés, les différents stades de l'analyse sont les suivants: aspiration et injection du réactif dans la cuve à réaction, agitation, aspiration de la prise d'essai, equilibrage thermique, remise au zéro du pont de mesure, injection de l'échantillon, mesure, vidange.

Pour enchainer ces étapes, il a été nécessaire d'inclure un organe de commande ou programmateur. Ce dernier est constitué d'un cylindre entrainé par un moteur et portant des cames qui établissent les contacts électriques de commande des électrovannes, de l'agitateur et de l'appareil de mesure.

Cet appareil à enthalpimétrie à injection effectue les analyses d'une manière séquentielle, de façon continue ou répétitive. Sa mise en route est instantanée et un dosage dure 3 min. Dans ces conditions il est possible d'optimiser les réactifs et d'ajuster la cadence des analyses à la demande.

APPLICATIONS

Avec cet appareil automatique, nous avons étudié des réactions de neutralisation, de complexation et d'oxydo-réduction. A titre d'exemple nous allons citer trois dosages parmi ceux qui ont été étudiés au laboratoire.

Neutralisation

L'acide nitrique a été dosé, dans le domaine de concentration 0.3–3 M, à l'aide de soude 0.2 M. Le volume de réactif était de 25 ml, celui de la prise d'essai de 1.5 ml. Les calculs d'erreurs basés chaque fois sur dix résultats de mesure conduisent au niveau de confiance 95%, à des valeurs du rapport: écart type/valeur moyenne voisines de 1%: 0.5 à 1.3%.

Exemple: acidité théorique, 1.03 M; trouvée, 1.02 ± 0.01 M.

Complexation

L'ion uranyle a été dosé par l'ion sulfate dans le domaine de concentration 10 à 300 g/l en UO_2^{2+} à acidité constante 1 M. A 20 ml de solution de sulfate d'ammonium 3 M, était ajoutée une prise d'essai de 2 ml de solution de nitrate d'uranyle. Les calculs d'erreurs effectués de manière identique à ceux mentionnés ci-dessus conduisent à des valeurs écart type/valeur moyenne, égales à 1%–1.5%.

Exemple: teneur en uranium théorique, 155 g/l; trouvée, 155 ± 2.0 g/l.

Oxydo-réduction

Les ions cerium(IV) ont été dosés par les ions fer(II) en milieu sulfurique 0.5 M.

Le domaine de concentration a été 0.2 à 1 M/l. A 25 ml de solution de sel de Mohr 0.2 M dans l'acide sulfurique 0.5 M on ajoutait 2 ml de solution de nitrate cériammonique dans l'acide sulfurique 0.5 M. Les valeurs du rapport écart type/valeur moyenne calculé comme précédemment, oscillent entre 0.6 et 1 %.

Exemple: teneur en Ce(IV) théorique, 0.5 M; trouvée, 0.5 ± 0.002.

La limite inférieure de concentration atteinte au cours de nos essais a été de 10^{-2} M/l. A de telles concentrations on inverse l'ordre d'arrivée ainsi que les volumes des liquides. Par exemple, pour doser l'ammoniaque dans le domaine 10^{-2}–10^{-1} M/l nous ajoutions 2 ml d'acide nitrique 4 M à 25 ml de solution à doser.

DISCUSSION

Cette méthode qui fait intervenir les variations d'enthalpie ΔH permet de choisir à des fins analytiques des réactions chimiques difficilement utilisables au sein d'autres méthodes basées sur des variations d'enthalpie libre ΔG.

$$\Delta G_{\mathrm{T,P}} = \Delta H_{\mathrm{T,P}} - T\Delta S = -RT \log K$$

$$\Delta H_{\mathrm{T,P}} = -Q_{\mathrm{P}}$$

Ainsi l'acide borique dont la constante d'acidité a une valeur faible $K_1 = 5.8 \cdot 10^{-10}$ peut être dosé avec de la soude par enthalpimétrie à injection car sa chaleur de neutralisation est suffisamment grande $\Delta H = -10.2$ kcal/mole.

La réaction choisie doit avoir une cinétique rapide. On peut doser successivement plusieurs éléments mais la difficulté de trouver des réactifs sélectifs augmente avec le nombre d'éléments à doser et avec la variété des ions présents dans la solution.

La variation de température mesurée est de l'ordre de quelques centièmes de degré. La mesure est d'autant plus précise qu'on diminue les phénomènes thermiques secondaires dus à la dissolution, à la dilution, à l'agitation, aux échanges avec le milieu extérieur, au passage du courant dans la thermistance. Certains facteurs, telle la chaleur d'agitation, sont relativement négligeables. Par contre, d'autres, telle l'influence de la température extérieure, peuvent être plus importants. On peut pallier à l'influence de ces différents termes au moyen d'une enceinte thermostatée ou d'un réglage électrique.

De toute façon, il est possible de vérifier la réponse de l'appareil à l'aide d'un échantillon connu. L'automatisation de l'appareillage permet d'atteindre de très bonnes reproductibilités et les résultats sont obtenus avec des erreurs relatives voisines du pourcent.

Cet appareil a été conçu pour résister au mieux aux agents corrosifs. Prochainement des essais seront effectués en enceinte α ce qui constitue un milieu plus défavorable qu'un laboratoire conventionnel. Les vérins pneumatiques confèrent à cet appareil une grande robustesse et une très bonne fiabilité.

Par rapport aux instruments commerciaux actuels, l'appareil décrit présente comme avantages de rendre automatique le mode opératoire, de numériser le signal de mesure et de convertir ce dernier en valeur élaborée de concentration de l'élément à doser.

La tendance actuelle, dans l'industrie, étant à la construction de grandes unités, les instruments d'analyse ont un rôle important à jouer dans le développement de l'automatisation de telles unités. Cet enthalpimètre rejoint le nombre des appareils d'automatisation des contrôles chimiques qui trouvent leurs applications dans des domaines aussi variés que: les industries du sucre, des engrais, du pétrole, l'hydrométallurgie, les industries pharmaceutiques et la lutte contre la pollution.

RÉSUMÉ

Un appareil entièrement automatique à enthalpimétrie à injection est décrit. Il comprend un automate de prélèvement de l'échantillon et de transfert des réactifs, fonctionnant à air comprimé, une cellule de réaction et un dispositif de mesure rendu automatique et numérique par un servomécanisme nouveau. Le capteur utilisé est une thermistance qui fournit un signal proportionnel à la concentration de l'élément à doser. Comme applications, ont été réalisés des dosages basés sur des réactions de neutralisation, de complexation et d'oxydo-réduction. La précision de ces dosages est voisine de 1%. L'analyse est effectuée d'une manière séquentielle de façon discontinue ou répétitive.

SUMMARY

A completely automatic apparatus based on injection enthalpimetry is described. The sample is taken automatically and reagent is added by means of pneumatic pipettes. The detector is a thermistor, and automation is achieved by means of a new servomechanism; a digital read-out can be provided. Typical applications were tested with oxidation–reduction, complexing and neutralisation reactions. The precision of the analyses was about 1%. Analyses are performed sequentially, either discontinuously or repetitively.

ZUSAMMENFASSUNG

Eine Apparatur für die Automatisierung von Analysen mittels Thermistoren wird beschrieben. Die Probenahme und die Zugabe der Titrierlösung werden pneumatisch ausgeführt. Der Detektor—ein Thermistor—wandelt die Reaktionswärme in ein elektrisches Signal um, welches der Konzentration des zu bestimmenden Elementes proportional ist. Ein neuer Servomechanismus ergibt eine digitale Anzeige. Beispiele für Neutralisierungs-, Redox- und Komplexierungsreaktionen werden gegeben. Die Präzision der Titration ist 1%. Die verschiedenen Analysen können diskontinuierlich oder kontinuierlich ausgeführt werden.

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THE DETERMINATION OF NICKEL, ZINC, COBALT AND MANGANESE IMPURITIES IN CADMIUM BY PULSE POLAROGRAPHY

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Cadmium is often recovered as a by-product of the zinc industry. Both elements are rather easy separated, but zinc always constitutes a major impurity element in pure cadmium products. Nickel, cobalt and manganese generally are present in lower amounts.

Emission spectrography is frequently used for the determination of these and other elements. Without any separation down to a few p.p.m. can be determined; after enrichment 0.02–0.05 p.p.m. cobalt and 0.01–0.05 p.p.m. nickel[1] and 0.05 p.p.m. nickel, zinc and cobalt in cadmium have been determined[2]. After preliminary separations, colorimetric methods can also be used.

Classical d.c. polarography allows the determination of about 20 p.p.m. of zinc[3–5] and less than 1 p.p.m. nickel[6]; 1 p.p.m. of both elements have been determined by cathode-ray polarography[7]. Without separation, 20 p.p.m. zinc has been determined by square-wave polarography[8].

More recently, mass spectroscopic techniques have been developed for the determination of many trace impurities in cadmium sulphide; the detection limits for most impurities are 10 p.p.b.[9]

The present investigation deals with the determination by pulse polarography of traces of nickel, zinc, cobalt and manganese in cadmium and its compounds. This technique has already been applied for the determination of bismuth, copper and lead[10], thallium[11], antimony, tin and arsenic[12] and indium[13] in cadmium products. The reduction waves of nickel(II), zinc(II), cobalt(II) and manganese(II) were used in the polarographic analysis. These occur at potentials more negative than the cadmium(II) reduction wave, rendering necessary a prior separation from the cadmium matrix. This was performed by electrolytic deposition of cadmium on mercury at a controlled potential.

EXPERIMENTAL

Apparatus and reagents

Pulse polarograph, Southern type A 1700 Mark II; the derivative method of operation was used[10].

Electromechanical potentiostat, constructed as described by LAMPHERE AND ROGERS[14] and providing an output voltage and current of up to 50 V and 5 A respectively. The control sensitivity is ± 2 mV.

Mercury-cathode electrolysis cell of the H-type, with fine-porosity sintered

Pyrex disc diaphragm, 4 cm in diameter. The mercury working electrode compartment of Erlenmeyer form had a capacity of about 250 ml and a pool area of *ca.* 40 cm^2; about 80 ml of twice vacuum-distilled mercury was used as cathode. A stopcock with sealed platinum contact permitted withdrawal of the mercury, the electrical contact being maintained. The cell was immersed partially in a stirred water bath at room temperature for cooling.

Several analytical-grade reagents were further purified, especially to reduce the zinc content. Sulphuric acid and pyridine were redistilled from a quartz apparatus. Concentrated stock solutions of lithium thiocyanate and lithium hydroxide in water were electrolysed for 24 h under a nitrogen atmosphere in separate electrode compartments on a mercury cathode at -1.6 V *vs.* S.C.E. Water, mercury, nitrogen, hydrochloric, acetic and nitric acid were purified as previously described[10]. All other reagents were of analytical grade and used without further purification. Nickel(II), zinc(II), cobalt(II) and manganese(II) stock solutions were prepared from the analytical-grade sulphates and standardized.

Polarographic data

For the polarographic determination of cobalt and manganese, various procedures can be considered depending on whether a reduction wave of the di- or trivalent species or an oxidation wave is used. In theory, some reactions involving the trivalent species could allow the determination of manganese and cobalt without previous separation. However, interferences may be expected from the cadmium matrix, from other impurities present in excess, or from the oxidation slope of mercury. For example in 0.4 *M* cadmium chloride–3 *M* triethanolamine and in the presence of ammonia to keep the cadmium in solution, the manganese(II) oxidation peak merges partially with the mercury oxidation slope, preventing the use of a high instrumental amplifier gain. In 0.5 *M* cadmium chloride–3 *M* ethylenediamine, the cathodic copper(II) and anodic cobalt(II) peaks nearly coalesce. Furthermore, the solubility of cadmium in these electrolytes is often rather low. Preference was therefore given to the reduction reactions of the divalent species of the elements under investigation after their previous separation from the cadmium matrix.

The first experiments were aimed at the polarographic analysis in an ammonia–ammonium chloride solution. As in many supporting electrolytes, zinc seriously interfered with cobalt, but generally the latter was present in much lower amounts than zinc. In cathode-ray polarography, cobalt(II) has been reported to give an adsorption peak in the presence of dimethylglyoxime, free from interferences, and about 200 times more sensitive than the diffusion-controlled peak[15]. However, this peak could not be obtained with the derivative pulse-technique. Furthermore, the supporting electrolyte did not give satisfactory results for low zinc concentrations. At high instrumental amplifier gain, the polarogram showed a peak coinciding with the zinc peak and having a comparable shape; the height of this peak was irreproducible and increased on prolonged deaeration both with nitrogen and argon. No improvement was obtained after electrolysing the solution on mercury at a controlled potential.

Numerous other electrolytes were tried, such as thiocyanate and acetate. In thiocyanate media the cadmium(II) and zinc(II) peaks nearly coincided with those of nickel(II) and cobalt(II), respectively. In acetate media, the nickel(II) and zinc(II) peaks were not separated. Promising features were, however, shown by an acetate–thiocyanate mixture. When thiocyanate was added to a solution of the elements under investigation in 0.1 *M* acetate, nickel(II) was reduced at a more positive potential. At a thiocyanate concentration of 0.025 *M*, well separated peaks were obtained with peak potentials of about −0.63(Cd), −0.80(Ni), −1.11(Zn), −1.37(Co) and −1.62(Mn) *vs.* mercury pool. A typical pulse polarogram is given in Fig. 1.

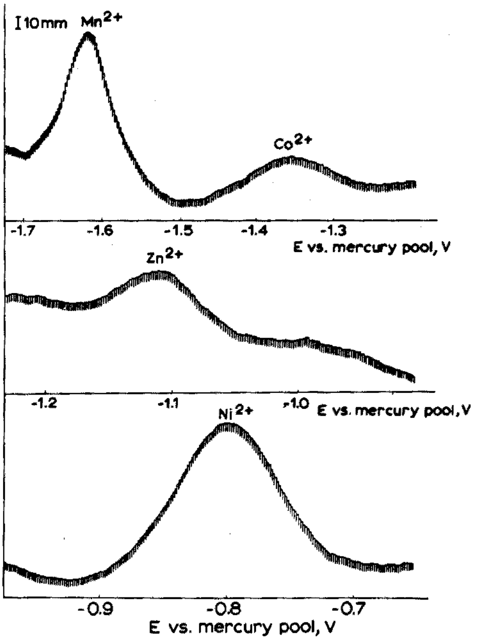

Fig. 1. Pulse polarogram of $3 \cdot 10^{-6}$ *M* Ni(II), $2 \cdot 10^{-7}$ *M* Zn(II), $4.6 \cdot 10^{-7}$ *M* Co(II) and $4.4 \cdot 10^{-7}$ *M* Mn(II) in 0.1 *M* LiAc + 0.025 *M* LiSCN. Conditions: sensitivity 1/5, pulse amplitude 35 mV, current integration over 9 drop lives, polarization rate 60 min/V (Ni, Zn) and 30 min/V (Co, Mn).

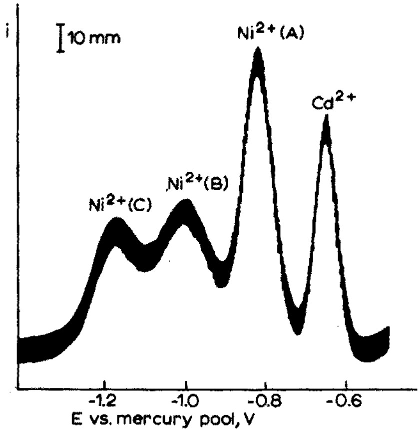

Fig. 2. Pulse polarogram of $7.35 \cdot 10^{-5}$ *M* Ni(II) and $9.80 \cdot 10^{-6}$ *M* Cd(II) in 0.1 *M* LiAc + 0.025 *M* LiSCN. Conditions: sensitivity 1/80, pulse amplitude 35 mV, current integration over 9 drop lives, polarization rate 7.5 min/V.

At higher thiocyanate concentrations, the cadmium and nickel peaks and also the zinc and cobalt peaks further approached each other. For manganese, when a large excess of acid was present, the hydrogen reduction peak was not fully separated from the preceding, but more sensitive, manganese(II) peak. Lithium thiocyanate and acetate are preferable to the other alkali and ammonium compounds for low concentrations of manganese. In conventional d.c. polarography a potassium thiocyanate–ammonium acetate mixture was used by STOUT *et al.*[16] at pH 4.6 for the simultaneous determination of nickel and zinc in plant ash and by SCOTT[17] for the determination of the same elements in aluminium. On the upper plateau of the nickel wave he found a small kink, which was not a true nickel maximum.

When polarograms of each element were recorded separately, nickel at concentrations higher than about 10^{-6} *M* was found to give three peaks with peak potentials of about −0.80(A), −0.97(B) and −1.14(C) V *vs.* mercury pool (Fig. 2). This behaviour of nickel at relative low thiocyanate concentrations has already been studied[18–20]. The most negative peak is attributed to the reduction of hydrated nickel ions, while the two more positive peaks are associated with the reduction of nickel–thiocyanate complexes. The peak potentials of the third peak and the zinc peak differed by 40 mV. The heights of the three peaks were nearly proportional to the nickel concentration in the $2.5 \cdot 10^{-5}$–$7.5 \cdot 10^{-5}$ M range, the second and third peak being about half as high as the first one. At lower nickel concentrations, the relative heights of the second and third peak decreased. At the $6 \cdot 10^{-6}$ and $3 \cdot 10^{-6}$ M levels, the height of the middle peak amounted, respectively, to *ca.* 37 and 18% of the first one. Below 10^{-6} M, only the most positive peak remained and could be used for analytical purposes. From here on, this peak is referred to as the nickel(II) peak. The supporting electrolyte was thus not suitable for the determination of zinc in the presence of large amounts of nickel. However, the zinc content of cadmium generally is appreciably higher than that of nickel, and the method is about 5 times less sensitive for nickel than for zinc. This accounts for the fact that in this investigation the contribution of nickel at the zinc peak potential was mostly negligible.

Iron interfered with cobalt, as the iron(II) and cobalt(II) reduction peaks were only separated less than 50 mV.

The concentrations giving a peak height of 10 mm in the pure supporting electrolyte at maximal amplifier gain, were about 10^{-8} M for zinc and manganese, $5 \cdot 10^{-8}$ M for nickel and $8 \cdot 10^{-8}$ M for cobalt. In the same sequence, the peak half-widths were *ca.* 95, 75, 160 and 75 mV. Cobalt, and to a smaller extent nickel, behaved irreversibly. The sensitivities and peak potentials were nearly constant in the pH range 6–7, which was therefore used throughout this work. The linear relationship between concentration and peak height was verified by calibration curves.

The reduction wave of peroxide interfered with that of zinc(II). At high oxygen concentrations, when the solution in the polarographic cell was only partially deaerated or even not at all, the peroxide reduction had an asymmetrical and irregular peak shape, with a peak half-width value of about 450 mV. At low peroxide concentrations, such as arise from the reduction of dissolved oxygen on the mercury pool before and during deaeration, no peak was obtained. The wave had a nonlinear rising part over ± 200 mV, on which the zinc peak was superimposed; then a plateau nearly parallel to the residual current curve was attained. A peak in this plateau could be measured accurately. Even when the solution was deaerated before being brought into contact with the mercury pool, detectable traces of peroxide were always present. Its wave height was not reproducible under identical working conditions, but was always less than 75 mm at half the maximal instrumental amplification. At best, this setting could be used for zinc, resulting in a detection limit of $2 \cdot 10^{-8}$ M. The peroxide interference could probably have been avoided by means of an external reference electrode[21], but the zinc content of the cadmium samples investigated did not necessitate the use of the higher amplifier gains and the solution had not even to be deaerated before the mercury pool was added.

The sensitivity was about 5 times greater for cadmium than for nickel. Their peak potential difference allowed the determination of nickel up to a cadmium : nickel molar concentration ratio of 200 : 1 when a pulse amplitude of 7 mV was used, which resulted in an incidental five-fold decrease in the detection limit of nickel. After separation, the cadmium remaining in solution interfered when low nickel concentrations were determined at high instrumental amplification. In this case a supporting electrolyte which would provide better separation of the nickel and cadmium peaks and would enhance the nickel sensitivity was desirable. Pyridine and ammonia were therefore investigated.

Frequently, pyridine is used together with an equimolar amount of pyridinium chloride. In a 0.25 *M* solution of both reagents, an unidentified peak appeared at high instrumental sensitivity, nearly coinciding with the nickel peak. The same occurred in the purest pyridine commercially available and also in twice-redistilled pyridine. In the presence of pyridinium chloride, a trace organic compound present or formed probably reacted at the D.M.E. at the nickel peak potential. The height of the interfering peak decreased on raising the pH and a smooth base line was obtained in 0.25 *M* pyridine–0.05 *M* potassium chloride. In this medium the cadmium–nickel peak potential difference amounted to 230 mV, the nickel peak half-width was 70 mV, and the pulse polarographic sensitivity of nickel as defined above, was 10^{-8} *M*. The cadmium–nickel molar concentration ratio could exceed 750 : 1 and zinc did not interfere. A typical pulse polarogram is shown in Fig. 3. In comparison with thiocyanate–acetate, pyridine–potassium chloride has several advantages: the sensitivity of nickel is increased five-fold and larger cadmium concentrations may be present or a pulse amplitude of 35 mV may be used.

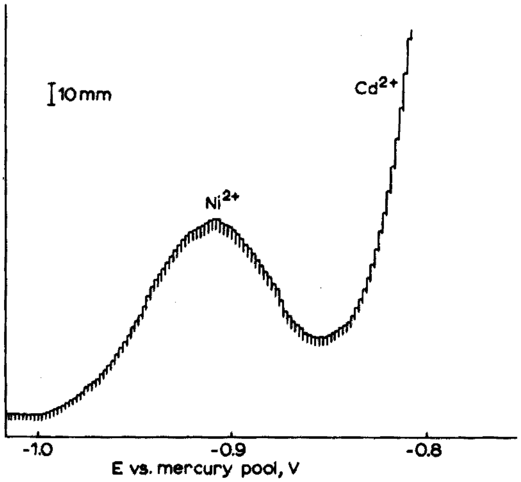

Fig. 3. Pulse polarogram of $1.84 \cdot 10^{-6}$ *M* Ni(II) in 0.25 *M* pyridine + 0.05 *M* KCl, representing 0.072 p.p.m. Ni in analytical grade $CdCl_2 \cdot 2\frac{1}{2} H_2O$ (sample 5 from Table II, 15 g weight). Conditions: sensitivity 1/5, pulse amplitude 7 mV, current integration over 9 drop lives, polarization rate 60 min/V.

In 1 *M* ammonia–1 *M* ammonium chloride the cadmium and nickel peaks are separated by 320 mV. The nickel peak half-width and the pulse polarographic sensitivity amount, respectively, to 120 mV and $2 \cdot 10^{-8}$ *M*. On the whole, pyridine was preferred to ammonium hydroxide.

Separation

Ion exchange[5,22,23], extraction[7,24,25] and electrolytic deposition of cadmium[4,26,27] can be used for the separation of the elements under investigation from large amounts of cadmium.

Preference was given to the electrolytic deposition of cadmium, as it enables the simultaneous separation of the four elements under investigation. Polarographic half-wave potentials, deposition potentials on platinum[27] and data on controlled potential electrolysis on mercury[26] indicate that in several electrolytes, such as hydrochloric and sulphuric acid, cadmium can be electrodeposited while the elements under investigation remain in solution.

Electrolysis on platinum, being less troublesome than on mercury, was first investigated. From 0.3 *M* hydrochloric and sulphuric acid at a cathode potential of −0.9 V *vs.* S.C.E., rough, crumbly cadmium deposits were obtained; the distribution was not homogeneous, being especially dense at the edges of the electrode. With a diaphragm cell, the loose deposit was concentrated just opposite the junction between the compartments. On a copper-plated electrode, a uniform deposit was obtained initially, but when the electrode had become entirely covered with cadmium, particles of the deposit were lost. Accordingly, preference was given to electrolysis on mercury.

The electrolyses were performed in 0.25 *M* hydrochloric acid at a cathode potential of −0.85 to −0.90 V *vs.* S.C.E. Hydrochloric acid was chosen, because it is easy to purify and to remove, and iron can be extracted from it. The mercury–solution interface was vigorously stirred by a rotating propeller-type glass stirrer to prevent accumulation of deposited metal on the surface layer. After the electrolysis, the whole solution was recovered as some evaporation could occur if heat was developed in the earlier stages of the electrolysis, depending on the resistance of the cell (fritted disc). The polarograms of the electrolysed solutions were rather unstable at high amplifier gain and contained an unidentified peak, probably caused by peroxide. Good results were obtained when the solution was evaporated to dryness, and the residue heated to 400° and redissolved.

Preliminary experiments showed that nickel, zinc, cobalt and manganese remained in solution quantitatively. The efficiency of deposition of cadmium was improved by replacing the cathode with fresh mercury after much of the metal has been deposited; 10 g of cadmium, dissolved in a volume of 100 ml, could be deposited to a final concentration of less than $5 \cdot 10^{-6}$ *M* in less than 5 h, when the mercury was twice renewed. Iron also remained in solution. After addition of a few drops of nitric acid, the electrolysed solution was evaporated, the residue was dissolved in 8 *M* hydrochloric acid, and the solution was extracted with diisopropylether to remove iron. After evaporation of the aqueous phase, the pulse polarogram of the residue dissolved in the supporting electrolyte, had a rather unstable base line and contained unidentified peaks, probably from organic compounds. Stable polarograms were obtained after the residue had been heated at 400° for 1 h, and recovery of the elements to be determined was quantitative. In order to prevent zinc losses, a few drops of sulphuric acid were added to the solution before evaporation and the excess of acid was removed by heating on a hot-plate (*ca.* 300°). The residue was dissolved in the minimum amount of hydrochloric acid (1:1) and after evaporation under an i.r. lamp, was redissolved in the supporting electrolyte, as the heated sulphate residue did not dissolve quantitatively.

Procedure

Dissolve a suitable amount of cadmium metal in hot hydrochloric acid (25%), adding at intervals a few drops of nitric acid. Cool and transfer the solution to the mercury-cathode electrolysis cell and dilute to a volume of about 100 ml with water. Adjust the potential of the stirred mercury cathode at -0.85 to -0.90 V *vs.* S.C.E. To speed up the electrolysis, especially for samples containing large amounts of cadmium, renew the mercury when the current has dropped to about 50 mA and again at 20 mA. When the current has fallen to a nearly constant value of a few mA, drain off the mercury while electrical contact is maintained.

Collect the solution quantitatively in a beaker, add a few drops of nitric acid and evaporate nearly to dryness. Dissolve the residue in 25 ml of 7.75–8 *M* hydrochloric acid, transfer to a 100-ml separating funnel and extract twice with 25-ml portions of diisopropylether. Treat the combined ethereal extracts with 20 ml of 7.75–8 *M* hydrochloric acid. Combine the aqueous solutions. Add a few drops of sulphuric acid, evaporate and remove the excess of acid by heating on a hot-plate (*ca.* 300°). Heat the residue in a furnace at 400° for 1 h. Dissolve the residue in a small amount of warm hydrochloric acid (1:1), evaporate under an I.R. lamp and redissolve in the supporting electrolyte (0.1 *M* lithium acetate–0.025 *M* lithium thiocyanate). Transfer the solution to a 10-ml flask and dilute to the mark with the supporting electrolyte. Record a pulse polarogram and determine nickel, zinc, cobalt and manganese by the standard addition method.

For cadmium compounds, proceed in the same way after dissolving in water and adding hydrochloric acid. Take a polarogram of a blank solution prepared in the same way.

RESULTS

Special attention must be paid to possible contamination of the sample with zinc from reagents and common materials used in the various stages of the analysis. For instance, an appreciable amount of the initial large irreproducible blank values obtained arose from the heating of the extraction residue in an electrical oven with rust-proofed walls. Water from a copper still, redistilled in a two-stage quartz apparatus also contains an appreciable amount of zinc when the content of the compartments enriched with zinc is not regularly removed.

In spite of very careful purification of the reagents and despite taking a number of other precautions such as the protection of open vessels from atmospheric dust, a blank value of $1.36 \cdot 10^{-7} \pm 0.20 \cdot 10^{-7}$ *M* was obtained. This concentration is relatively high with respect to the *ca.* $2 \cdot 10^{-8}$ *M* that in practice can be detected in the pure supporting electrolyte. However, it was much lower than the concentrations measured for the commercial cadmium samples analysed ($> 5 \cdot 10^{-6}$ *M*). Therefore, no further attempt was made to obtain better purification of the reagents, in order to obtain still lower blank values. If an accuracy of the same order as the blank is considered to be acceptable for the determination of zinc concentrations, the detection limit can be estimated at 0.01 p.p.m. for a 10-g sample and a final volume of 10 ml.

Under the same sample and volume conditions, down to about 0.02 p.p.m. cobalt ($4 \cdot 10^{-7}$ *M*) and 0.003 p.p.m. manganese ($5 \cdot 10^{-8}$ *M*) can be determined at a fifth of the maximal instrumental amplification and a pulse amplitude of 35 mV. For nickel, a pulse amplitude of 7 mV must generally be used, which limits the sensitivity to about 0.08 p.p.m. ($1.3 \cdot 10^{-6}$ *M*). This can be lowered to less than 0.01 p.p.m., if a pyridine–chloride supporting electrolyte is employed. Under the same conditions as for zinc, no blank values for nickel, cobalt and manganese were observed.

The whole procedure was applied to the analysis of synthetic samples prepared by adding known quantities of nickel, zinc, cobalt and manganese to a cadmium solution. The cadmium was previously freed from these elements by controlled-potential electrolytic deposition of cadmium on copper-plated platinum from a solution of the analytical-grade sulphate. The results are summarized in Table I.

In order to check the practical efficiency, the method was also applied to the analysis of various commercially available cadmium samples (Table II). The sensitivity for zinc and manganese is satisfactory and the zinc content is well above the

TABLE I

DETERMINATION OF NICKEL, ZINC, COBALT AND MANGANESE IN CADMIUM

(5-g samples; final volume, 10 ml)

Ni added (μg)	*Ni found (μg)*	*Yield (%)*	*Zn added (μg)*	*Zn found (μg)*	*Yield (%)*
52.4	52.0	99.2	58.6	58.8	100.3
5.87	5.51	93.9	32.7	32.9	100.6
2.94	2.84	96.6	6.54	6.62	101.2
1.17	1.42	121.4	0.654	0.679	103.8
0.734	0.869	118.4	0.327	0.350	107.0

Co added (μg)	*Co found (μg)*	*Yield (%)*	*Mn added (μg)*	*Mn found (μg)*	*Yield (%)*
52.4	51.8	98.9	49.4	49.5	100.2
5.89	5.80	98.5	27.5	27.6	100.4
2.95	2.89	98.0	5.49	5.47	99.6
0.589	0.562	95.4	0.549	0.563	102.6
0.295	0.266	90.2	0.275	0.289	105.1

TABLE II

DETERMINATION OF NICKEL, ZINC, COBALT AND MANGANESE IN COMMERCIALLY AVAILABLE CADMIUM SAMPLES

(5–15 g samples; final volume, 10 ml)

Product	*Grade*	*Nickel (p.p.m.)*	*Zinc (p.p.m.)*	*Cobalt (p.p.m.)*	*Manganese (p.p.m.)*
Cadmium metal	Pure	3.26	30.3	2.47	0.53
Cadmium metal	Analytical	1.19	11.7	0.12	0.14
Cadmium metal	Analytical	0.12	0.45	0.041	0.076
Cadmium metal	Ultra pure	<0.08	0.24	<0.02	<0.003
$CdCl_2 \cdot 2\frac{1}{2}\ H_2O$	Analytical	<0.08 0.072[a]	0.33	<0.02	0.050
$CdCl_2 \cdot 2\frac{1}{2}\ H_2O$	Analytical	<0.08 0.047[a]	0.73	<0.02	0.097
$3CdSO_4 \cdot 8\ H_2O$	Analytical	0.065	1.85	0.036	0.56

[a] Determined in 0.25 *M* pyridine–0.05 *M* potassium chloride.

detection limit of the procedure used. The contents of nickel and cobalt in three samples are below the detection limit with an acetate–thiocyanate supporting electrolyte. When a higher sensitivity is desired, larger sample weights would permit further lowering of the absolute detection limit. However, in this case nickel is better determined separately in a pyridine–potassium chloride supporting electrolyte.

SUMMARY

A pulse-polarographic method for the simultaneous determination of traces of nickel, zinc, cobalt and manganese in cadmium and its compounds is described. Interference from the reduction of the cadmium matrix was eliminated by a prior electrolytic deposition of cadmium on a mercury cathode at a controlled potential of −0.90 V *vs.* S.C.E. Iron in excess interfered with the determination of cobalt and was therefore extracted from the electrolysed solutions. The polarographic determination was performed in 0.1 *M* lithium acetate –0.025 *M* lithium thiocyanate as supporting electrolyte. A sample weight of 10 g and a final volume of 10 ml allowed the determination of about 0.08 p.p.m. nickel, 0.01 p.p.m. zinc, 0.02 p.p.m. cobalt and 0.003 p.p.m manganese. Less than 0.01 p.p.m. nickel could be determined with a 0.25 *M* pyridine–0.05 *M* potassium chloride supporting electrolyte. Several synthetic samples and commercially available cadmium products were analysed.

RÉSUMÉ

Une méthode pulse-polarographique est décrite pour le dosage simultané de traces de nickel, zinc, cobalt et mangnèse dans le cadmium et ses composés. L'interférence provenant de la réduction de la matrice de cadmium est éliminée par un dépôt électrolitique préalable du cadmium sur la cathode de mercure, à potentiel de 0.9 V *vs.* E.C.S.

ZUSAMMENFASSUNG

Es wird eine pulspolarographische Methode zur Simultanbestimmung von Nickel-, Zink-, Kobalt- und Manganspuren in Cadmium und seinen Verbindungen beschrieben. Eine Störung durch Reduktion der Cadmium-Matrix wurde vermieden durch vorhergehende elektrolytische Abscheidung des Cadmiums an einer Quecksilberkathode bei einem kontrollierten Potential von −0.90 V gegen Standard-Kalomelelektrode. Überschüssiges Eisen störte bei der Kobaltbestimmung und wurde daher aus den elektrolysierten Lösungen extrahiert. Die polarographische Bestimmung wurde mit 0.1 *M* Lithiumacetat–0.025 *M* Lithiumthiocyanat als Trägerelektrolyt ausgeführt. Eine Probe von 10 g und ein Endvolumen von 10 ml erlaubten die Bestimmung von etwa 0.08 p.p.m. Nickel, 0.01 p.p.m. Zink, 0.02 p.p.m. Kobalt und 0.003 p.p.m. Mangan. Weniger als 0.01 p.p.m. Nickel konnten mit 0.25 *M* Pyridin–0.05 *M* Kaliumchlorid als Trägerelektrolyt bestimmt werden. Verschiedene synthetische Proben und handelsübliche Cadmium-Produkte wurden analysiert.

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SHORT COMMUNICATIONS

The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique

Part VIII. The analysis of sulfide minerals and ores

The analysis of sulfide minerals and ores is generally based on an oxidizing attack, either in the wet way or by a fusion. The former method is universally applied in routine analysis of the technically important sulfide ores. For process control purposes, the oxidation of sulfide in the wet way has the disadvantages of being slow and of leaving the gangue unattacked. It has been demonstrated that sulfide minerals[1] and ores[2] are decomposable by a mixture of hydrofluoric and perchloric acids; when this attack is made in a bomb, the decomposition time can be reduced considerably. The application of atomic absorption spectrophotometry to the determination of silver, zinc, cadmium, copper and lead in sulfide minerals is described by RÚBESKA[3].

The present communication describes the use of a bomb technique and a mixture of hydrofluoric, hydrochloric and nitric acids for the decomposition, not only of the sulfide species, but also of the gangue of sulfide minerals and ores. In the sample solution, or in aliquot portions of it, iron, copper, lead, zinc, silicon, aluminium, magnesium, calcium, sodium, potassium, titanium and manganese are determined by atomic absorption spectrophotometry.

Experimental

The instruments, apparatus, reagents and solutions were the same as used previously[4]. As analytical results for sulfide ores are usually reported, not as oxides, but as elements, it is recommended to take this into account when preparing the primary standard solutions. In the sulfide minerals and ores the content of the various components may vary within a wide concentration range, hence the preparation of the series of secondary standard solutions is not described.

In the preparation of sample and secondary standard solutions the various interferences have to be considered; for a discussion of the precautions to avoid interferences, a previous paper[4] should be consulted.

Silicon, aluminium, magnesium, calcium and titanium were determined with acetylene–nitrous oxide flames and the other elements with acetylene–air flames.

Procedure

Transfer 0.2000 g of the sample to the bomb, add 2.5 ml of hydrofluoric acid, 2 ml of hydrochloric acid and 2 ml of nitric acid, close the bomb without delay, heat while stirring to 110 ± 5° and decompose at that temperature for about 10 min. Cool the bomb (without applied voltage) in running water. Open the bomb and add quickly by pipette 25 ml of saturated boric acid solution, heat and mix until a clear solution is obtained. Transfer the solution to a 100-ml volumetric flask, dilute quickly to volume with water and transfer at once to a plastic bottle.

Determine iron*, lead, silicon, aluminium, magnesium, sodium, potassium, titanium and manganese in the main solution, and the other elements in appropriate aliquot portions. Make the determinations and calculations as described in a previous paper[4].

Results

The present scheme was tested by decomposing samples of Norwegian origin of pyrrhotite, chalcopyrite and pyrite; the results of repeated analyses of a sulfide ore are given in Table I.

TABLE I

ANALYTICAL DATA IN PERCENT BY WEIGHT FOR THE NORDIC REFERENCE SAMPLE ASK-KISMALM (SULFIDE ORE FROM BLEIKVASSLI, NORWAY), SERIES I, BOTTLE NO. 37[a]

	$\bar{X}$	S	C
Silicon (as SiO_2)	7.45	0.30	4.0
Aluminium (as Al_2O_3)	0.27	0.01	2.7
Magnesium (as MgO)	0.078	0.002	2.5
Calcium (as CaO)	0.054	0.013	24
Sodium (as Na_2O)	0.064	0.015	23
Potassium (as K_2O)	0.058	0.007	12
Titanium (as TiO_2)	0.0057	0.0006	11
Manganese (as MnO)	0.078	0.002	2.5
Zinc (as Zn)	9.4	0.25	2.7
Copper (as Cu)	0.142	0.003	2.1
Lead (as Pb)	2.04	0.04	2.0
Iron (as Fe)	35.0	0.6	1.7

[a] $\bar{X}$ = average of 5 analyses.
S = standard deviation.
C = relative standard deviation.

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* Iron was determined with the burner turned 90° from its standard position.

Some observations on the determination of zinc by atomic fluorescence spectrometry under conditions favourable for analysis

Although the relative merits of atomic emission, atomic absorption and atomic fluorescence spectrometry have recently been the subject of controversial discussion[1,2], there seems to be general agreement that for zinc and a group of elements whose principal resonance lines lie low in the ultraviolet (*ca.* 220 nm), the detection limits obtainable with currently available instrumentation are superior when the fluorescence technique is used. Results reported so far for the determination of zinc by atomic fluorescence are summarised in Table I, but most of the references quoted are concerned with the optimisation of experimental parameters, rather than the analysis of practical samples. Recently we have reported[3] that 100-fold excesses of 48 cations and 18 anions caused no interference in the determination of a 10^{-5} *M* zinc solution in an air–propane flame, and KLAUS[12] has determined zinc in biological materials. The object of the present investigation was to examine the effect of flame composition and burner type on the interferences in, and sensitivity of, the determination of zinc.

TABLE I

REPORTED DETECTION LIMITS FOR ZINC

Flame	*Burner type*[a]	*Detection limit*	*Source*	*Ref.*
Air–propane	Ch.	0.003	Osram vapour lamp	3
Air–propane	Ch.	0.6	150 W xenon arc	3
Air–hydrogen	Ch.	0.6	150 W xenon arc	3
Oxy–hydrogen	T.C.	0.1	450 W xenon arc	4
Hydrogen–ent. air	T.C.	0.03	450 W xenon arc	4
Oxy–hydrogen	T.C.	0.04	Osram vapour lamp	5
Oxy–acetylene	T.C.	0.04	Osram vapour lamp	5
Oxy–hydrogen	T.C.	0.6	150 W xenon arc	6
Oxy–hydrogen	T.C.	0.0001	Osram vapour lamp	7
Air–hydrogen	T.C.	0.0005	Phillips vapour lamp	8
Air–hydrogen	Ch.	0.0002	Electrodeless dis. tube	14
Nitrogen separated air–hydrogen	Ch.	0.005[b]	Electrodeless dis. tube	9
Air–propane	Ch.	0.002	Electrodeless dis. tube	10
Air–hydrogen	T.C.	0.00004	Electrodeless dis. tube	11

[a] Ch. = chamber type; T.C. = total consumption type.
[b] Result obtained with a solar-blind photomultiplier as a detector.

Experimental

The modified Southern Instruments A 1740 Grating Flame Photometer used has been described previously[13]. The source of irradiation employed was a microwave-powered zinc electrodeless discharge tube[14], placed immediately behind an asbestos screen with a 3 cm × 1.5 cm slit, as close as possible to the relevant burner. A Beckman total consumption burner was used to burn turbulent, approximately stoichiometric oxy–hydrogen and air–hydrogen flames, and for air–acetylene (or hydrogen) the original A 1740 burner head was replaced by a Unicam SP900 air–acetylene head *via* a suitable stainless-steel adaptor. The resulting burner was used to burn pre-mixed air–hydrogen and air–acetylene flames, both slightly fuel-rich.

Solutions. 1000-p.p.m. solutions were made up from analytical reagent-grade zinc sulphate, and zinc metal dissolved in the minimum volumes of hydrochloric acid and nitric acid.

Diverse ions. Solutions were made up for a range of metals, from chlorides and nitrates; analytical reagent-grade salts were used whenever possible.

Results and discussion

Calibration curves. Figure 1 shows the calibration curves obtained in the four flames investigated. Zinc chloride, nitrate and sulphate were found to give identical calibration curves within the limits of experimental error in all four flames. Measurements were made at the height in the flame which gave the optimum signal-to-noise ratio at low concentrations: all measurements were made with a nominal 6-nm bandpass and a 10-sec integration period. A 0.1-p.p.m. zinc solution was nebulised between each reading to ensure that no significant source drift had occurred. The earlier incidence of curvature in the calibration curves obtained with the turbulent flames can be partially attributed to greater self-absorption. This arises because of the existence of appreciable populations of ground-state atoms outside this type of flame at the heights used for measurement, *i.e.* 10 cm and 7 cm for oxy–hydrogen and air–

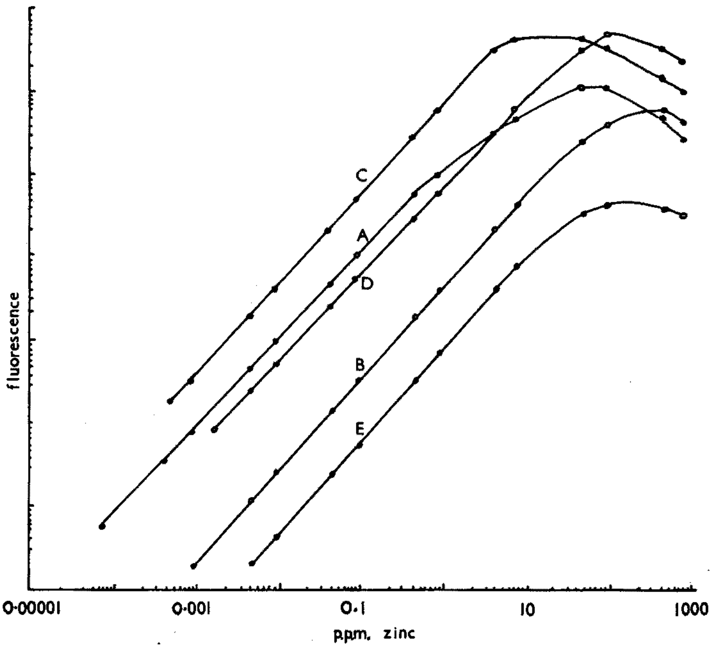

Fig. 1. Calibration curves for zinc in: (A) Oxy–hydrogen, (B) air–hydrogen (pre-mixed), (C) air–hydrogen (turbulent), (D) air–acetylene (pre-mixed), (E) fuel-lean oxy–hydrogen (turbulent).

hydrogen respectively. When a small, very fuel-lean oxy–hydrogen flame was used on the total consumption burner, the incidence of curvature was reduced.

Detection limits. The detection limits obtained are shown in Table II. The detection limit was taken as the concentration for which the signal is twice the standard deviation at that concentration: the use of the integration facility does not readily permit the use of signal–noise ratios for the calculation of a detection limit.

TABLE II

DETECTION LIMITS FOR ZINC AT 213.9 nm[a]

Flame	*Burner type*	*Detection limit (p.p.m.)*
Air–acetylene	Chamber	0.002
Air–hydrogen	Chamber	0.001
Air–hydrogen	Total consumption	0.0005
Oxy–hydrogen	Total consumption	0.0001

[a] All detection limits were measured under optimum signal–noise conditions with the same electrodeless discharge tube source.

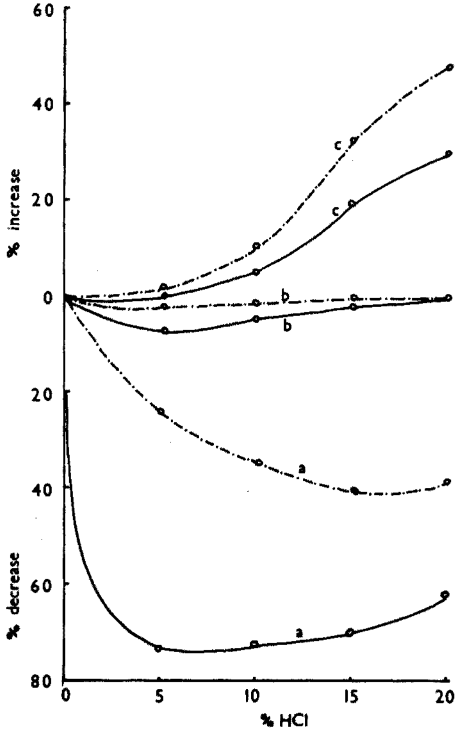

Fig. 2. Effect of hydrochloric acid on the fluorescence from (a) 0.1 p.p.m., (b) 1.0 p.p.m. and (c) 10.0 p.p.m. zinc in turbulent flames: (—) oxy–hydrogen and (-.—.) air–hydrogen.

Effect of hydrochloric acid. BRATZEL *et al.*[15] studied the effect of hydrochloric acid on the fluorescence of cadmium in a turbulent, fuel-rich oxy-hydrogen flame, and found that although enhancement was obtained at high concentrations (100 p.p.m. of cadmium), depression occurred at lower concentrations. A similar type of effect was found here for zinc, in both of the turbulent flames investigated (Fig. 2), but to a lesser extent in the pre-mixed air–hydrogen flame. GIDLEY AND JONES[16] have reported interference of hydrochloric acid in the determination of zinc which they attributed to absorbance by molecular species, and undoubtedly viscosity, surface tension and density effects also play an important part, but these effects should give a similar decrease in signal over the range investigated. This was found to be the case only when the pre-mixed air–acetylene flame was used, and with this flame, although the calibration curve was appreciably less sensitive, it was not distorted at constant acid concentrations. When turbulent flames were used, however, the fluorescence emission profiles were found to vary appreciably with both acid concentration, and also with zinc concentration, which indicates that zinc compound formation plays an important part in the interference mechanism in turbulent flames, by affecting the ground-state atom distribution.

Cationic interferences. The interference effects of 24 cations were examined at 1000-fold excess in each of the flames investigated (Table III). Although all of the interferences encountered in the turbulent flames were enhancements, attributable to scatter of the source radiation, which is very significant at the wavelength used for zinc, some of the results appear initially to be anomalous, and the effect of increasing amounts of interfering ion was therefore examined in detail for Al, Ca, Cu, Mg and Na. The scatter signal from the interfering cations alone was also examined; when this signal was subtracted from the total signal, corrected curves were obtained. These curves were generally of the form shown in Fig. 3, and were similar to the interference effect often encountered in atomic absorption, indicating that the apparent interference can differ from the true interference. However, 20,000-fold amounts of aluminium gave enhancements of 50% and 100 % in turbulent oxy–hydrogen and air–

TABLE III

EFFECT OF 1000-FOLD EXCESS (w/w) OF VARIOUS CATIONS ON THE DETERMINATION OF 0.1 p.p.m. ZINC BY FLUORESCENCE AT 213.9 nm

Flame	*% Interference from–to*	*Cations*
Oxy–hydrogen, turbulent	0–5	Al, Bi, Ca, Cd, Cr, Hg, In, K, Mg, Mn, Na, Se
	5–10	Cu, Mo
	10–20	Co, Fe, Ni, Pb, Tl
	>20	Ba, Sn, V
Air–hydrogen, turbulent	0–5	Cd, Cr, Cu, Hg, In, K, Na, Se, Tl
	5–10	Al, Co, Ni, Pb, Sn
	10–20	Ca, Mg, Mo, V
	>20	Ba, Bi, Fe, Mn
Air–hydrogen, pre-mixed	0–5	Al, Cd, Co, Cr, Cu, Hg, Na, Ni, Pb, Se, Tl
	5–10	Ba, Bi, Ca, Fe, In, K, Mg, Mo, Sn, V
	10–20	Mn
	>20	None
Air–acetylene, pre-mixed	0–5	Al, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, In, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sn, Tl, V
	>5	None

hydrogen flames, respectively, which could not be attributed to scatter alone. The effect was found to be due to appreciable changes in the fluorescence emission-height profile, *i.e.* the ground-state atom distribution in the flame. In pre-mixed air–acetylene flames, the same concentration of aluminium gave a 6% decrease in signal.

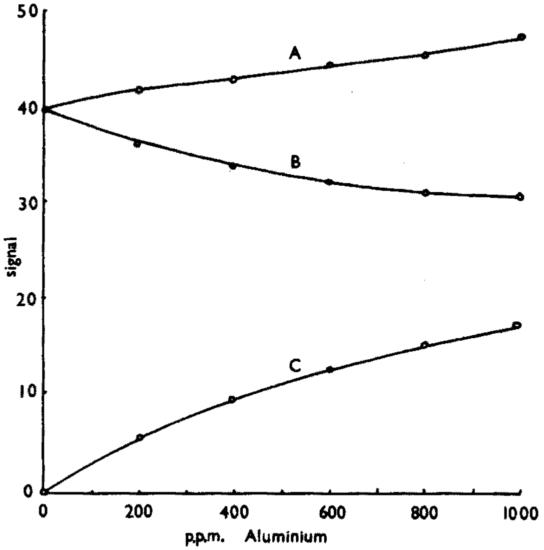

Fig. 3. Effect of aluminium on zinc fluorescence (0.1 p.p.m. zinc). (A) Uncorrected curve, (B) corrected curve, (C) curve from aluminium alone. Oxy–hydrogen (turbulent) flame.

Conclusions

The results obtained indicate that turbulent oxy–hydrogen flames are most suitable for the determination of very small traces of zinc when the foreign ion content is low, but that the laminar, pre-mixed air–acetylene flame is more suitable for the determination of zinc in the presence of variable amounts of diverse ions, although the detection limit obtained is less favourable than in the cooler flame. The hotter flame also appears to be much less susceptible to interference caused by variation in ground-state atomic distribution than the turbulent hydrogen flames.

It is clearly most important from a practical viewpoint that thermally efficient flames such as air–acetylene, rather than cool ones such as air–hydrogen, should be used for atomic fluorescence as for atomic absorption.

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The determination of calcium in steel by optical emission spectrometry

Certain non-metallic inclusions in steel have a deleterious effect on steel properties, particularly fatigue strength and surface finish. Inclusions may be classified as inherent or exogenous, the former resulting from deoxidation additions and precipitation during cooling, and the latter from included debris such as refractory lining and slags[1]. Generally, exogenous inclusions in steel are undesirable and electron probe micro-analyses in these laboratories have shown the presence of $CaO.6Al_2O_3$ inclusions containing about 8% (w/w) calcium oxide. KEISSLING AND LANGE[2] have reported $3CaO.Al_2O_3.3SiO_2$ inclusions containing about 40% (w/w) calcium oxide, and FRANKLIN *et al.*[3] have shown that inclusions containing significant calcium levels can originate from impurities present in ferro-alloy additions.

Calcium, unlike aluminium and silicon which are usually added to steel, may be used as a trace element to monitor the extent and origin of certain exogenous inclusions. Calcium determinations can assist deoxidation studies when calcium alloys are used to finish certain steels and can provide quantitative information to supplement electron probe micro-analyses.

Most steels contain less than 20 μg/g of calcium and methods for the determination usually involve a dissolution and separation technique, before analysis. SCHOLES[4], HEADRIDGE AND RICHARDSON[5] and TAYLOR AND BELCHER[6] used atomic absorption spectrophotometry, VASSILAROS AND MCKAVENEY[7] used a mercury cathode separation and rotating-disk optical emission spectrography, and ADACHI *et al.*[8] precipitated calcium fluoride before determination by optical emission spectrography. These procedures are destructive of the sample, have blank difficulties and are time-consuming.

TAYLOR AND BELCHER[6] have established the calcium concentration of a series of steel samples and thereby allowed an investigation of the rapid determination of calcium in plain carbon and stainless steels by point-to-plane, direct-reading, optical emission spectrometry[9]. The rapid reporting of calcium concentrations together with the other elements of importance could further assist the quality control of steelmaking.

Experimental

Spectrometer. Jarrell-Ash 2 m; direct reading model 66-105; dispersion, 0.42 nm/mm; wavelength ranges, 175–210 and 220–420 nm; vacuum, 0.65 N/m^2.

Electrical parameters. Power circuit—pulse arc, 5 Ω, 50 μH, 19 μF, 11A r.f., 900 V, 100 discharges/sec. Initiator circuit—high voltage spark, 13 kV, 2.5 nF, residual inductance, 30 Ω primary, < 1 Ω secondary, 3A r.f.

Electrode system. Silver 6.55 mm diam., ASTM C5A tip, gap 4 mm, argon 10 l/min, sample negative, finished on 80-grit Al_2O_3 discs.

Exposure conditions. Pre-flush, 10 sec; pre-burn, 20 sec; integration, 30 sec (time terminated).

Slit widths and wavelengths. Entrance slit, 25 μm; exit slit, Ca 315.89 nm, 75 μm; exit slit, Ca 396.85 nm, 75 μm.

Results and discussion

A study of wavelengths within the range of the spectrometer[10–12], indicated that Ca 396.85 nm could be sufficiently sensitive and free from interference for the determination of trace levels of calcium in steel. The suitability of Ca 315.89 nm for the determination of calcium in chromium-free steels was investigated, since this wavelength is used frequently for the analysis of oxides. Ca 317.93 nm and Ca 393.37 nm respectively, were not considered suitable because of potential interference by B, Mo, Ti and Cr, and by iron.

The excitation conditions chosen for the investigation are similar to a suggested method of THE AMERICAN SOCIETY FOR TESTING AND MATERIALS[9] for the spectrochemical analysis of steel; however, the method has not previously been applied to the determination of calcium. The integration period was terminated by time rather than reference to iron as internal standard, because the iron contents of the samples ranged from 52 to 98%. The relatively long pre-burn (20 sec) and integration times (30 sec) are used to minimise segregation and sample history effects although shorter times are applicable in quality control situations.

The calcium concentration and the alloy composition of the steels[6] used in the study are shown in Table I. The calibration graphs obtained with Ca 396.85 nm and Ca 315.89 nm are shown in Fig. 1, but the high chromium steels have not been plotted for Ca 315.89 nm. Excellent sensitivity and freedom from interference was obtained with Ca 396.85 nm. The expected serious interference by Cr 315.88 nm on Ca 315.89 nm was confirmed and for the chosen conditions, 1% chromium was equivalent to an interference level of 20 μg/g calcium; however, useful results can be obtained provided that chromium contents are low ($Cr < 0.1\%$).

TABLE I

CALCIUM CONCENTRATION AND ALLOY COMPOSITION OF STEELS USED IN STUDY

Sample no.[a]	*Nominal composition (%)*	*μg/g Ca*
NBS 1167	0.1C, 0.3Mn, 0.04Cr, 97Fe	1
BCS SS31	0.5C, 0.4Mn, 0.1Cr, 98Fe	14
BCS SS35	0.3C, 0.7Mn, 0.2Cr, 98Fe	20
BHP SS69	3.8Si, 1.1Nb, 0.03Cr, 95Fe	47
BHP SS78	0.5Si, 0.5Mn, 13Cr, 86Fe	18
BHP SS112	1.0Mn, 21Ni, 24Cr, 52Fe	36
BHP SS113	0.5Mn, 5Ni, 26Cr, 67Fe	18
BHP SS128	1.2Mn, 10Ni, 19Cr, 68Fe	3

[a] NBS = National Bureau of Standards (U.S.A.).
BCS = British Chemical Standard.
BHP = Broken Hill Proprietary Co., Ltd.

Inclusions may be heterogeneously distributed in steel, and since calcium is associated mainly with exogenous inclusions, a study of the attainable precision and any influencing factors was warranted. British Chemical Standard SS35 was selected for a precision study and metallographic and electron probe micro-analyses, because this steel was known to be specially melted and tested for homogeneity for use as a spectrographic standard.

The inclusions present in BCS SS35 were found to be small, being generally less than 5 μm and evenly dispersed. The calcium-bearing inclusions were found to be galaxite with an analysed composition of 58% Al_2O_3, 40% MnO, 1% CaO and 0.2% MgO. The relatively small size and the low calcium content of the inclusions would contribute to the good precision (Table II) (relative standard deviation or Sr* = 0.035 at 20 μg/g) obtained with the Ca 396.85 nm line and confirms the inherent precision of the developed procedure when applied to homogeneous steel samples. The poorer signal/-background ratio for Ca 315.89 nm is evident in Fig. 1 and is reflected by the poorer precision (relative standard deviation or Sr = 0.093) shown in Table II; however, this

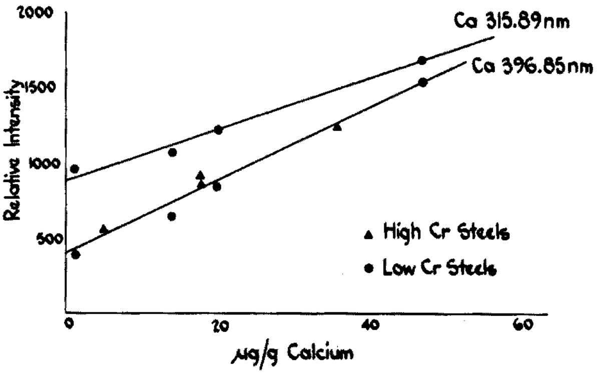

Fig. 1. Calibration graphs obtained with Ca 396.85 nm and Ca 315.89 nm for steels listed in Table I.

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*For definition of Sr see R. W. FENNELL AND T. S. WEST, *Pure and Applied Chemistry*, Vol. 18, No. 3, 1969.

TABLE II

A STUDY OF THE PRECISION OBTAINED WITH STEEL SAMPLE BCS SS35

Data	*Ca 396.85 nm*	*Ca 315.89 nm*[a]
n	12	12
Range (μg/g)	19.0–21.5	19.0–26.0
Mean (μg/g)	20.1	22.5
1s (μg/g)	0.7	2.1
Relative standard deviation	0.035	0.093

[a] Uncorrected for chromium interference.

level of precision is not uncommon for this concentration level in optical emission spectrometry.

The proposed procedure may be applied to the routine analysis of steel samples and the results can be related to the parameters used to assess inclusion levels in particular steel grades or to assist calcium deoxidation studies. Increased data concerning calcium levels should become available and the information should prove valuable to investigations relating to non-metallic inclusions in steel.

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The accurate determination of trace amounts of europium in aluminium

The high neutron-absorption cross-section of europium makes a precise determination of its value important. Recent requests for well-defined samples to perform such measurements created the problem of accurate determination of this element. The samples were prepared by a high-frequency levitation technique[1] as Eu/Al alloys at the 1%, 20 p.p.m. and 2 p.p.m. Eu levels. This communication reports the accuracy that can be achieved in the determination of europium at these levels.

Many papers describe the determination of traces of rare earths in different materials. Most recent analyses have been done by neutron activation procedures[2-5] or by high-voltage spark spectrography combined with chemical separations[6,7]. Although these methods offer satisfactory sensitivities, their accuracy does not appear to have been adequately demonstrated. The mass spectrometric stable isotope-dilution method has been recently used for the determination of rare-earth elements in rocks and minerals with variable results[8], but possible systematic errors were not considered and again the accuracy was not fully evaluated.

Outline of the stable isotope-dilution method

If an unknown amount (N_T moles) of a bi-isotopic element is spiked with a known amount (N_S moles) of an isotopically enriched sample, the atom ratio $q = N_T/N_S$ and the weight ratio $p = M_T/M_S$ of the two amounts can be calculated[9] when the resulting isotopic blend (isotopic ratio R_B) is measured:

$$q = \frac{R_S - R_B}{R_B - R_T} \cdot \frac{1 + R_T}{1 + R_S}$$

$$p = \frac{R_S - R_B}{R_B - R_T} \cdot \frac{1 + \gamma R_T}{1 + \gamma R_S}$$

where γ = ratio of the relative atomic masses concerned. The subscripts T and S refer to the sample (target) and to the spike, respectively.

For the present determination, an enriched ^{151}Eu sample was available for use as a spike: ^{151}Eu, 92.009±0.059 atom %; and ^{153}Eu, 7.991±0.059 atom %; hence $R_S = {}^{151}\mathrm{Eu}/{}^{153}\mathrm{Eu} = 11.514$.

The europium used in the preparation of the alloys was verified to be natural: ^{151}Eu, 47.86±0.19 atom %; and ^{153}Eu, 52.14±0.19 atom %; hence $R_T = {}^{151}\mathrm{Eu}/{}^{153}\mathrm{Eu} = 0.918$.

Further[10], $\gamma = 150.919838/152.921242$.

It is possible to choose the amount M_S of spike to be added so as to minimize the propagated statistical uncertainty on q and p. An optimum ratio p or q of approximately 0.5 is found, considering the variance of q or p:

$$\sigma^2(p) = \mathrm{f}[p, R_T, R_S, \sigma^2(R_T)\ \sigma^2(R_S)]$$

The actual determination then proceeds as follows: (*a*) determination of R_T by measuring the isotopic composition of the europium used; (*b*) determination of R_S by measuring the isotopic composition of the spike; (*c*) determination of N_S per gram of solution by chemical analysis of the spike; (*d*) weighing and dissolution of alloy samples (the isotope dilution calculation will yield N_T and the mass of the alloy sample will allow calculation of the concentration (N_T/g)); (*e*) blending of sample and spike solution aliquots so that $q \simeq 0.5$, the solution aliquots being accurately weighed; (*f*) determination of R_B in the spiked europium samples, after removal of the excess aluminium.

Preparation of samples for mass spectrometric measurements

Assay of the spike. The europium spike was determined by titration with EDTA solution which had been standardized against primary standard zinc.

The reproducibility of the EDTA titration was 0.1% (s, $n=8$). The ^{151}Eu sample in the oxide form was calcined at 900° overnight to insure stoichiometric reaction (Eu/Eu_2O_3 conversion factor = 0.86292; Eu atomic weight = 151.080).

The oxide was dissolved in hydrochloric acid, diluted to a definite volume and weighed. Several weighed aliquots of the resulting solution were assayed by titration with EDTA solution at pH 5.8 (hexamethylenetetramine buffer) in the presence of xylenol orange indicator. The reproducibility of the titrations was 0.29% (s, $n=5$); the results agreed within 0.13% with the theoretical Eu_2O_3 stoichiometry. A spectrographic analysis of the spike sample indicated 0.02% samarium and 0.05% calcium as impurities. The samarium contribution determination was corrected for in the calculation of the final result. Calcium does not interfere in the EDTA titration under the conditions used.

An aliquot of the spike base solution was diluted in order to arrive at a ^{151}Eu solution which contained 7.81 μg of europium per g. Errors from the metrological determinations were negligible (maximum error of the complete procedure <0.01%). Experience of rare-earth titrations with EDTA in known solutions at the same semi-micro level (a total amount of about 10 mg of enriched ^{151}Eu sample was available for the determination) has shown agreement between observed and known values within the statistical uncertainty of the present determination. From all the considerations given, the total accuracy of the ^{151}Eu solution is estimated to be 0.5%.

Blending of sample and spike. Because of the large difference of the europium/aluminium ratio in the three samples analyzed (1%, 20 p.p.m., 2 p.p.m.), the amounts used for the determination were different depending on the europium content.

For the 20-p.p.m. europium sample, about 1 g of alloy was used, while for the 2 p.p.m. and 1% europium samples the analyses were carried out on 2 g and 0.1 g respectively. Samples were dissolved in hydrochloric acid and weighed aliquots of the spike solution were added in order to achieve a Eu sample/Eu spike ratio of about 0.5.

Separation of europium and aluminium. Solvent extraction was chosen for the separation of europium from the large excess of aluminium which hampered the isotopic analysis. Many chelate systems can be used for the extraction of the rare earths; a common and successful one is the lanthanide-1-(2′-thenoyl)-3,3,3-trifluoroacetone (TTA) system. The extraction behaviour of the rare-earth chelates with TTA has been thoroughly studied[11-13] and analytical procedures for their isolation have been given[14,15]. Since aluminium can be co-extracted by TTA, sulfosalicylic acid was used as a masking agent for the effective separation of europium[16].

According to tests carried out with ^{152}Eu and ^{154}Eu as tracers, the procedure allows an excellent and reproducible recovery (87±1%) of europium. This value can amount to 98% when the starting aqueous phase is treated twice more with TTA.

Spectrophotometric determinations of aluminium in the final aqueous phases of the extraction scheme showed that the europium/aluminium separation factor is large: $D_{\mathrm{Eu}}/D_{\mathrm{Al}}=9\cdot10^4$.

For the determination of the 20-p.p.m. europium samples, 200 ml of an aqueous 20% (w/v) sulfosalicylic acid solution was added to the spiked solution containing 1 g of the 20-p.p.m. europium sample in about 150 ml. A pH of 4.65 ± 0.05 was obtained by means of concentrated ammonia solution.

The resulting solution was mixed for 30 min with 10 g of TTA dissolved in 100 ml of xylene. The europium was then back-extracted from the organic phase by mixing it for 10 min at 60° with two 25-ml portions of *M* hydrochloric acid. After washing with 25 ml of xylene, the hydrochloric acid phase was concentrated to 0.5 ml and analyzed by mass spectrometry. For the other samples, the procedure was essentially the same, provided that an adequate amount of aluminium masking agent was used.

Measurement of isotopic composition of the blends

The isotopic measurements were performed on a 12″–90° thermal ionization mass spectrometer with tungsten filaments. The ions measured were $^{151}\mathrm{Eu}^+$ and $^{153}\mathrm{Eu}^+$. Samples of 10–50 μg deposited on a tungsten filament yielded sufficiently strong and stable ion currents ($\sim10^{-12}$ A) to be measured on a plate collector. Two filaments loads were measured for each sample and from each load one $^{151}\mathrm{Eu}/^{153}\mathrm{Eu}$ ratio value was determined as the average of 6–10 measured isotopic ratios. The mean of the two load values was taken as the result R_{B} for the sample concerned. The computed europium concentrations in each alloy sample are summarized in Table I. Similarly, the spike was isotopically analyzed (R_{S}), and europium was extracted from a prepared alloy (R_{T}).

Determination of europium in pure aluminium

Aluminium. Four samples of pure aluminium were dissolved, spiked and other-

TABLE I

ISOTOPIC COMPOSITION OF THE BLENDS

($R_{\mathrm{T}}=0.918$; $R_{\mathrm{S}}=11.514$. Concentration of Eu in spike solution: 7.81 μg Eu/g)

Sample number	*Concentration of Eu in alloy (weight p.p.m.)*	*Sample number*	*Concentration of Eu in alloy (weight p.p.m.)*
L1 (20 p.p.m.)	15.09[a]	L1A (2 p.p.m.)	1.978
L2 (20 p.p.m.)	19.53	L1B (2 p.p.m.)	1.941
L3 (20 p.p.m.)	19.62	L1C (2 p.p.m.)	1.966
Pure Al	$\leqq$ 0.020	L5A (1%)	9884.24
L1 (20 p.p.m.)	19.59	L5B (1%)	9798.11
L2 (20 p.p.m.)	19.34	L5C (1%)	9812.27
L3 (20 p.p.m.)	19.55	Pure Al	0.079
Pure Al	$<$ 0.02	Pure Al	$<$ 0.02
L1 (20 p.p.m.)	19.59	Blank reagents	$<$ 0.02
L2 (20 p.p.m.)	19.29		
L3 (20 p.p.m.)	19.33		
L1 (20 p.p.m.)	19.10		
L1 (20 p.p.m.)	19.63		

[a] Obviously the first determination was subject to an unidentified gross error; it was rejected.

wise treated in the same way as the alloys in order to determine a possible europium content. In three cases, ≦0.02 p.p.m. was found, and in a fourth, 0.08 p.p.m. As the sensitivity of the method is calculated to be of the order of 0.02 p.p.m., the "natural" europium content of the aluminium is ≦0.02 p.p.m., the 0.08 p.p.m. figure possibly being caused by a slight europium contamination.

The complete procedure was performed without any aluminium or alloy sample in order to determine its blank europium level, which was found to be <0.02 μg.

Results and discussion

The results as well as the different uncertainties which lead to the final accuracy are summarized in Table II. It can be concluded that a final accuracy of 1.3% on the 20-p.p.m. determination and 4% on the 2-p.p.m. determination can be achieved.

TABLE II

RESULTS AND DIFFERENT UNCERTAINTIES

Nominal Eu content of the alloys	*1%*	*20 p.p.m.*	*2 p.p.m.*
Mean	0.9831% ($n=3$)	19.46 p.p.m. ($n=10$)	1.963 p.p.m. ($n=3$)
Statistical uncertainties			
s_{int}	0.0064 (0.65%)	0.13 (0.65%)	0.013 (0.65%)
s_{ext}	0.0046 (0.53%)	0.18 (0.93%)	0.019 (0.96%)
$\bar{s}_{\text{ext}}$	0.0027 (0.31%)	0.057 (0.30%)	0.011 (0.56%)
$t_{0.05}\bar{s}_{\text{ext}}$	0.0114 (1.3%)	0.13 (0.66%)	0.047 (2.4%)
Uncertainties on systematic error corrections (%)			
Spike definition	0.5	0.5	0.5
Spike/sample blending	0.05	0.01	0.01
Possible mass spectrometric bias	0.15	0.15	0.15

The determination is believed to be specific because of the nature of the method (only the interaction of the known amount of europium spike isotopes with the unknown amount of europium sample isotopes is measured). The internal standard deviation s_{int} calculated by normal propagation of error is independent of the concentration of the element over a wide range of concentrations (2 p.p.m.–1%) at a high precision level (0.65%). The uncertainty on the chemical definition of the spike—in this case 0.5%—must be added to the precision of the determination as a possible maximum systematic uncertainty. The blending error resulting from the weighing of aliquots of sample and spike is almost negligible (0.01–0.05%).

Since the mass spectrometer was not calibrated for europium, the mass spectrometric measurements are subject to systematic errors. From experience with other ions ($Na_2BO_2^+$ and U^+), this possible error is estimated to be maximally 0.3%. If this is included in the final value of the isotope-dilution determination, one finds a possible error on the europium content of the alloy of 0.15%.

In the case of the 1% europium sample a direct chemical determination of europium in presence of aluminium is possible by EDTA titration[16]. This determination was carried out and the result was 0.986_1. The reproducibility of the titrations was 0.4% (s, $n=8$). The result agrees with the result obtained by isotopic dilution within 0.3%.

This work was carried out as part of the "Sample Preparation and Assaying" activity of CBNM. The samples described can be obtained on request. Each sample is issued with certified chemical concentration, isotopic composition and weight.

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Application of atomic absorption spectrometry to the determination of cobalt in cobalt(III) complexes

Most of the conventional methods for the determination of cobalt are based on formation of complexes with the trivalent metal ion. When the samples to be analysed contain the metal in the form of inert complexes, these must first be broken down. Detailed investigations have shown that in the case of various complexes this destructive treatment before the determination of cobalt can be avoided if atomic absorption spectrometry with a laminar propane–air flame is employed.

Experimental

A sample of pure complex (50 mg) containing ligands such as ammonia, ethylenediamine (en), trimethylenediamine (tn), nitro, cyanide, and EDTA was dissolved in 1 l of water containing 2 drops of wetting agent (household liquid detergent was satisfactory) and 5 ml of concentrated hydrochloric acid. The absorption of the resulting solution was measured on a Zeiss spectrophotometer PMQII fitted with the flame accessory FA2. As recommended by Zeiss the slit burner with a laminar air–propane flame was used. The hollow-cathode lamp current was 15 mA and absorbances were measured at the 2407.25 Å resonance line with a bandpass of 0.7 Å. The final result for each complex was based on three solutions, the absorbances of which were measured three times each by integration of the absorbance over 1 min.

The purity of the samples was checked by electrogravimetry using an IKA electrolysis apparatus EN 401 (Janke und Kunkel, Staufen im Breisgau, Western Germany) fitted with Fischer electrodes of platinum gauze (nos. 72139 and 72140, Johnson, Matthey and Co., Ltd.). In a standard procedure devised by BROPHY[1] about 0.2 g of cobalt is electrolyzed for 20 min at 2 A in a cold bath containing 20 ml of concentrated ammonia liquor, 5 g of sodium disulfite and 12 g of ammonium chloride in 300 ml of water. It was found necessary to modify this procedure by further addition of 25 g of sodium sulfite and heating the solution to 60° for satisfactory electrolysis of most of the complexes.

TABLE I

COMPARISON OF THE RESULTS FROM ATOMIC ABSORPTION SPECTROMETRY (a.a.) WITH THOSE FROM ELECTROGRAVIMETRY (e.g.)

	Calc.	*A.a.*	*E.g.*
$[Co(H_2O)_6]Cl_2$	24.77	Standard	24.80 ± 0.02
$[Co(NH_3)_6]Cl_3$	22.03	$21.9_6 \pm 0.0_6$	22.22 ± 0.02
$[Co(en)_3]Cl_3 \cdot 3H_2O$	14.75	$14.6_2 \pm 0.0_9$	14.76 ± 0.01
$[Co(en)_2(tn)]Cl_3 \cdot 2H_2O$	14.89	$14.9_8 \pm 0.0_6$	—[a]
$[Co(tn)_3]Cl_3 \cdot 2H_2O$	13.91	$13.8_0 \pm 0.1_7$	13.85 ± 0.05
$[Co(NH_3)_5Cl]Cl_2$	23.53	$23.4_2 \pm 0.1_0$	23.44 ± 0.02
$[Co(NH_3)_5NO_2]Cl_2$	22.58	$22.7_5 \pm 0.2$	22.70 ± 0.08
$[Co(NH_3)_5ONO]Cl_2$	22.58	$22.7_8 \pm 0.1_3$	22.63 ± 0.02
$[Co(NH_3)_4CO_3]NO_3 \cdot \frac{1}{2}H_2O$	22.83	$22.9_8 \pm 0.1_0$	22.99 ± 0.02
cis-$[Co(en)_2Cl_2]Cl \cdot 1\frac{1}{2}H_2O$	18.86	$18.8_2 \pm 0.0_8$	18.92 ± 0.01
trans-$[Co(en)_2(NO_2)_2]NO_2 \cdot 2H_2O$	16.69	$16.6_8 \pm 0.0_8$	—[a]
$NH_4[Co(EDTA)]$	19.07	$9.4_8 \pm 0.2_0$	0.00
$K_3[Co(CN)_6]$	23.19	$13.4_5 \pm 0.4$	0.00

[a] Sufficient material was not available for the determination.

Results and discussion

Table I shows the excellent agreement of the atomic absorption results with both the electrogravimetric and calculated values for all but the EDTA and hexacyano complexes. The low result for the EDTA complex may be caused by a partial transformation of cobalt to oxide by the thermal decomposition of the metal–carboxylate bond. For the cyano complex the low result may be explained by the high thermal stability of the transition metal cyanides resulting in an incomplete decomposition of the complex in the flame.

The relative precision of the atomic absorption spectrophotometric method was found to be 0.6%, and that of the electrogravimetric method to be 0.2%. However, the accuracy of the two methods appears to be very similar. As only 10 ml of solution is required for a single determination corresponding to a sample size of less than 1 mg, we may conclude that atomic absorption spectrometry can serve as a convenient method for the microdetermination of cobalt in these types of complex. The propane–air flame will suffice for the determination in amine and nitro complexes, while EDTA and cyano compounds will need a hotter flame.

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BOOK REVIEW

Methods of Biochemical Analysis, Edited by DAVID GLICK, Vol. 17, Interscience Publishers–J. Wiley & Son, Inc., New York, 1969, viii + 428 pp., price 155 s.

Four of the articles in this latest volume in the series deal with important methods of wide application and four are concerned with the determination of particular compounds. M. A. LESSLER AND G. P. BRIERLEY deal with oxygen electrode measurements in biochemical analysis. This technique is of great current interest and the article, although relatively brief, is a timely addition to the series. Practical aspects of liquid scintillation counting are described by Y. KOBAYASHI AND D. V. MAUDSLEY in a long contribution which also deals in detail with sample preparation. W. O. CASTER gives a critical evaluation of the gas chromatographic technique for identification and determination of fatty acid esters, with particular reference to the use of analog and digital computer methods. Current methods are reviewed, particularly from the stand-point of the quantitation of results using conventional instrumentation and automatic data handling procedures. The longest article in this volume is by M. ROTH who deals exhaustively with the fluorimetric assay of enzymes. This contribution occupies nearly one hundred pages and includes a bibliography of 423 references. The first of the reviews dealing with particular compounds is by R. BRODERSEN AND J. JACOBSEN and is concerned with the separation and determination of bile pigments. Recommended procedures for the determination of bilirubin and its conjugates are described. E. ROBINS discusses the measurement of phenylalanine and tyrosine in blood, describing fluorimetric methods and bacterial inhibition assay. A. KAPLAN writes on the determination of urea, ammonia and urease. Finally JANE E. SHAW AND P. W. RAMWELL contribute a topical account of the separation, identification and estimation of prostaglandins together with an extensive list of references. It will be clear from this list of contents that *Methods of Biochemical Analysis* continues to keep abreast of modern techniques and for this reason continues to fulfil its purpose and to provide an invaluable service for biochemical research.

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