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GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

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

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

Manuscripts

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

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

Figures should be drawn in Indian ink on drawing or tracing paper with all lettering in **thin** pencil. Standard symbols be used in line drawings; the following are available to the printers:

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References should be given at the end of the paper and should be numbered in the order of their appearance in the text (**not** arranged alphabetically). Abbreviations of journal titles should conform to those adopted by the *Chemical Abstracts List of Periodicals*, 1961 Edition and supllements. The recommended form for references to journal papers and books is as follows:

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

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

Summaries are published in English, French and German; authors must always provide a summary in the language of the paper, and are encouraged to supply translations where convenient. No summaries are needed for Short Communications.

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Analytica Chimica Acta has three issues to the volume, and four vols. will appear in 1970. Subscription prices: \$ 17.50 or Dfl. 63.— per volume; \$ 70.00 or Dfl. 252.— for 1970, plus postage. Additional cost for copies by airmail available on request. For subscribers in the U.S.A. and Canada, 2nd class postage paid at New York, N.Y. For advertising rates apply to the publishers.

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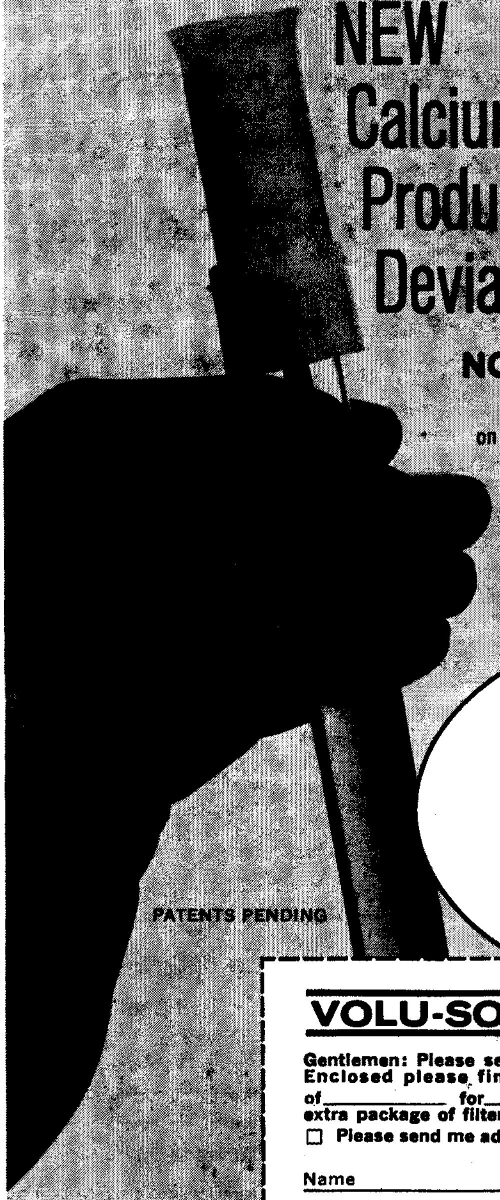

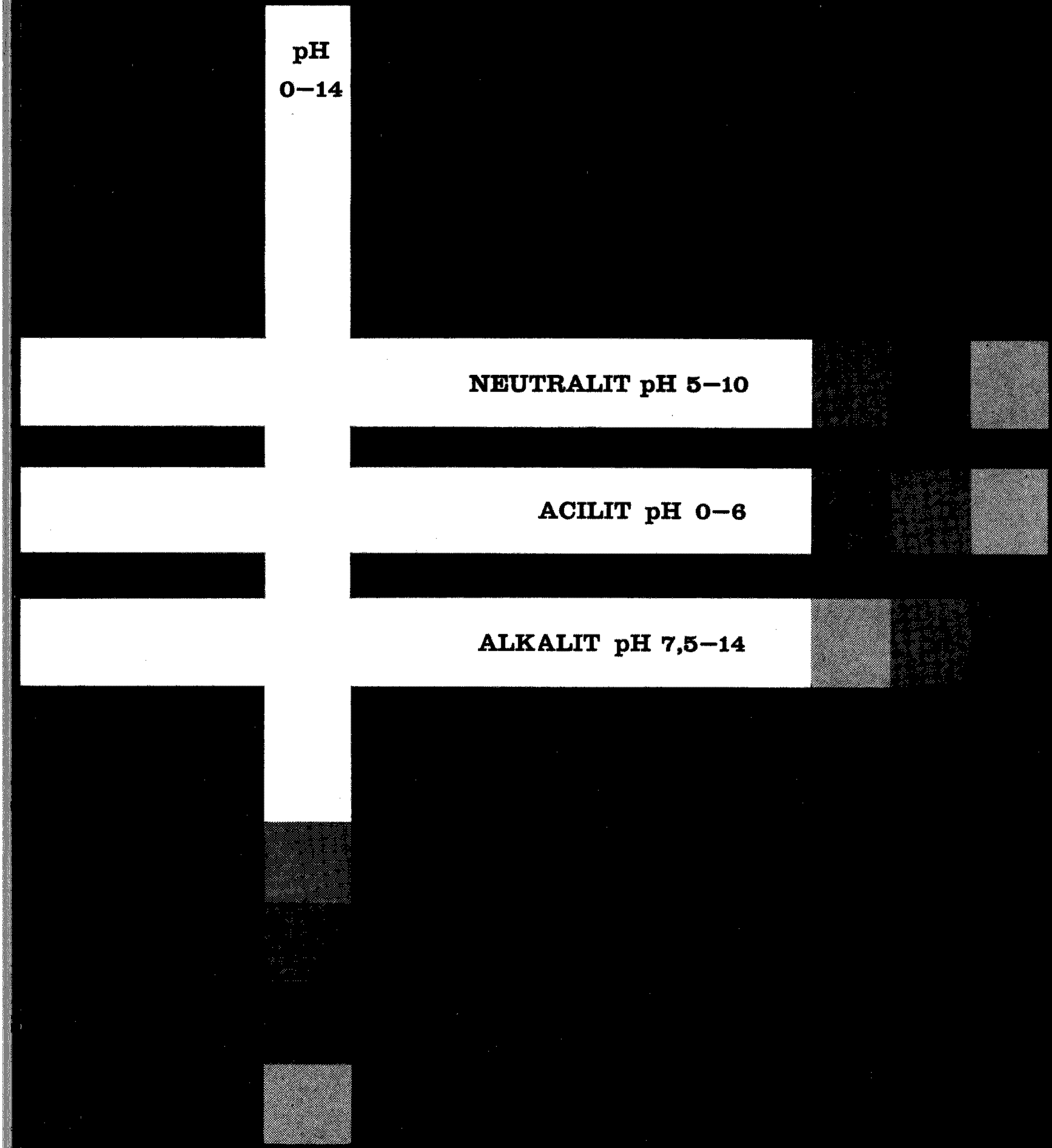
pH
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NEUTRALIT pH 5–10
ACILIT pH 0–6
ALKALIT pH 7,5–14

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 49, No. 2, February 1970

TITRATIONS WITH COMPLEXING AGENTS FORMING MONONUCLEAR AND BINUCLEAR COMPLEXES WITH METALS

The general theory of titrations with complexing agents forming metal complexes in which the metal:ligand ratios are 1:1 and 2:1 is discussed, and rules are given for the calculation of conditional constants. The theory is applied to the titration of manganese and copper with triethylenetetraminehexaacetic acid (TTHA). Curves plotting the conditional stability constants of the 1:1 and 2:1 complexes as functions of pH are given. Values of pM at the two equivalence points for the two metals are presented as functions of pH. The curves offer a simple means of predicting the courses of complexation titrations under varying experimental conditions. Moreover, the curves enable a choice of the optimum experimental conditions including the selection of a suitable indicator and an estimation of the attainable accuracy. When the correctness of the theory and the values of the constants used was tested by carrying out visual and photometric titrations, satisfactory agreement was obtained.

L. Harju and A. Ringbom,
Anal. Chim. Acta, 49 (1970) 205–219

COMPLEXIMETRIC TITRATIONS WITH TRIETHYLENETETRAMINEHEXAACETIC ACID

The potentialities of TTHA as a reagent for the compleximetric titration of various metals are discussed, and particular attention is paid to the conditions under which 1:1 and 2:1 complexes are formed. The conditional constants for the formation of 2:1 and 1:1 complexes are calculated and presented graphically as functions of pH for the metals Ag, Al, Ba, Sr and Ca, Cd, Co(II), Cu(II), Fe(III), Hg(II), La and two lanthanides (Nd,Er), Mg, Mn, Ni, Pb, Th, and Zn. The pM values at the two equivalence points at different pH values are also given. General comments on the constants and their use are presented.

L. Harju and A. Ringbom,
Anal. Chim. Acta, 49 (1970) 221–230

Inorganic Macromolecules Reviews

The Chemistry, Physics and Technology of Macromolecular Inorganic Compounds and Materials

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

The principal aim of the journal is to contribute actively to the study and exploitation of inorganic macromolecules by providing a review periodical which covers all aspects of their science and technology.

Inorganic macromolecules will be interpreted broadly to embrace both natural and synthetic systems. The Reviews thus will help bridge the gap existing between organic polymer science, glasses and ceramics and should be of interest to chemists, physicists, polymer scientists, materials scientists and materials engineers working in this field. Reviews will be published in English, French or German, though preferably in English.

The first two issues will contain the proceedings of the International Symposium on Inorganic Polymers held April 9, 10 and 11, 1969 at the Northern Polytechnic, London.

Some forthcoming papers:

Polymer chemistry of boron cluster compounds
H.A. Schroeder (Connecticut, U.S.A.)

Nitrogen-sulphur compounds
M. Becke-Goehring (Heidelberg, Germany)

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

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

Inorganic Polymers
L. Holliday (London, Great Britain)

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

Further information, specimen copies and hints to authors will be sent by the publisher on request. Subscription orders may be placed with your usual supplier or with the publisher

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AZONOL A. A NEW METALLOCHROMIC REAGENT
PHOTOMETRIC DETERMINATION OF COBALT AND SCANDIUM

3-(4-Antipyrinylazo)-2,4-pentanedione (azonol A) forms brick-red and wine-red complexes with Co(II), Pd(II), Ni, Fe(II), Cu(II), Zn, Cd, Hg(II), Pb(II), Mn(II), Sc, Y, lanthanons, Zr, Hf, Th and Bi, in the pH range of 1.00–10.00. The complexes usually have a metal:ligand ratio of 1:2, except for the thorium and bismuth complexes which are 1:3. Complexation with cobalt(II) at pH 1.10 in the presence of EDTA allows a selective determination of cobalt; of 25 cations studied, only 4-fold molar ratios of vanadium(V), 6-fold molar ratios of palladium(II), copper(II) and scandium and 8-fold molar ratios of zinc and iron(II) caused interference in the determination of 0.5 μmole of cobalt(II). Amongst 15 anions, 20-fold molar ratios of oxalate and 30-fold molar ratios of cyanide caused low results. Scandium can be determined at pH 1.10 in presence of cyanide; only bismuth, thorium, hafnium and iron(III) interfere seriously.

B. Budesinsky and J. Svecova,
Anal. Chim. Acta, 49 (1970) 231–240

ELECTROCHEMICAL CHARACTERISTICS OF 2-METHYL-1,4-NAPHTHOQUINONE (VITAMIN K_3)
A COULOMETRIC MICROMETHOD OF DETERMINATION

Electrochemical characteristics of 2-methyl-1,4-naphthoquinone (vitamin K_3) were studied by polarography, controlled potential coulometry, and cyclic voltammetry. A polarographic procedure in acetate and phosphate buffers and a microcoulometric method of determination of this compound with electrogenerated cerium(IV) ion are described.

G. J. Patriarche and J. J. Lingane,
Anal. Chim. Acta, 49 (1970) 241–246

ANION-EXCHANGE CHROMATOGRAPHY OF HYDROXY ACIDS WITH AUTOMATIC ANALYSIS OF THE ELUATE

An automatic method is described for the analysis of complex mixtures of monoprotic hydroxy acids. The acids are separated by anion-exchange chromatography and the eluate is analyzed in a four-channel analyzer by (*a*) chromic acid oxidation, (*b*) the carbazole reaction, and by periodate oxidation with subsequent determination of (*c*) the formation of formaldehyde and (*d*) the periodate consumption.

B. Carlsson and O. Samuelson,
Anal. Chim. Acta, 49 (1970) 247–254

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,
Dfl. 65.00, £7.10.0.

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

INFRA RED INSTRUMENTATION AND TECHNIQUES

by A. E. MARTIN

5½ x 8½″, x + 180 pages, 13 tables, 94 illus., 86 lit.refs., 1966,
Dfl. 32.50, 75s.

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

ENERGY TRANSFER IN RADIATION PROCESSES

Chemical, Physical and Biological Aspects

Proceedings of the International Symposium held in Cardiff, 1965

edited by G. O. PHILLIPS

5½ x 8½″ ,xvi + 182 pages, 10 tables, 81 illus., 273 lit.reft., 1966,
Dfl. 32.50, 75s.

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

MASS SPECTROMETRIC ANALYSIS OF SOLIDS

edited by A. J. AHEARN

5½ x 8½″ ,viii + 175 pages, 13 tables, 46 illus., 242 lit.refs., 1966,
Dfl. 30.00, 70s.

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

RADIOCHEMICAL SURVEY OF THE ELEMENTS

Principal characteristics and applications of the elements and their isotopes

by M. HAISSINSKY
and
J.-P. ADLOFF

6 x 9″, ix + 177 pages, 1965, Dfl. 32.50, 75s.

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

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METHYLENEIMINODIACETIC ACID DERIVATIVES OF SOME 7-HYDROXYCOUMARINS AS ANALYTICAL REAGENTS

Fifteen derivatives of 7-hydroxycoumarin methyleneiminodiacetic acid were prepared and examined for their analytical reactions, in an attempt to improve the selectivity and sensitivity of the calcein blue type of reagent. However, most of the derivatives behaved similarly in their reactions with metal ions. The 3-carboxy-7-hydroxycoumarin complexone fluoresced most intensely and is recommended as an indicator for the titration of copper(II) with EDTA solutions: end-points are satisfactory even with 10^{-3} M solutions. Other metals can be determined by addition of EDTA and back-titration with copper(II) solution. Determinations of 0.06–6 μg of copper by quenching of fluorescence are suggested.

M. A. Salam Khan and W. I. Stephen,
Anal. Chim. Acta, 49 (1970) 255–260

STUDIES WITH DITHIZONE

PART XXI. A NOVEL BICYCLIC OXIDATION PRODUCT OF DITHIZONE

The purple compound $C_{13}H_{10}N_4S$ produced by the oxidation of dithizone has been shown to be a novel bicyclic compound of structure 3-phenylazobenzo-1,3,4(4H)thiadiazole. The absorption spectrum of its green conjugate acid and blue anion and the infrared spectrum of the parent compound and its deuteration product are reported. The association through hydrogen-bonding indicated in the solid by X-ray crystallography has been confirmed by infrared measurements of solutions in carbon tetrachloride.

H. M. N. H. Irving, U. S. Mahnot and D. C. Rupainwar,
Anal. Chim. Acta, 49 (1970) 261–266

IDENTIFICATION AND DETERMINATION OF IMPURITIES IN SALICYLANILIDE

In studies on the production of salicylanilide an assay method for salicylanilide itself and methods for the identification and determination of impurities were required. In addition to the starting materials (aniline and salicylic acid) four impurities were isolated and identified: salicylsalicylanilide, *ar*-phosphonosalicylanilide, 4-hydroxybenzanilide, and the *p*-hydroxybenzoate of 4-hydroxybenzanilide. Salicylanilide was assayed by direct ultraviolet spectrophotometry in basic methanol solution. Salicylic acid and phosphonosalicylanilide were extracted from a salicylanilide–chloroform solution with dilute sodium bicarbonate solution. Aniline and salicylsalicylanilide were determined by passing a methanolic solution of salicylanilide through Dowex 2, acetate-form, resin. Aniline, and methyl salicylate resulting from alcoholysis of salicylsalicylanilide, were contained in the eluate. All impurity concentrations were determined by ultraviolet spectrophotometry.

N. E. Skelly,
Anal. Chim. Acta, 49 (1970) 267–274

Photoluminescence of Solutions

With Applications to Photochemistry and Analytical Chemistry

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

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

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

Comprehensive Analytical Chemistry

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

VOLUME IIB: Physical Separation Methods

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

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

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

Atomic-Absorption Spectroscopy

and Analysis by Atomic-Absorption Flame Photometry

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

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

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

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X-RAY FLUORESCENCE ANALYSIS OF NICKEL–IRON THIN FILMS WITH STANDARDS PREPARED BY THE PYROLYSIS OF METAL ORGANIC COMPOUNDS

A rapid method of preparing Ni–Fe thin-film standards for X-ray fluorescence and similar applications is described. The procedure consists of applying a mixture of metal organic compounds to an appropriate substrate followed by firing the specimen in a reducing atmosphere. Standards prepared in this manner are used to perform non-destructive X-ray fluorescence analysis of thin-film samples. Relative precision at the 1.0% level is attained.

W. D. SHELBY AND P. CUKOR,
Anal. Chim. Acta, 49 (1970) 275–278

THE ELECTROCHEMICAL REDUCTION OF SOME PALLADIUM(II)–PYRIDINE COMPLEXES

The reduction of the palladium(II) complexes of pyridine, 2-methyl, 3-methyl and 4-methylpyridine has been studied. The reductions were irreversible in all cases, with no evidence of any dissociation of the complexes before reduction. Adsportion of the ligands at the mercury cathode was observed chronopotentiometrically. A comparison is made of the analytical capabilities of polarography and chronopotentiometry for the systems investigated.

S. I. WOODBURN, M. W. BLACKMORE AND R. J. MAGEE,
Anal. Chim. Acta, 49 (1970) 279–286

PRECISE DETERMINATION OF OXYGEN AND SILICON IN CHONDRITIC METEORITES BY 14-MeV NEUTRON ACTIVATION WITH A SINGLE TRANSFER SYSTEM

Improved methods for the determination of oxygen and silicon by 14-MeV neutron activation are described. A single-transfer system is employed to attain a precision approaching that of biaxial rotator systems. Analyses of six samples of the Allende chondrite are given and a correlation is found between oxygen and silicon abundances.

J. W. MORGAN AND W. D. EHMANN,
Anal. Chim. Acta, 49 (1970) 287–299

COLORIMETRIC DETERMINATION OF SOME AROMATIC COMPOUNDS WITH A FORMALDEHYDE–SULPHURIC ACID REAGENT

A simple colorimetric determination of several aromatic compounds with the help of a formaldehyde–sulphuric acid reagent has been developed. Hydrocarbons, ethers and other unreactive molecules can be determined. The nature of the coloured reaction products is briefly discussed.

M. R. F. ASHWORTH, G. CAPPEL AND E. HAMMER,
Anal. Chim. Acta, 49 (1970) 301–307

INORGANIC ELECTRONIC SPECTROSCOPY

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

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

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

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

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

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

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

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

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

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THE TITRATION OF ORGANIC COMPOUNDS WITH CHROMIUM(II) SOLUTIONS

(in German)

Procedures and standard deviations are reported for the titration with chromium(II) of a number of compounds of interest in pharmaceutical and dyestuff chemistry. Two methods are described by which the reduction can be carried out in neutral or alkaline medium, in the presence of EDTA. Depending on the nature of the functional groups, reduction can be reversible or irreversible. In mixtures, components of the two categories can be determined separately if the titration with chromium(II) solution is followed by titration with a strong oxidant.

W. Büchler, P. Gisske und J. Meier,
Anal. Chim. Acta, 49 (1970) 309–315

THE COMPOSITION AND ION-EXCHANGE BEHAVIOR OF ZINC HEXACYANOFERRATE(II) ANALOGUES

The dependence of the composition of zinc hexacyanoferrate(II) complexes on the mixing ratio of sodium hexacyanoferrate(II) and zinc nitrate solutions is demonstrated, and the ion-exchange behavior of the different complexes is described. Depending on the mixing ratios of the two components, $Zn_2Fe(CN)_6$ or $Na_2Zn_3[Fe(CN)_6]_2$, or mixtures of these compounds, may be formed. The adsorption rate for cesium(I) on zinc hexacyanoferrate(II) is extremely slow, whereas it is very rapid on disodium trizinc hexacyanoferrate(II). The Zn–Cs and Na–Cs exchange rates for the different complexes are discussed.

S. Kawamura, H. Kuraku and K. Kurotaki,
Anal. Chim. Acta, 49 (1970) 317–322

DECOMPOSITION OF OXIDE AND SULPHIDE MINERALS AND ORES BY FUSION WITH AMMONIUM SALTS

The use of fusion with ammonium salts for the decomposition of some oxide and sulphide ores and minerals has been investigated. Iron pyrites, zincblende, copper ore, copper concentrates, lead concentrates, Nimba iron ore, burnt pyrites, and manganese ore can be completely decomposed by ammonium hydrogen sulphate or ammonium hydrogen sulphate containing ammonium nitrate or ammonium chloride additives. In some cases repetitive fusions are necessary. The cooled melt can be leached with a mineral acid to produce a solution shown to be suitable for the quantitative analysis of the major metallic component(s) of the sample.

A. A. Verbeek, J. B. B. Heyns and R. A. Edge,
Anal. Chim. Acta, 49 (1970) 323–333

TREATISE ON ELECTROCHEMISTRY

Second, completely revised edition

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

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

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

OXIDATION AND COMBUSTION REVIEWS

edited by C. F. H. Tipper,

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

Volume 1

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

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

Volume 2

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

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

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

ATMOSPHERIC OXIDATION AND ANTIOXIDANTS

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

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

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

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RAPID COMPLEXIMETRIC DETERMINATION OF ALUMINIUM AND TITANIUM IN COMMON ORES AND SILICATES

A rapid compleximetric method is presented for the determination of aluminium and titanium in ores and silicates such as bauxite, clay, ilmenite, cements and ceramic products. Excess of EDTA is added to an aliquot of the acid sample solution, the pH is adjusted with hexamine and the excess of EDTA is titrated with a combined solution of copper and zinc in the presence of xylenol orange and PAN as indicators. For the simultaneous titration, fluoride is added to release the EDTA combined with both aluminium and titanium. For the stepwise titration, phosphate is added to release the EDTA combined with titanium, and then fluoride is added to release the EDTA combined with aluminium. The method avoids the problem of titanium hydrolysis encountered by previous workers.

A. Nestoridis,
Anal. Chim. Acta, 49 (1970) 335–341

THE DETERMINATION OF PARACETAMOL AND ASPIRIN IN MIXTURES BY NON-AQUEOUS POTENTIOMETRIC TITRIMETRY OR BY ULTRAVIOLET SPECTROPHOTOMETRY

(Short Communication)

A. G. Fogg, P. J. Sausins and J. R. Smithson,
Anal. Chim. Acta, 49 (1970) 342–345

THE LIQUID-STATE ELECTRODE (A PRELIMINARY COMMUNICATION)

(Short Communication)

J. Růžička and J. Chr. Tjell,
Anal. Chim. Acta, 49 (1970) 346–348

THE AMPEROMETRIC AND INDIRECT POLAROGRAPHIC DETERMINATION OF PALADIUM(II) WITH SELENOPHENE-2-ALDOXIME

(Short Communication)

L. S. Bark and M. Jain,
Anal. Chim. Acta, 49 (1970) 349–351

ADHESION AND ADHESIVES

2nd, completely revised, edition

edited by R. Houwink and G. Salomon

Volume 1

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

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CONTENTS:

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

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CONTENTS:

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TITRATIONS WITH COMPLEXING AGENTS FORMING MONONUCLEAR AND BINUCLEAR COMPLEXES WITH METALS

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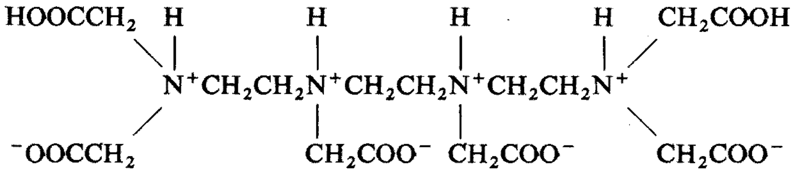
(Received October 14th, 1969)

Multidentate complexing agents are often able to bind more than one metal ion. Depending on the experimental conditions, compounds with a metal–ligand ratio of either 1:1 or 2:1 may be formed.

As an example, triethylenetetraminehexaacetic acid (TTHA = H_6L) may be considered. This reagent, introduced by FROST[1] in 1956, has the structure



and has thus ten coordinating groups. Various authors have investigated the properties and reactions of this complexing agent. Its remarkable analytical potential has been made clear particularly by PŘIBIL AND VESELÝ[2], who utilized the fact that some metals react with the reagent in a molar ratio of 2:1, whereas others form 1:1 compounds. By appropriate combination of TTHA with other complexing agents, they succeeded in analysing solutions containing several metals.

It is not, however, possible to distinguish between metals forming exclusively 1:1 complexes with TTHA, on one hand, and metals forming exclusively 2:1 complexes on the other. Which product is formed depends not only on the metal ion but also on the experimental conditions, above all on the pH of the solution. For instance, if copper is titrated with TTHA at pH 4, practically only the 2:1 complex is formed, but a titration performed in alkaline solution—in the opposite direction to avoid precipitation of copper hydroxide—can be based on the formation of a 1:1 complex.

Several other metals also form both 1:1 and 2:1 complexes; which of these predominates depends on the experimental conditions.

THEORY OF TITRATIONS WITH COMPLEXING AGENTS FORMING MONONUCLEAR AND BINUCLEAR COMPLEXES

From an analytical point of view it seems desirable to define clearly the conditions favouring the formation of each of the two complexes. Particularly important for the analyst are the answers to the questions: what compound is formed, how complete is the reaction, what are the optimum experimental conditions and the best indicator for a particular titration, how high an accuracy can be attained?

At first sight, the problem seems relatively simple. In principle, the problem of titrating a metal ion, M,with a complexing agent, L, forming the compounds M_2L and ML is the same as the neutralisation of a dibasic acid, say H_2L. (Or, more correctly, the titration in the opposite direction, *i.e.* hydrogen ions with L anions.) Is not the theoretical treatment of a compleximetric titration then quite analogous to the treatment of an acid–base titration?

However, some differences are obvious. The complexation reactions leading to M_2L and ML are accompanied by a large number of side reactions, particularly important among which are the reactions with hydrogen and hydroxide ions. TTHA, for instance, is a hexabasic acid forming many acid ions; moreover, it is theoretically possible that several acid or basic metal complexes are formed, *e.g.* MHL, MH_2L, MOHL, $M(OH)_2L$, M_2HL, M_2H_2L, M_2OHL, $M_2(OH)_2L$, etc.

The complications caused by the side reactions can be largely eliminated if the theory of the titrations is based on the concept of the *conditional constant*[3]. If, for a given reaction, the value of this "constant" is known at various pH values, this means that the pM values at the equivalence point are also known; a suitable indicator can then be easily chosen, and the maximum titration error can be read directly from the common error diagram[3].

In 1960 WÄNNINEN[4] showed how the titration of a metal to ML is affected by the formation of M_2L complexes. Here, the opposite problem is also encountered: the formation of M_2L is considered as the main reaction and the effect of the formation of the 1:1 complex on the main reaction must be established; other side reactions producing various acid or basic complexes must also be included in the theoretical treatment.

The results of such calculations can conveniently be presented as curves plotting the conditional constants as functions of pH. Such graphic presentations allow one to determine the courses of various reactions under various conditions. The curves enable an immediate choice of the optimum experimental conditions to be made without any more or less involved calculations.

In practice, the complexing agent is usually the titrant in compleximetric titrations of metals; the first equivalence point occurs when M_2L is formed, the second equivalence point when ML is formed. However, the theoretical treatment will be somewhat simplified if we consider the equivalence points as the end-points of titrations in the opposite direction in accordance with the reactions $L+M=ML$ and $ML+M=M_2L$.

Titration to ML

If the stability constant of the complex formed is denoted by $K_{ML}^{M,L}$, the conditional constant is

$$K_{(ML)'}^{M',L'} = \frac{[(ML)']}{[M'][L']} = \frac{\alpha_{ML}}{\alpha_M \alpha_L} K_{ML}^{M,L} \tag{1}$$

i.e. by inserting appropriate α coefficients (side-reaction coefficients), all side reactions are taken into consideration. Primed concentrations thus include the products of side reactions. For details of the concepts used, the reader is referred to reference 3. Owing to the many side reactions, the conditional constants are furnished with more superscripts than usual, in order to avoid any ambiguity. The dissociating compound is always indicated by a subscript and the dissociated components by superscripts; primes are appended to any species involved in one or more side reactions. This notation is the same as that used for acids and bases in Chapter V of reference 3.

The over-all α coefficients are functions of the individual α coefficients as given by the following expressions:

$$\alpha_{ML} = \alpha_{ML(H)} + \alpha_{ML(OH)} - 1 \tag{2}$$

$$\alpha_L = \alpha_{L(H)} \tag{3}$$

$$\alpha_M = \alpha_{M(OH)} + \alpha_{M(ML)} - 1 \tag{4}$$

The α coefficients have their usual meanings and are easily calculated from the equilibrium constants. $\alpha_{M(ML)}$, which accounts for the formation of M_2L may deserve some comments.

$$\alpha_{M(ML)} = \frac{[M]+[M_2L]}{[M]} = 1+[ML]\, K_{M_2L}^{M,ML} = 1 + \frac{[(ML)']}{\alpha_{ML}} K_{M_2L}^{M,ML} \tag{5}$$

If M_2L is also involved in side reactions leading to acid or basic complexes, we have

$$\alpha_{M(ML)} = 1 + \frac{\alpha_{M_2L}\, [(ML)']\, K_{M_2L}^{M,ML}}{\alpha_{ML}} \tag{6}$$

At the equivalence point, $[(ML)']$ approximately equals the total concentration of metal, C_M. If $\alpha_{M(ML)}$ predominates over $\alpha_{M(OH)}$, and if unity in eqn. (5) can be neglected, we can write

$$\alpha_M \approx \frac{\alpha_{M_2L(H)}\, C_M\, K_{M_2L}^{M,ML}}{\alpha_{ML}} \tag{7}$$

and the conditional constant will be

$$\log K_{(ML)'}^{M',L'} \approx \Delta\log K + 2\log \alpha_{ML(H)} - \log \alpha_{L(H)} - \log \alpha_{M_2L(H)} - \log C_M \tag{8}$$

where $\Delta\log K$ is the difference $\log K_{ML}^{M,L} - \log K_{M_2L}^{M,ML}$.

In eqns. (7) and (8) all acid complexes are taken into account. If basic complexes are formed, corresponding expressions are valid.

The equations given are valid at points not too far from the equivalence point; it is thus assumed that [(ML)′] does not differ greatly from C_M in magnitude.

According to common rules, [M] at the equivalence point is given by

$$[\mathrm{M}]_{\mathrm{eq}} = \frac{[\mathrm{M}']_{\mathrm{eq}}}{\alpha_{\mathrm{M}}} = \frac{(C_{\mathrm{M}}/K_{(\mathrm{ML})'}^{\mathrm{M}',\mathrm{L}'})^{\frac{1}{2}}}{\alpha_{\mathrm{M}}} \tag{9}$$

It may be noted that if $\alpha_{\mathrm{M(ML)}}$ predominates among the α_{M} coefficients, $\mathrm{pM_{eq}}$ will be independent of the total concentration of the metal. If the formation of M_2L is the only side reaction, eqn. (9) will be simplified to

$$[\mathrm{M}]_{\mathrm{eq}} = \frac{1}{(K_{\mathrm{ML}}^{\mathrm{M,L}}\, K_{\mathrm{M_2L}}^{\mathrm{M,ML}})^{\frac{1}{2}}} = \beta_{\mathrm{M_2L}}^{-\frac{1}{2}} \tag{10}$$

where $\beta_{\mathrm{M_2L}}$ is the cumulative stability constant of M_2L. This expression corresponds to the common expression for [H] at the first equivalence point in the titration of a dibasic acid.

If another ion, N, is present, a coefficient $\alpha_{\mathrm{L(N)}}$ has to be added to eqn. (3). This coefficient

$$\alpha_{\mathrm{L(N)}} = 1 + [\mathrm{N}]\, K_{\mathrm{NL}}^{\mathrm{N,L}} + [\mathrm{N}]^2\, K_{\mathrm{N_2L}}^{\mathrm{2N,L}} \tag{11}$$

Usually, one of the α coefficients predominates and the other coefficients can be neglected.

Titration to M_2L

We consider this case also as a titration with M as titrant, *i.e.* $ML + M = M_2L$. The conditional constant is

$$K_{(\mathrm{M_2L})'}^{\mathrm{M}',(\mathrm{ML})'} = \frac{[(\mathrm{M_2L})']}{[\mathrm{M}']\,[(\mathrm{ML})']} = \frac{\alpha_{\mathrm{M_2L}}}{\alpha_{\mathrm{M}}\,\alpha_{\mathrm{ML}}}\, K_{\mathrm{M_2L}}^{\mathrm{M,ML}} \tag{12}$$

The nature of the α coefficients will be clear from the following equations:

$$\alpha_{\mathrm{M_2L}} = \alpha_{\mathrm{M_2L(H)}} + \alpha_{\mathrm{M_2L(OH)}} - 1 \tag{13}$$

$$\alpha_{\mathrm{M}} = \alpha_{\mathrm{M(OH)}} \tag{14}$$

$$\alpha_{\mathrm{ML}} = \alpha_{\mathrm{ML(H)}} + \alpha_{\mathrm{ML(OH)}} + \alpha_{\mathrm{ML(diss)}} - 2 \tag{15}$$

$\alpha_{\mathrm{ML(diss)}}$ is a measure of the dissociation of ML, *i.e.* the formation of free or acid L ions. Consequently,

$$\alpha_{\mathrm{ML(diss)}} = \frac{[\mathrm{ML}]+[\mathrm{L}']}{[\mathrm{ML}]} = 1 + \frac{1}{[\mathrm{M}]\, K_{\mathrm{ML}}^{\mathrm{M,L}'}} \tag{16}$$

[M] varies greatly during a titration. However, the conditions at the equivalence point and in its vicinity are of particular interest. $\alpha_{\mathrm{ML(diss)}}$ remains close to unity as long as $[\mathrm{M}]_{\mathrm{eq}} \gg 1/K_{\mathrm{ML}}^{\mathrm{M,L}'}$ and the dissociation will then be slight. If $\alpha_{\mathrm{ML(diss)}}$ considerably exceeds unity, it means that the concentration of ML can be ignored; the metal in the system is present either as M_2L or as M. In the cases considered in this paper, $\alpha_{ML(diss)}$ always equals unity.

The interference of another metal, N, can be taken into consideration in a way similar to that used in the consideration of the titration to ML, *i.e.* by including a coefficient $\alpha_{ML(N)}$ in eqn. (15). Then, for the reaction $ML + N = NL + M$

$$\alpha_{ML(N)} = \frac{[ML]+[NL]}{[ML]} = 1 + \frac{[N]\,K_{NL}}{[M]\,K_{ML}} \tag{17}$$

Whether N interferes or not depends not only on the difference between log K_{ML} and log K_{NL} and on the concentration of N, but also on the values of $\alpha_{ML(H)}$ or $\alpha_{ML(OH)}$ (since the over-all α coefficient is the sum of all individual coefficients). The value of [M] at this equivalence point can be approximately estimated, but an exact value demands somewhat laborious calculations (*e.g.* iteration).

The conditions leading to a successful compleximetric titration can be easily defined if the conditional constants governing the equilibria of the system are known. We have applied the theoretical principles developed, to the titration of manganese and copper with TTHA since we feel that understanding of these principles will be effectively promoted by some examples demonstrating their use in practice. It may be noted that a similar treatment was given in a paper by WIKBERG AND RINGBOM[5] for the titration of silver with TTHA. A more complete review elucidating the possibilities of titrating other metals with TTHA will be given in the following paper of this issue[6].

EXPERIMENTAL

Reagents

For most of the experiments a sample of TTHA from Geigy Chemical Co., Basel, was used. Later, a sample from J.T. Baker Chemical Co., Phillipsburgh, N.J., was employed.

Apparatus

A Metrohm Spectrocolorimeter E 1009 combined with a Metrohm Potentiograph E 336 was used for the photometric titrations.

TITRATION OF MANGANESE WITH TTHA

As far as we know, no stability constants of Mn–TTHA complexes have been determined. Investigations conducted at this laboratory by HARJU, the results of which will be published later, gave the following logarithmic values (concentration constants, $\mu = 0.1$, temp. $= 25°$):

$K_{MnL}^{Mn,L}$	$K_{MnHL}^{H,MnL}$	$K_{MnH_2L}^{H,MnHL}$	$K_{Mn_2L}^{Mn,ML}$
14.5	8.74	3.45	6.54

On the basis of these values, the conditional constants can be calculated from the equations given in the previous section.

For the titration of manganese to the 2:1 complex, the conditional constant

$$\log K_{M_2L}^{M',(ML)'} = -\log \alpha_{M(OH)} - \log \alpha_{ML(H)} + \log K_{M_2L}^{M,ML} \tag{18}$$

The other α coefficients given in eqns. (12)–(15) can be disregarded. Since $\log K_{MnOH}^{Mn,OH} = 3.4$, the coefficient $\alpha_{M(OH)}$ will not affect the result unless the pH exceeds about 10 (*cf.* ref. 3). The conditional constant is plotted as a function of pH in Fig. 1.

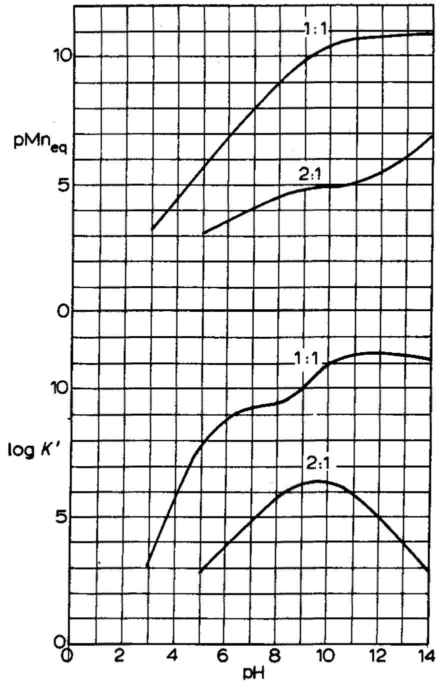


Fig. 1. Conditional constants and pMn$_{eq}$ values as functions of pH in titrations of manganese(II) with TTHA to the 1:1 and 2:1 complex. C_{Mn} is assumed equal to 10^{-3} *M*.

The conditional constant for the continued titration to the 1:1 complex can be calculated from the previously given eqn. (8).

$$\log K_{(ML)'}^{M',L'} = \Delta\log K + 2\log \alpha_{ML(H)} - \log \alpha_{L(H)} - \log C_M \tag{19}$$

The coefficient $\alpha_{M_2L(H)}$ in eqn. (8) can be disregarded. For the calculation of $\alpha_{L(H)}$ the following logarithmic acid stability constants determined by BOHIGIAN AND MARTELL[8] were used: 10.19, 9.40, 6.16, 4.16, 2.95, 2.42. The obtained values of log $\alpha_{L(H)}$ were

pH	1	2	3	4	5	6	7	8	9	10	11
log $\alpha_{L(H)}$ =	29.30	23.43	18.25	14.16	10.83	7.98	5.65	3.61	1.74	0.47	0.06

Since it is likely that also proton complexes containing more than six protons exist, the values at very low pH values (< *ca.* 2.5) are probably a little too low. However, they are seldom needed in analytical work.

The conditional constants calculated for $C_M = 10^{-3}$ are plotted against pH in Fig. 1, curve B.

For titration purposes it is still desirable to know pM_{eq} which is obtained from the common equation

$$[M]_{eq} \approx \frac{(C_M/K')^{\frac{1}{2}}}{\alpha_M} \tag{20}$$

where K', *i.e.* the conditional constant for the reaction in question, is taken from Fig. 1.

The pMn_{eq} values for 2:1 titrations as well as for 1:1 titrations are also presented as functions of pH in Fig. 1.

On the basis of Fig. 1 it is possible to choose appropriate conditions for the titrimetric determination of manganese. For instance, if manganese is titrated at pH 10 to a pMn value of 5, Mn_2L is formed, but if the indicator changes colour at pMn 10, then MnL is formed. If suitable indicators are available and the precision of detecting the end-point can be estimated (say, to ± 0.5 pMn unit), the attainable accuracy can be read from the common error diagram with log $K'C$ as abscissa[3]. (It should be remembered that at the first equivalence point, when M_2L is formed, the total concentration of the metal is not C_M but $\frac{1}{2}C_M$.)

The conditional constant for the formation of Mn_2L is rather small, for it never exceeds $10^{6.5}$. Hence the accuracy of a visual titration will be low. However, the constant is sufficiently high in value for results of satisfactory accuracy if the end-point is detected photometrically. In Fig. 2, the result of a titration with eriochrome black T as indicator at pH 9.5 is presented.

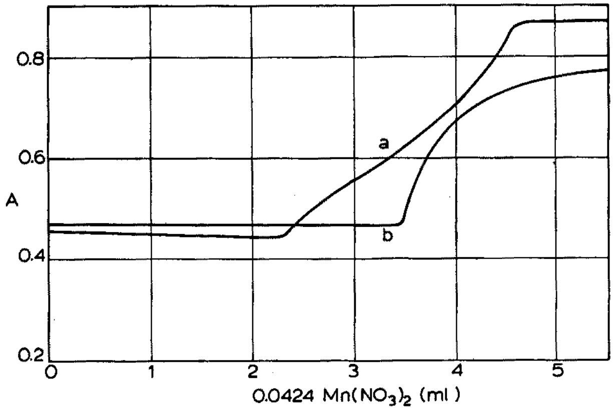
The indicator changes colour at pMn 8.8 approximately[6]. A glance at Fig. 1 reveals that the transition point appears *after* the first equivalence point where $pMn_{eq} = 5$ (titration to Mn_2L), but *before* the second equivalence point where $pMn_{eq} = 10$ (titration to MnL). According to an earlier suggested terminology[3], the indicator functions in the first case as a "high sensitivity indicator", and in the second case as a "low sensitivity indicator". The equivalence points will appear as break points in both cases, and the titration curve in Fig. 2, relating to a titration in reverse direction, is in good agreement with theory, *i.e.* both ways of titration can be used.

In Fig. 3 the results of two photometric titrations with methylthymol blue are presented. At pH 7 a "medium sensitivity" curve arises, but since the conditional constant is about 5, the jump is not very steep. If the pH is increased to 11.8, the break at the 1:1 equivalence point will be very sharp, as can be seen in Fig. 3.

The precipitation of manganese hydroxide can be avoided if the initial titration is performed in neutral solution, *i.e.* it is thus not necessary to titrate in the opposite direction in an alkaline solution.

To avoid oxidation of manganese(II), small amounts of ascorbic acid should be added before titration of an alkaline solution.

According to Figs. 1–3, visual titrations are most precise at a pH of 11.8 with methylthymol blue as indicator. The 1:1 compound is then formed, and the colour change is very sharp. The error diagram indicates errors below 0.1%, if 10^{-3} *M* solutions are titrated. Performed titrations gave satisfactory results.



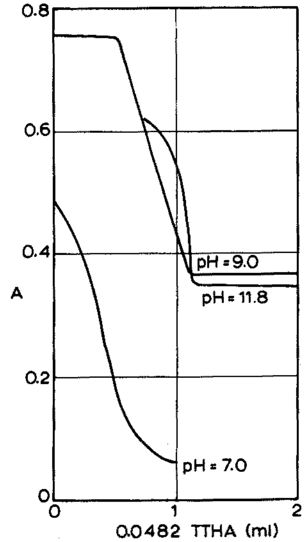


Fig. 2. Stepwise photometric titration of TTHA with manganese(II) and eriochrome black T as indicator. λ = 530 nm; C_{Ind} = $1.4 \cdot 10^{-5}$ *M*. Initial volume = 70 ml; $\mu \approx 0.1$. (a) 2 ml 0.0482 *M* TTHA; pH = 9.5 (H_3BO_3–NaOH). (b) 3 ml 0.0482 *M* TTHA; pH = 10.0 (H_3BO_3–NaOH). Theoretical equivalence points: (a) 2.27 ml, 4.54 ml. (b) 3.41 ml, 6.82 ml.

Fig. 3. Photometric titration of 1 ml of 0.0507 *M* $MnSO_4$ with TTHA using methylthymol blue as indicator. λ = 600 nm; C_{Ind} = $1.4 \cdot 10^{-5}$ *M*; volume = 70 ml; $\mu \approx 0.1$; pH 7.0 (imidazole), pH 9.0 (NH_3–NH_4Cl), pH 11.8 (NH_3–NH_4Cl). Theoretical equivalence points: 0.53 (2:1 complex) and 1.05 (1:1 complex).

TITRATION OF COPPER WITH TTHA

Values of the stability constants of various copper–TTHA complexes have been given by BOHIGIAN AND MARTELL[8] and by KLAUSEN *et al.*[9]. However, calculations on the basis of these constants, which differed considerably, did not agree with experimental data. This fact led to a closer examination of the reported values. It turned out that BOHIGIAN AND MARTELL[8], when measuring the pH of solutions containing copper and ligand in the ratio 1:1, assumed that [Cu_2L] could be disregarded compared to [Cu]. In reality, however, [Cu_2L]/[Cu] exceeds unity in the pH range in question, as shown by recorded spectral curves and titrations. Moreover, all the mentioned authors assumed that no acid binuclear complexes are formed. However, experiments showed that Cu_2HL and Cu_2H_2L exist. If the structure of the TTHA molecule is considered, the existence of such acid complexes is quite probable.

Details of the determinations will be given in a separate paper[7]. Here, only the logarithmic values obtained are given (concentration constants, $\mu=0.1$, temp. = 25°):

$K_{\mathrm{CuL}}^{\mathrm{Cu,L}}$	$K_{\mathrm{CuHL}}^{\mathrm{H,CuL}}$	$K_{\mathrm{Cu_2L}}^{\mathrm{Cu,CuL}}$	$K_{\mathrm{Cu_2L}}^{\mathrm{2Cu,L}}$	$K_{\mathrm{Cu_2HL}}^{\mathrm{H,Cu_2L}}$	$K_{\mathrm{Cu_2H_2L}}^{\mathrm{H,Cu_2HL}}$
19.2	8.0	13.4	32.6	3.0	2.7

The calculations of the conditional constants were based on eqns. (1)–(15) and were performed as shown in the above treatment of manganese complexes. However, the coefficient $\alpha_{\mathrm{M_2L(H)}}$, which is equal to unity for manganese complexes, must be taken into consideration, as protonation favours the formation of 2:1 complexes in acid solutions. For $K_{\mathrm{CuOH}}^{\mathrm{Cu,OH}}$, which is needed to calculate $\alpha_{\mathrm{Cu(OH)}}$, a value of $10^{6.0}$ was used.

The conditional constants are plotted as functions of pH in Fig. 4. The calculated values for $\mathrm{pCu_{eq}}$ are also presented there.

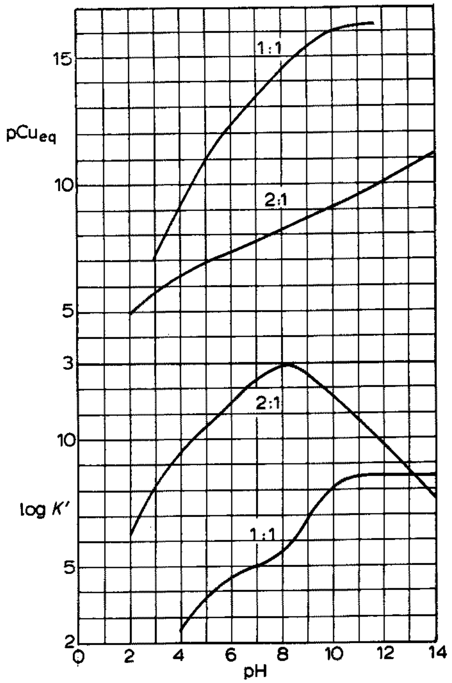


Fig. 4. Conditional constants and $\mathrm{pCu_{eq}}$ as functions of pH in titrations of copper(II) with TTHA to the 2:1 and 1:1 complex. C_{Cu} is assumed equal to 10^{-3} *M*.

A comparison with the corresponding curves for manganese complexes in Fig. 1 reveals that whereas a titration of manganese to MnL is more advantageous than a titration to $\mathrm{Mn_2L}$, the opposite is true for copper. The conditional constant of $\mathrm{Cu_2L}$ is remarkably high in value at all pH values above 2. The maximum value of 10^{13} is attained at pH 8. The conditional constant of CuL is too small in acidic solutions for a successful titration, but in basic solutions the values are sufficiently high as they exceed 10^8 at pH 10.

The correctness of the above deductions can be checked by photometric titration. Since all the formed copper compounds differ in colour, titrations without

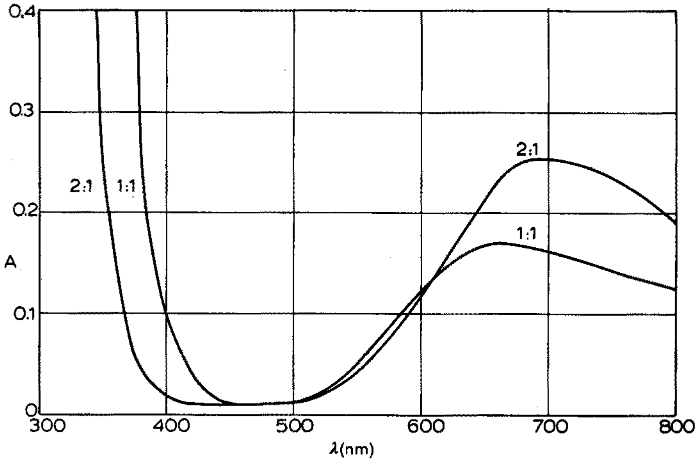


Fig. 5. Absorbance curves for copper(II)–TTHA chelates. $C_{TTHA} = 2 \cdot 10^{-3}$ *M*. For the solution of the 1:1 complex, pH = 10.0 (H_3BO_3–NaOH); for the solution of the 2:1 complex, pH = 2.35 (HNO_3). $\mu \approx 0.1$, 25°.

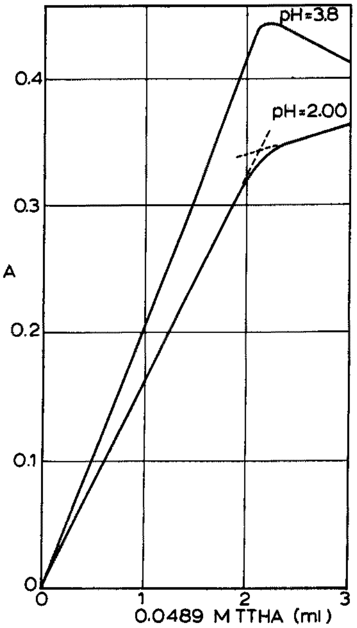
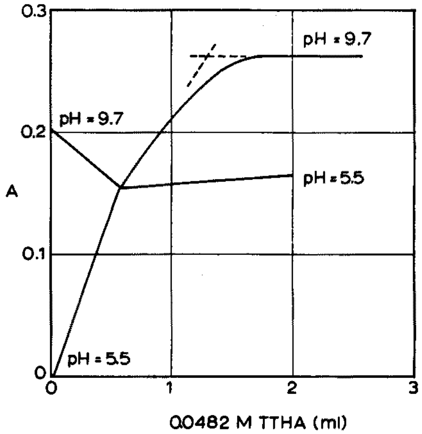


Fig. 6. Photometric titration of copper(II) with TTHA without indicator. λ = 700 nm. 3.52 ml 0.0570 *M* $Cu(NO_3)_2$; volume = 98.5 ml; $\mu \approx 0.1$. pH = 3.8 (HCOOH–NaOH), pH = 2.0 (HNO_3). Theoretical 2:1 equivalence point at 2.05 ml.

an indicator are also possible. Absorbance curves of the 2:1 and 1:1 complexes recorded under appropriate experimental conditions are presented in Fig. 5.

The results of a number of titrations without indicator are presented in Figs. 6 and 7. It can be seen that in acidic solution no break appears at the 1:1 point, whereas a break occurs at the 2:1 point. The break is rather sharp except at pH values below 2.



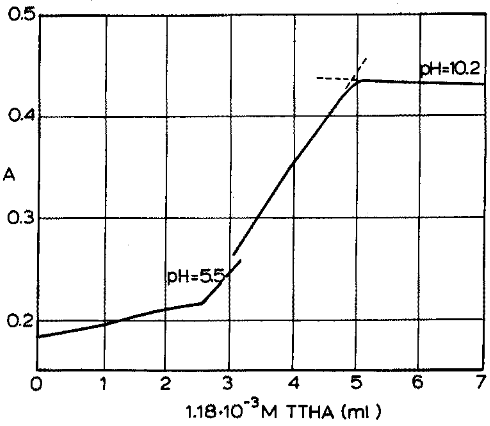


Fig. 7. Photometric titration of 1 ml of 0.0517 *M* $CuCl_2$ solution with TTHA without indicator. $\lambda = 650$ nm; volume $\approx$ 70 ml; $\mu \approx 0.1$; pH 5.5 (urotropine), pH 9.7 (NH_3–NH_4Cl). Theoretical equivalence points: 0.54 ml (2:1 complex), 1.07 ml (1:1 complex).

Fig. 8. Photometric titration of copper(II) with TTHA without indicator. $\lambda = 330$ nm; volume $\approx$ 20 ml. pH 5.5 (urotropine), pH 10.2 (H_3BO_3–NaOH). Theoretical equivalence points: 2.50 ml (2:1 complex), 5.00 ml (1:1 complex).

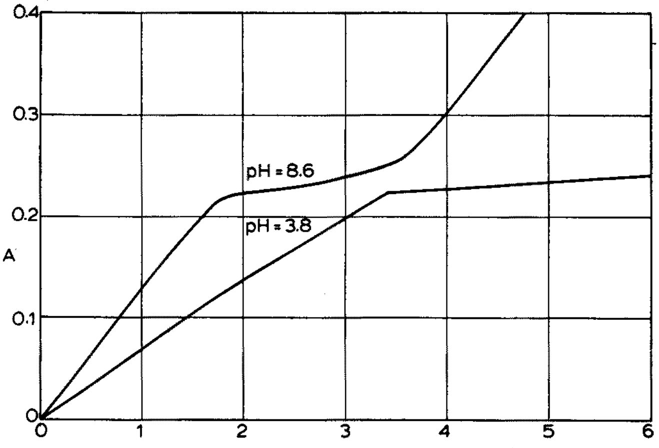
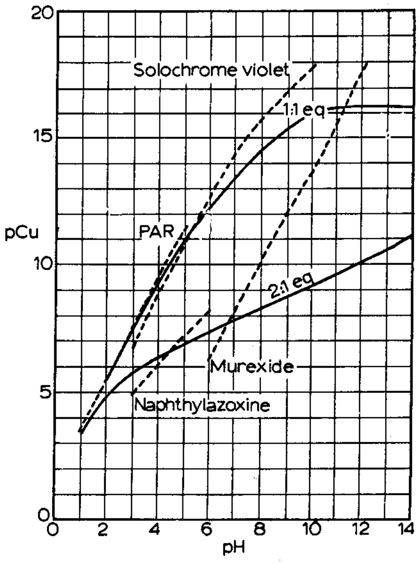


Fig. 9. Photometric titration of 2.00 ml of 0.0489 *M* TTHA with copper(II) solution without indicator. $\lambda = 600$ nm; volume $\approx$ 90 ml; $\mu \approx 0.1$. pH 3.8 (HCOOH–NaOH), pH 8.6 (H_3BO_3–NaOH). Theoretical equivalence points: 1.72 ml (1:1 complex) and 3.43 ml (2:1 complex).

Stepwise titrations with two break points are also possible, as shown in Figs. 8 and 9, relating to cases where the pH was changed during the titration. All the curves are in excellent accordance with the values of the conditional constants in Fig. 4. In alkaline solution, with an excess of copper (II), the absorbance may be affected by precipitation of copper(II) hydroxide.

It is possible to estimate the value of an equilibrium constant from a rounded curve. The titration at pH 2 giving the absorbance curve presented in Fig. 6, gave for $K^{2\mathrm{Cu},\mathrm{L}}_{\mathrm{Cu_2L}}$ the value $10^{31.6}$, which is in satisfactory agreement with the value of $10^{32.6}$ determined by other methods[7].



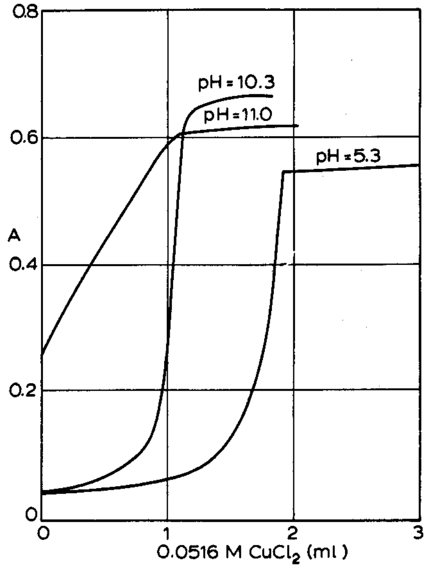


Fig. 10. $p\mathrm{Cu}_{\mathrm{eq}}$ as function of pH when titrating a 10^{-3} *M* Cu(II) solution with TTHA to the 1:1 and the 2:1 complex. Values of $p\mathrm{Cu}_{\mathrm{trans}}$ for PAR, solochrome violet, murexide and naphthylazoxine are also plotted as functions of pH.

Fig. 11. Photometric titration of 1.00 ml of 0.0489 *M* TTHA with copper(II) solution using PAR as indicator. $\lambda = 520$ nm; $C_{\mathrm{Ind}} = 4 \cdot 10^{-6}$ *M*; volume ≈ 70 ml; $\mu \approx 0.1$. pH 5.3 (urotropine), pH 10.3 (H_3BO_3–NaOH), pH 11 (H_3BO_3–NaOH). Theoretical equivalence points: 0.95 ml (1:1 complex), 1.90 ml (2:1 complex).

The transition points of some indicators (taken from ref. 3) are presented graphically together with the $p\mathrm{M}_{\mathrm{eq}}$ values at the two equivalence points at various pH values in Fig. 10. The titration curves shown in Figs. 11–14, which were performed with various indicators, have the forms expected from the values of the conditional constants. In other words, if $p\mathrm{Cu}_{\mathrm{trans}} \ll p\mathrm{Cu}_{\mathrm{eq}}$, a "low sensitivity" curve arises, whereas if $p\mathrm{Cu}_{\mathrm{trans}} \gg p\mathrm{Cu}_{\mathrm{eq}}$, a "high sensitivity" curve is obtained; if $p\mathrm{Cu}_{\mathrm{trans}}$ and $p\mathrm{Cu}_{\mathrm{eq}}$ are of the same order of magnitude, a curve rounded at both sides arises. According to the curve in Fig. 14, $p\mathrm{Cu}_{\mathrm{trans}}$ of naphthylazoxine is not far from the equivalence point $p\mathrm{Cu}_{\mathrm{eq}} = 7.3$ at pH 5.8. No values of $p\mathrm{Cu}_{\mathrm{trans}}$ are given in the literature, but later

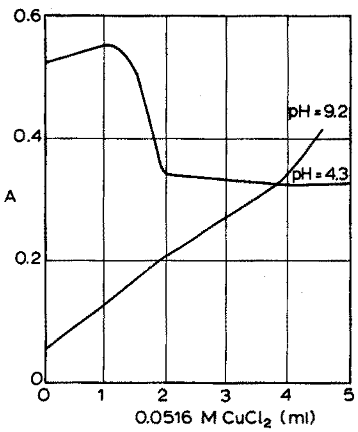
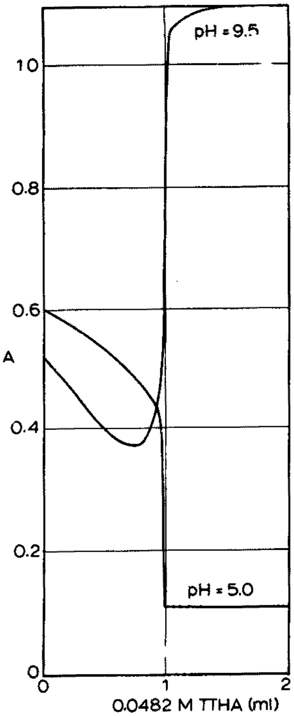


Fig. 12. Photometric titration of 2.00 ml of 0.0488 M TTHA with copper(II) solution using solochrome violet as indicator. λ = 580 nm; $C_{\text{Ind}} = 1.5 \cdot 10^{-5}\ M$; volume ≈ 70 ml; $\mu \approx 0.1$. pH 4.3 (HCOOH–NaOH), pH 9.2 (H_3BO_3–NaOH). Theoretical equivalence points: 1.88 ml (1:1 complex), 3.76 ml (2:1 complex).



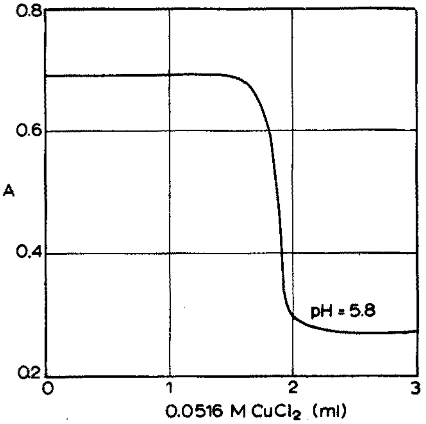


Fig. 13. Photometric titration of 2 ml of 0.0485 M $CuSO_4$ with TTHA solution using murexide as indicator. λ = 550 nm; $C_{\text{Ind}} = 4.3 \cdot 10^{-6}\ M$; volume ≈ 70 ml; $\mu \approx 0.1$; pH 5 (urotropine), pH 9.5 (NH_3–NH_4Cl). Theoretical equivalence point: 1.01 ml (2:1 complex).

Fig. 14. Photometric titration of 1.00 ml of 0.0489 M TTHA with copper(II) chloride solution using naphthylazoxine as indicator. λ = 570 nm; $C_{\text{Ind}} = 3 \cdot 10^{-5} M$; volume ≈ 70 ml; $\mu \approx 0.1$. pH 5.8 (urotropine). Theoretical equivalence points: 0.95 ml (1:1 complex) and 1.90 ml (2:1 complex).

investigations in this laboratory[10] gave the values inserted in Fig. 10: $pCu_{trans} \approx 7.9$ at pH 5.8.

The attainable accuracy can be estimated from the common error diagram when it is noted that in 2:1 titrations $\frac{1}{2}C_M$ represents the total metal concentration.

The determinations of manganese and copper represent two different cases where TTHA is used as a titrant. In practice, determinations of other metals may be more important; actually, this reagent offers good possibilities for the analysis of several multicomponent systems.

The value of TTHA as a titrant for the determination of various metals under various conditions will be discussed in more detail in the following paper.

The authors wish to thank E. R. KORTE, Ph. M., who revised the English text of this paper. This investigation has been supported by grants from Statens Teknologiska Kommission, Finland.

SUMMARY

The general theory of titrations with complexing agents forming metal complexes in which the metal:ligand ratios are 1:1 and 2:1 is discussed, and rules are given for the calculation of conditional constants. The theory is applied to the titration of manganese and copper with triethylenetetraminehexaacetic acid (TTHA). Curves plotting the conditional stability constants of the 1:1 and 2:1 complexes as functions of pH are given. Values of pM at the two equivalence points for the two metals are presented as functions of pH. The curves offer a simple means of predicting the courses of complexation titrations under varying experimental conditions. Moreover, the curves enable a choice of the optimum experimental conditions including the selection of a suitable indicator and an estimation of the attainable accuracy. When the correctness of the theory and the values of the constants used were tested by carrying out visual and photometric titrations, satisfactory agreement was obtained.

RÉSUMÉ

Une étude est effectuée sur les titrages à l'aide d'agents complexants, formant des complexes mono- et binucléaires avec les métaux. Un exemple d'application est présenté pour le titrage du manganèse et du cuivre, au moyen d'acide triéthylènetétraminohexacétique (TTHA). On examine l'influence du pH. Les courbes obtenues permettent de prévoir le cours de titrages par complexométrie, dans diverses conditions expérimentales. D'autre part, elles permettent de choisir les conditions optimales, ainsi que l'indicateur approprié.

ZUSAMMENFASSUNG

Es wird die allgemeine Theorie komplexometrischer Titrationen mit solchen Komplexbildnern diskutiert, die ein Metall:Liganden-Verhältnis von 1:1 und 2:1 bilden. Regeln zur Berechnung der Zustandskonstanten werden angegeben. Die Theorie wird auf die Titration von Mangan und Kupfer mit Triäthylentetraminhexaessigsäure (TTHA) angewandt. In Diagrammen wird die Stabilitätskonstante der 1:1- und 2:1-Komplexe in Abhängigkeit vom pH-Wert dargestellt. Die pM-Werte an den zwei Äquivalenzpunkten für die 2 Metalle werden als Funktion des pH-Wertes angegeben. Die Kurven bieten einen einfachen Weg zur Vorhersage des Verlaufes komplexometrischer Titrationen unter variierenden, experimentellen Bedingungen. Darüber hinaus ermöglichen die Kurven die Wahl optimaler Versuchsbedingungen einschliesslich der Auswahl eines geeigneten Indikators und einer Abschätzung dei ereichbaren Genauigkeit. Die praktische Überprüfung der Theorie ergab zufriedenstellende Übereinstimmung.

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COMPLEXIMETRIC TITRATIONS WITH TRIETHYLENETETRAMINE-HEXAACETIC ACID

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In a preceding paper[1], the general theory of compleximetric titrations with complexing agents forming metal complexes with metal:ligand ratios of both 1:1 and 2:1 was formulated. It was shown that the theoretical treatment is greatly simplified if the conditional constants of the two complexes are known at various pH values. The theory was illustrated by applying it to the titration of manganese and copper with triethylenetetraminehexaacetic acid (TTHA). The validity of the theory was tested by performing photometric titrations.

TABLE I

STABILITY CONSTANTS OF METAL–TTHA COMPLEXES

(μ = 0.1, temp. = 30° for Ba, Sr and Ca; 25° for all others)

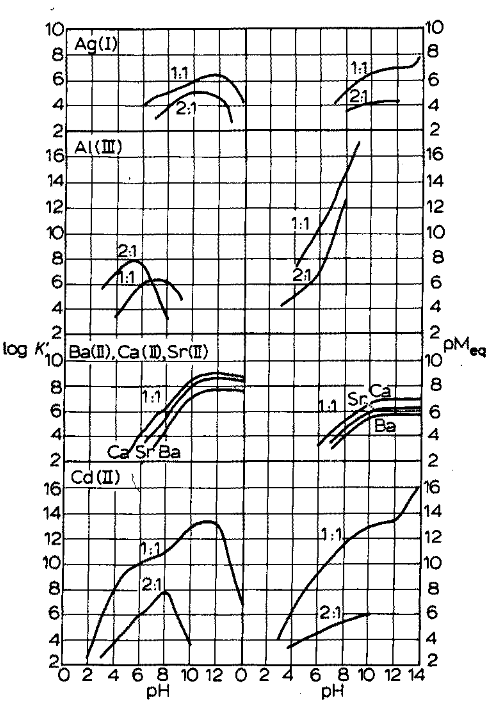
Metal ion	*Log*								
	K_{ML}	K^{H}_{MHL}	$K^{H}_{MH_2L}$	$K^{M}_{M_2L}$	β_{M_2L}	$K^{H}_{M_2HL}$	$K^{H}_{M_2H_2L}$	$K^{2OH}_{M2(OH)_2L}$	*Ref.*
Ag^+	8.67	9.11		5.22	13.89				3
Al^{3+}	19.7	5.85		8.9	28.6			15.9	2
Ba^{2+}	8.22	7.66	5.50	3.41	11.63				4
Ca^{2+}	10.06	8.34	3.68	4.10	14.16				4
Cd^{2+}	18.65	8.32	3.2	8.2	26.85				2
Co^{2+}	17.1	8.12		11.7	28.8	3.0	2.6		2
Cu^{2+}	19.2	8.00		13.4	32.6	3.0	2.7		2
Er^{3+}	23.19	4.50		3.73	26.92			13.0	2
Fe^{3+}	26.8	7.60	2.75	13.7	40.5			21.0	2
Hg^{2+}	26.8	6.3	3.6	12.3	39.1	3.6	2.7	12.8	2
La^{3+}	22.22	3.30		3.40	25.62				2
Mg^{2+}	8.43	9.30		5.95	14.38				2
Mn^{2+}	14.65	8.74	3.45	6.54	21.19				2
Nd^{3+}	22.82	3.93		3.93	26.75			11.5	2
Ni^{2+}	18.1	8.00		14.3	32.4	2.6	2.3		2
Pb^{2+}	17.1	8.20		11.0	28.1	3.0	2.6		2
Sr^{2+}	9.26	7.78	4.24	3.44	12.70				4
Th^{4+}	31.9	3.05							2
Zn	16.65	8.15		12.05	28.7	3.0	2.6		2

In this paper the theory is applied to the titration of a number of other metals with TTHA. For the general theory including the calculation of conditional constants the reader is referred to the previous paper. The stability constants used were predominantly determined experimentally; a few values were taken from the literature. A complete report of these determinations of stability constants will be given subsequently[2].

The values of constants used are collected in Table I.

The potentialities of compleximetric titrations with TTHA are particularly easy to grasp on the basis of curves plotting the conditional stability constants of the ML and M_2L complexes as functions of pH. Such curves are presented in Figs. 1–4, where the pM values at the two equivalence points are also plotted as functions of pH. When values are read from the curves, it should be remembered that the conditional constant of ML but not that of M_2L depends on the total concentration of the metal, C_M. The curves are drawn for the case where $C_M = 10^{-3}$.

The conditional constants used are presented in this paper in abbreviated form: Instead of the complete symbols $K^{M',L'}_{(ML)'}$ and $K^{M',(ML)'}_{(M_2L)'}$ (*cf.* ref. 1), we write K'_{ML} and K'_{M_2L}, respectively.



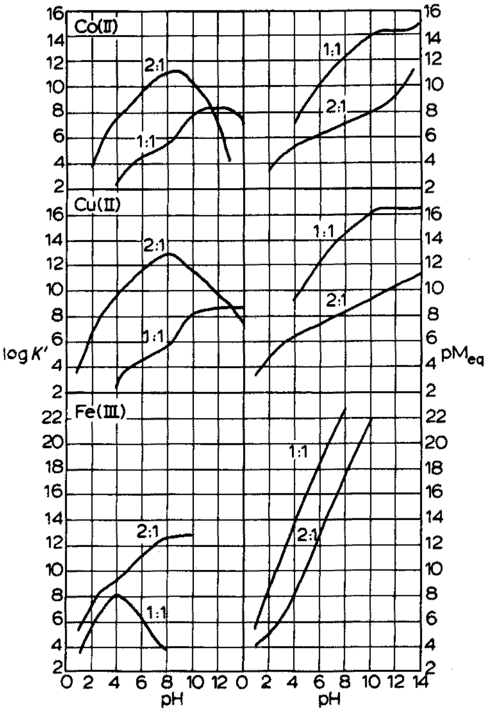
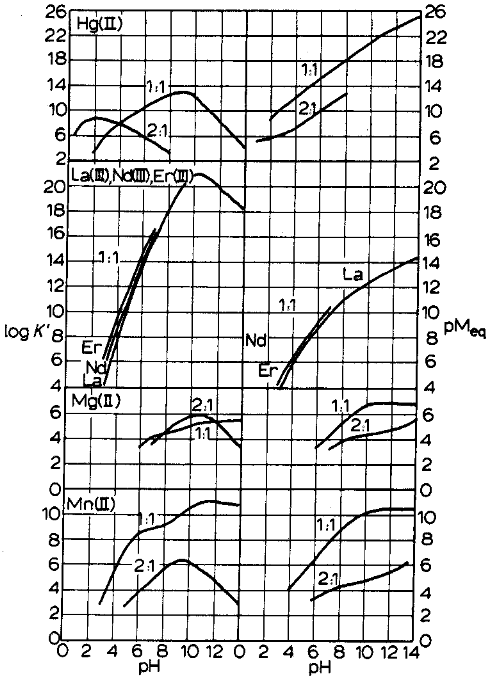


Fig. 1. Conditional constants and pM_{eq} values as functions of pH when titrating Ag, Al, Ba, Ca, Sr and Cd with TTHA to the 2:1 and 1:1 complexes. C_M is assumed to be 10^{-3} *M*.

Fig. 2. Conditional constants and pM_{eq} values as functions of pH when titrating Co(II), Cu(II), and Fe(III) with TTHA to the 2:1 and 1:1 complexes. C_M is assumed to be 10^{-3} *M*.



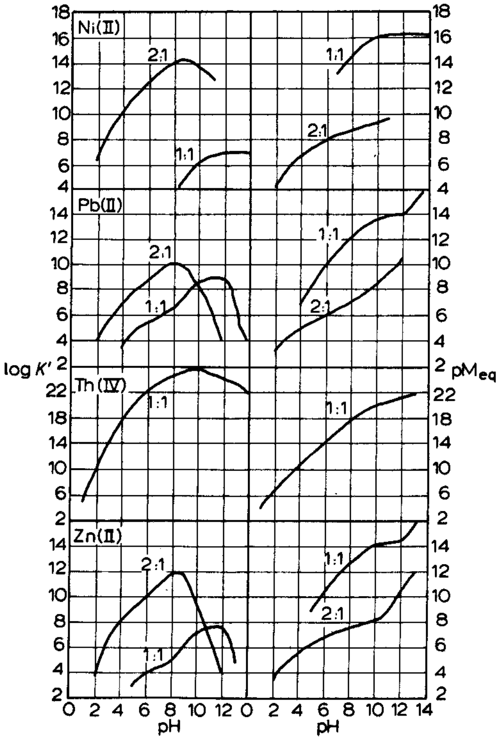


Fig. 3. Conditional constants and pM_{eq} values as functions of pH when titrating Hg(II), La, Nd, Er, Mg, and Mn with TTHA to the 2:1 and 1:1 complexes. C_M is assumed to be 10^{-3} *M*.

Fig. 4. Conditional constants and pM_{eq} values as functions of pH when titrating Ni, Pb, Th, and Zn with TTHA to the 2:1 and 1:1 complexes. C_M is assumed to be 10^{-3} *M*.

In all cases where $\alpha_{M(ML)}$ predominates over other α_M coefficients (*e.g.* $\alpha_{M(OH)}$), log K'_{ML} will decrease by one unit when C_M increases tenfold. On the other hand, in titrations to the 1:1 complex, pM_{eq} is independent of the total metal concentration, C_M, (provided that $[ML]K_{M_2L} \gg 1$), whereas pM_{eq} for the 2:1 titration depends on C_M; pM_{eq} will decrease by $\frac{1}{2}$ unit when C_M increases tenfold.

The conditional constants give information on the heights of the pM jumps in titrations. If a titration is performed potentiometrically, the change in potential is proportional to ΔpM. However, if K'_{ML} equals K'_{M_2L}, it does not follow that the two jumps on the titration curve are of exactly the same height. For the total metal concentration, one has to insert C_M if ML is formed, but $\frac{1}{2}C_M$ if M_2L is formed. The heights of the pM and the potential jumps and, consequently, the attainable precision will thus be somewhat smaller in the latter case. The accuracy and the precision can be conveniently estimated from the common error diagram[5] where the percentage error is presented as a function of log $(C_M K')$ at various values of $\Delta pM = pM_{end} - pM_{eq}$. If a metal is titrated to the 2:1 complex, $\frac{1}{2}C_M$ has to be taken as the total concentration of the metal. In other words, $\log(\frac{1}{2}C_M K') = \log(C_M K') - 0.3$ has to be taken as abscissa in the error diagram.

The minimum value of a constant for a successful visual titration is usually considered to be 10^6–10^7, assuming that a suitable indicator is available. If no suitable indicator is available, back-titration may be necessary. The appropriateness of various metal salts for back-titrations can be judged from Figs. 1–4. The rule is that the conditional stability constant of the TTHA complex formed by the metal of the back-titrant must not exceed the conditional constant of the complex formed by the metal to be determined. Otherwise, the back-titrant will react not only with the excess of TTHA, but also with the metal complex formed. This rule is always valid if the equilibrium is established rapidly. Exceptions are possible if an inert metal complex is formed.

For potentiometric and photometric titrations, a stability constant value of 10^5–10^6 is generally considered as the lower limit. However, graphic extrapolation methods yield results of good accuracy, even when the value of the constant is about 10^4, and accurate photometric titrations with a "dichrotitrator"[6], combined with the ECR (Exactly Correct Reference Solution) principle[7] may be possible even when the value of the stability constant is only about 10^2. These values refer, of course, to conditional constants.

General remarks on titrations with TTHA

TTHA is of major importance as a titrant for the analysis of solutions containing several metals. PŘIBIL *et al.*[8-11] have shown that, by appropriate combination of TTHA with other complexing agents forming only 1:1 complexes, the determination of several components may be possible. In this way, they succeeded in analysing various mixtures, *e.g.* of gallium and indium, of thorium and scandium, and of thorium and lanthanides. It is remarkable that solutions containing iron and various other metals (Ni, Bi, Al) can be analysed. For this purpose, PŘIBIL utilized the fact that the mononuclear iron(III)–EDTA complex is much more stable than the binuclear iron(III)–TTHA complex. The principle will be clear from Figs. 1–4. For instance, the logarithmic conditional constant of the iron(III)–EDTA complex at pH 4 is 14.7, whereas the logarithmic conditional constant of the 2:1 iron(III)–TTHA complex is below 10. For nickel, on the other hand, the two constants are about equal ($\log K' \approx 10$). Therefore, the TTHA ligand in the iron complex is readily displaced by two EDTA anions, whereas more stable or very inert metal–TTHA complexes will not react with EDTA. The excess of added complexing agent can be determined by back-titration with a lead or zinc salt solution. The titrated ligands can be differentiated since the EDTA anion binds one metal ion whereas the TTHA anion binds two metal ions.

Other authors[12-15] have also developed titration methods based on similar principles.

The courses of the curves in the alkaline range may raise some objections. First, polynuclear hydroxo complexes, which are not considered in the calculations, are known to exist and could influence the values of the conditional constants and the pM_{eq} values. Secondly, precipitation of metal hydroxides may occur if the pH value of the sample solution is sufficiently high.

The analyst is particularly interested in the conditions near the equivalence point where [M] is rather small, mostly considerably below "the mononuclear wall". Therefore, the calculations of the α coefficients can be based solely on the constants of the mononuclear complexes (for details, see ref. 5).

If there is a risk that metal hydroxides may precipitate—as is often the case when the solution is basic—it may sometimes be necessary to titrate in the reverse direction or to change the pH during the titration. At the 1:1 equivalence points the pM_{eq} values are, as a rule, so large that no precipitation occurs. At the 2:1 point, they may be so low for some metals that precipitation is possible in alkaline solution. Nevertheless, a titration may be performed if the pM jump is high. A few of the 2:1 curves of Figs. 1–4 are drawn up to a pH value a little above that where the metal hydroxide precipitates.

A few remarks on the titration of individual metals that may be useful are given below.

TITRATIONS OF VARIOUS METALS

Silver

Both conditional constants are below 10^7 at all pH values. Visual titrations can therefore scarcely be recommended, even if a suitable indicator were available. Potentiometric titrations[3] in basic solution (in the reverse direction) give one jump when silver and TTHA have reacted in the ratio 1:1, and another small jump when the ratio is 2:1. The optimum pH range is 10–11.

Aluminium

The conditional constant, K'_{Al_2L}, attains its maximum value, 10^8, at about pH 5.5. At slightly lower and higher pH values the constant decreases markedly and falls below 10^7 below pH 4 and above pH 6.5. This is in accordance with the experience of PŘIBIL AND VESELÝ[8], who recommended titrations at pH 5–5.5. The reaction is not very fast, and good aluminium indicators are hard to find. Heating and back-titration with a lead salt is therefore prescribed. (For appropriate indicators and pPb_{eq} values, see below under *Lead.*)

At pH 5.5, K'_{AlL} equals 5.5. When an excess of TTHA is present, a fraction of the formed Al_2L may therefore temporarily be transformed into AlL, but if equilibrium is established, this formation does not interfere (and was taken into consideration in the calculation of K'_{Al_2L}).

Barium, calcium and strontium

All the alkaline earth metals form predominantly 1:1 complexes with TTHA. The constants of the 2:1 complexes are also known and $\alpha_{M(ML)}$ reduces slightly the values of the conditional 1:1 constants. For titrations to the 2:1 complex, the reactions are too incomplete (non-conditional constants 10^3–10^4); the values of the conditional constants of the 2:1 complexes are not plotted in Fig. 1.

The 1:1 conditional constants are sufficiently high in value for successful titrations. However, they are smaller than the constants for 1:1 complexes of EDTA and many other derivatives of EDTA. Therefore, they are of interest mainly for the analysis of solutions containing several metals by combining TTHA with some other complexing agent.

Cadmium

The conditional 1:1 constant is larger than the 2:1 constant at all pH values and exceeds a value of 10^8 in the pH range 4–13 (maximum value $=10^{13}$ at pH 11). The maximum value of $K'_{\mathrm{Cd_2L}}$ equals $10^{7.8}$ at pH 8, but falls abruptly on both sides of this pH value. PŘIBIL AND VESELÝ[8] back-titrated to the 2:1 complex with lead nitrate at pH 5.5. According to the curves a high accuracy is scarcely attainable under these conditions. It is noteworthy that in basic solution up to pH 13, the 1:1 constant is very high. Titrations made with PAR (pyridylazoresorcinol) as indicator at pH 6 showed a noticeable colour change at the 2:1 equivalence point; but if the pH was then raised to 11.5, a second very sharp colour change could be observed at the 1:1 equivalence point.

Cobalt

Cobalt(II) should be titrated to the 2:1 complex. The conditional constant has its maximum value, $10^{11.2}$, at pH 9, but suitable indicators for direct titration are hard to find. PŘIBIL AND VESELÝ prescribe back-titration with lead nitrate at pH 5.5.

Copper

Copper can be titrated either to the 2:1 or to the 1:1 complex. For details, the reader is referred to the previous paper.

Iron(III)

The curves in Fig. 2 show that in titrations to the 2:1 end-point, the conditional constant values exceed 10^7 if pH is over 2. Titrations to the 1:1 complex are also possible; the optimum pH is about 4 (constant $\approx 10^8$). The formation of $\mathrm{Fe_2L}$ proceeds rapidly, but FeL is formed slowly. Various ways of detecting the end-point are possible, *e.g.* visual, photometric or potentiometric. Chromazurol S is a suitable indicator for the 2:1 titration at a pH of about 3.

Details about titrations of iron(III) with TTHA will be reported in a separate paper.

Mercury

Figure 3 shows that titrations to the 2:1 and 1:1 equivalence points are both possible. However, in acidic solutions (pH less than 4), precipitation of an acid mercury chelate may interfere. The formation of the 2:1 complex proceeds sufficiently fast, but the continued reaction to the 1:1 complex is rather slow. Potentiometric titration in the pH range 3–6 gives two jumps according to the theory.

PŘIBIL titrated mercury directly to the 2:1 complex with xylenol orange as indicator at pH 5.5, where pHg_{trans} equals 8.2 and pHg_{eq} is about 9.

A titration to the 1:1 complex is possible at pH 6.5 if methylthymol blue is used as indicator, and the titration is performed to the first shift to orange (or photometrically); pHg_{trans} equals 14.7 and pHg_{eq} is about 11.5.

Back-titrations with lead or zinc salts at pH 10 also give good results; HgL is then formed.

Lanthanum and lanthanides

The stability constants of the TTHA complexes of lanthanum and the rare-earth metals are remarkably high. K_{LaL}, for instance, is $10^{22.2}$, *i.e.* 6.5 logarithmic units larger than the stability constant of the La–EDTA complex. The 1:1 complexes predominate; $K^{La}_{La_2L}$ is only $10^{3.4}$.

Lanthanum can be titrated at pH 6 with xylenol orange or methylthymol blue as indicator[8]. At this pH pLa_{trans} is about 5.6 for both indicators. Since pLa_{eq} is about 9, the indicators are not sensitive enough, and titrations should be performed to a complete colour change (from reddish orange to clear yellow). The stability constant is so high that the theoretical error is below 0.2% in spite of the high ΔpLa value. Photometrically, the equivalence point, *i.e.* the break point on the absorbance curve, can be detected with great precision.

The rare-earth metals also form unusually stable complexes with TTHA. Table I contains the constants for neodymium ($\log K_{NdL} = 22.8$) and erbium ($\log K_{ErL} = 23.2$). The complexes are more stable than the corresponding complexes of EDTA and EDTA derivatives. It is likely that this fact can be favourably utilized for analytical purposes.

Magnesium

It is noteworthy that magnesium reacts with TTHA in a different way from the heavier alkaline earth metals. The conditional constants of the 2:1 and 1:1 complexes are of the same order of magnitude, between 10^4 and 10^6 in basic solution. Owing to the low values of the constants, TTHA offers only limited possibilities for the determination of magnesium. PŘIBIL titrated magnesium directly to the 2:1 complex at pH 9 with thymolphthalexone as indicator. Although this procedure implies almost the optimum conditions, the attainable accuracy can scarcely be high.

Manganese

Manganese can be titrated to the 2:1 complex as well as to the 1:1 complex. For details, the reader is referred to the preceding paper[1].

Nickel

The conditional constants of the nickel 2:1 complex are remarkably high; at pH 8–9 the values exceed 10^{14}. The 1:1 constants are very small, particularly in acidic solution.

PŘIBIL titrated nickel directly with murexide as indicator at pH 10–11 ($\log K'_{Ni_2L} = 13$). These conditions are in good agreement with theory since pNi_{eq} and pNi_{trans} both equal 9.2. The theoretical titration error will be negligible.

Lead

Lead is preferably titrated to the 2:1 complex at pH 5–6. $\log K'_{Pb_2L}$ is then between 8 and 9. When xylenol orange is used as indicator, $pPb_{trans} \approx 7.5$ and $pPb_{eq} \approx 7.6$. Therefore, lead should be titrated to the first shade in orange. Lead nitrate is an excellent back-titrant; the titration should then be performed to complete colour change.

At pH 11, K'_{PbL} exceeds K'_{Pb_2L}, but at pH values over 12, both constants will be small owing to the formation of plumbite ions.

Thorium

The conditional constants of the 1:1 thorium complex are very large; at pH 10 the constant equals 10^{24}. This value is considerably higher than that of the conditional Th–EDTA constant which never exceeds $10^{20.5}$. However, hydrolysis reactions make the values in alkaline solutions somewhat uncertain and consideration must be given to a possible precipitation of $Th(OH)_4$.

At pH 3, the conditional constant is still as high as 10^{14}. If xylenol orange is used as indicator, the theoretical error is considerably below 0.1%. Pyrocatechol violet can be used at pH 5, and, as theoretical calculations show, the titration error is then negligibly small.

The existence of a 2:1 Th–TTHA complex has not been proved.

Zinc

Zinc should be titrated to the 2:1 complex. Figure 4 shows that the conditional 1:1 constant exceeds 10^7 only in the pH range 10–12 and is considerably smaller than the 2:1 constant at lower pH values. Moreover, sufficiently sensitive indicators for a 1:1 titration are not available.

A visual titration at pH 6 with xylenol orange as indicator is appropriate. pZn_{eq} for a 10^{-3} M solution is then 6.7 and pZn_{trans} is about 6.5. The titration error is negligible. PŘIBIL titrated at pH 5.5; in this case, the theoretical error will also be below ±0.1%.

The difference in the behaviour of cadmium and zinc toward TTHA is remarkable.

CONCLUSIONS

TTHA is a complexing agent with properties differing markedly from those of previously used complexing reagents; therefore, it offers the analyst many new possibilities for solving various analytical problems. However, determination of these possibilities empirically demands extensive experiments; moreover, there is little guarantee that a method based on the results would be used under optimum conditions. In this and the preceding paper, the theory is presented graphically in the form of curves which in a simple and illustrative way make clear the course and the completeness of various reactions under varying experimental conditions.

The suggested approach seems particularly useful for judging the possibilities of compleximetric analysis of multicomponent systems.

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SUMMARY

The potentialities of TTHA as a reagent for the compleximetric titration of various metals are discussed, and particular attention is paid to the conditions under which 1:1 and 2:1 complexes are formed. The conditional constants for the formation of 2:1 and 1:1 complexes are calculated and presented graphically as functions of pH for the metals Ag, Al, Ba, Sr and Ca, Cd, Co(II), Cu(II), Fe(III), Hg(II), La and two lanthanides (Nd,Er), Mg, Mn, Ni, Pb, Th and Zn. The pM values at the two equivalence points at different pH values are also given. General comments on the constants and their use are presented.

RÉSUMÉ

On examine les possibilités d'utilisation de l'acide triéthylènetétraminohexaacétique (TTHA) pour le titrage complexométrique de divers métaux. On examine en particulier les conditions dans lesquelles les complexes 1:1 et 2:1 sont formés. Les constantes de formation de ces complexes sont calculées et présentées graphiquement en fonction du pH, pour les métaux suivants: Ag, Al, Ba, Sr, Ca, Cd, Co(II), Cu(II), Fe(III), Hg(II), La et quelques lanthanides (Nd, Er), Mg, Mn, Ni, Pb, Th et Zn. On indique également les valeurs pM aux deux points équivalents, à différents pH.

ZUSAMMENFASSUNG

Die Möglichkeiten von TTHA als Reagenz zur komplexometrischen Titration zahlreicher Metalle werden unter besonderer Berücksichtigung von 1:1- und 2:1-Komplexen diskutiert. Die Zustandskonstanten solcher Komplexe werden berechnet und graphisch als Funktionen des pH-Wertes für folgende Metalle wiedergegeben: Ag, Al, Ba, Sn und Ca, Cd, Co(II), Cu(II), Fe(III), Hg(II), La und einige Lanthaniden, Mg, Mn, Ni, Pb, Th und Zn. Ferner werden die pM-Werte an den 2 Äquivalenzpunkten bei verschiedenen pH-Werten aufgeführt. Zu den Konstanten und ihrer Verwendung werden allgemeine Bemerkungen gemacht.

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AZONOL A. A NEW METALLOCHROMIC REAGENT

PHOTOMETRIC DETERMINATION OF COBALT AND SCANDIUM

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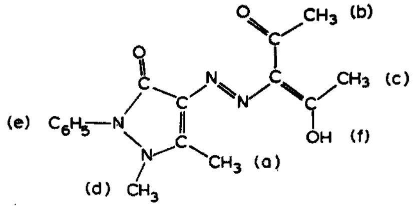
β-Diketones are well known complexing reagents used in many branches of chemistry, and a combination of a β-diketone with a suitable chromogenic system should have interesting possibilities. The azo dyestuffs appeared most convenient for this purpose because α-arylazo-β-diketones have been known for over 50 years[1-4]. However, when some of the recommended syntheses[1] were re-examined, yellow products, which were not in agreement with the structure assumed, were obtained; these products had very poor complexing and metallochromic properties. Accordingly, the preparation of the required substances was examined in detail. Suitable conditions of preparation which differ substantially from the usual conditions of preparation of azo dyestuffs were established. The coupling is performed at room or elevated (up to 100°) temperatures, and prolonged contact of the starting β-diketones with alkaline medium is avoided. The first substance of this type, azonol A, *i.e.* 3-(4-antipyrinylazo)-pentane-2,4-dione, I, and its principal analytical properties are described in this paper.



I

EXPERIMENTAL

Apparatus

All photometric measurements were made with a double-beam Cary 14 recording spectrophotometer. Quartz cells (1 cm) were used throughout. An Orion Model 801 pH-meter with a glass and calomel electrode pair, was used for pH measurements. NMR spectra were scanned with a Varian A-60 High Resolution NMR Spectrometer.

Preparation of the reagent

Dissolve 4.06 g of 4-aminoantipyrine in 20 ml of water and 5 ml of 12 *M* hydrochloric acid. Cool to 0°, stir mechanically and add a solution of 1.40 g of sodium nitrite in 10 ml of water, keeping the temperature at 0 ± 3°. Add 2.00 g of pentane-2,4-dione in 50 ml of water under the same conditions. Transfer the combined solution to a funnel and add it dropwise into a well-stirred solution of 40 ml of 5 *M* sodium hydroxide without cooling. The temperature varies between 20° and 30°. Let stand for 1 h, filter with suction through a glass sinter of medium porosity, and crystallize from 30 ml of 50% aqueous ethanol (yield *ca.* 1 g).

The product forms dark brick-red needles, m.p. 148–150°. The R_F value is 0.70 (blue spot) on Whatman paper No. 1 at 20° in *n*-butanol–12 *M* hydrochloric acid (4:1, fresh solution). A product of similar yield and quality may also be obtained if the sodium hydroxide solution is dropped into the combined solution of diazonium salt and pentane-2,4-dione.

The product was analyzed with the following results: 61.2% C, 5.8% H, 17.7% N; required for $C_{16}H_{18}N_4O_3$: 61.1% C, 5.8% H, 17.8% N. The NMR spectrum of the product gives in $CDCl_3$, with tetramethylsilane as internal standard, the following peaks (in p.p.m., see I): (a) 2.07, (b), (c) 2.60, 2.72, (d) 3.22, (e) 7.41, (f) 15.54.

Reagents

Azonol A solution. Prepare a $5.00 \cdot 10^{-4}$ *M* solution daily by dissolving 15.7 mg of the substance in 20 ml of ethanol and diluting to 100 ml with water.

Metal ion solutions. $1.00 \cdot 10^{-4}$ *M* and $1.00 \cdot 10^{-2}$ *M* stock solutions of the metal salts (usually nitrates or perchlorates) were used.

The pH was adjusted by means of perchloric acid and hexamine buffer (pH 1.10–6.90), glycine and sodium hydroxide (pH 8.24–10.14) and sodium hydroxide (pH 10.93–12.95). The ionic strength between pH 1.10 and 12.95 was kept constant (0.10 *N*) by means of sodium perchlorate[5]. Acidities higher than pH 1.10 were achieved with hydrochloric acid and below pH 0.00 they were expressed as the Hammett function $H°$. Hydrochloric acid was used because of the ease of oxidation of the reagent in the presence of perchloric or nitric acid concentrations higher than 1.00 *M*.

Determination of cobalt(II) and scandium

Add 3 ml of 0.05 *M* EDTA-disodium salt solution (for determination of cobalt(II)) or 0.05 *M* potassium cyanide solution (for determination of scandium) to a sample solution containing 0.1–0.5 µmole of cobalt(II) or scandium. Adjust to pH 4–7 by means of 0.5 *M* perchloric acid and 0.5 *M* sodium hydroxide. Add 5.0 ml of 0.5 *M* perchloric acid and mix. Then, add 5.00 ml of $5.00 \cdot 10^{-4}$ *M* reagent solution, dilute to 25 ml in a volumetric flask and mix. After 10 min, measure the absorbance at 610 nm of the reagent blank against sample solution. Construct the calibration curve for the given range of cobalt(II) or scandium concentrations under the same conditions. Straight lines should be obtained.

RESULTS AND DISCUSSION

Sensitivity of determination

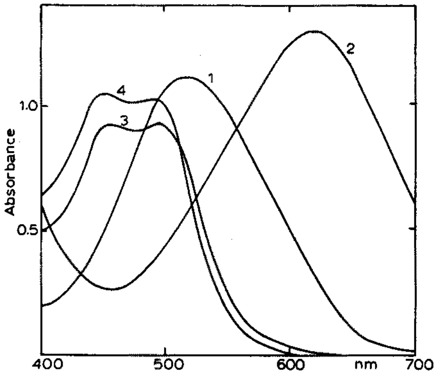
The sensitivity was expressed in the form of effective molar absorptivity for cobalt(II) and scandium corresponding to the linear part of the dependence between relative absorbance (blank minus sample solution) and the total concentration of metal. The results compared with sensitivities for other ions are presented in Table I.

TABLE I

EFFECTIVE MOLAR ABSORPTIVITIES FOR 610 nm AND pH 1.10[a]

Ion	*Molar absorptivity*	*Ion*	*Molar absorptivity*
Bi	38,800[b]	Cu(II)	13,800
Th	35,000[b]	Ni	10,000
Sc	26,000	Zn	1,200
Y	2,600	Hg(II)	12,000
La	$<$1,000	Mn(II)	$<$1,000
Al	$<$1,000	Hf	12,000
Fe(II)	6,000	Zr	3,100
Pd(II)	13,800	Ti(IV)	$<$1,000
Co(II)	24,400	Cr(III)	$<$1,000

[a] Calcium has molar absorptivity 3,900 for 445 nm and pH 12.07.
[b] Complexes of metal–ligand ratio of 1:3 are formed.



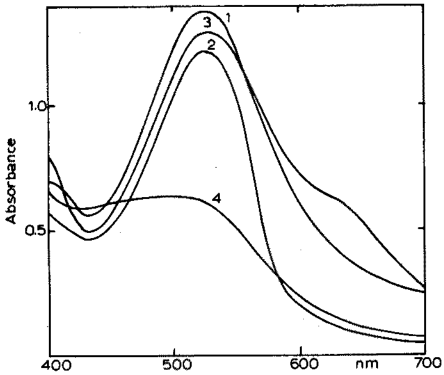


Fig. 1. Absorbance spectra of azonol A at different acidities. (1) $H^\circ = -2.60$; (2) pH 1.10; (3) pH 5.27; (4) pH 10.93; $c_L = 1.00 \cdot 10^{-4}$ *M*.

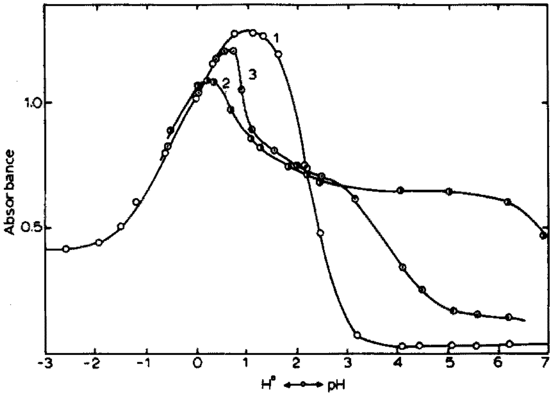
Fig. 2. Absorbance spectra of scandium (1, 2) and cobalt(II) (3, 4) complexes with azonol A. (1) and (3) pH 1.10; (2) and (4) pH 5.27; $c_L = 1.00 \cdot 10^{-4}$ *M*, $c_M = 4.00 \cdot 10^{-4}$ *M*.

Spectral characteristics

Typical spectral curves corresponding to the appearance of individual proton complexes (see below) of the ligand are presented in Fig. 1. Similar curves of the scandium and cobalt(II) complexes are shown in Fig. 2.

Influence of acidity and adherence to Lambert–Beer law

The dependence on pH of the absorbance of the reagent, and its cobalt(II) and scandium complexes is shown in Fig. 3. The maximum absorbance of both ions is at about pH 2.5. Unfortunately, this acidity is the least suitable for the determination, owing to the rapid change of the absorbance of the reagent alone around this pH value, and because of many interfering reactions. A pH of about 1.10, corresponding to the blue form of the reagent, is more suitable because changes in the reagent absorbance with pH are then small and because of the suppression of many interfering reactions. Figure 4 shows that the Lambert–Beer law is obeyed for both cobalt(II) and scandium up to $2.00 \cdot 10^{-5}$ *M* metal ion concentrations.



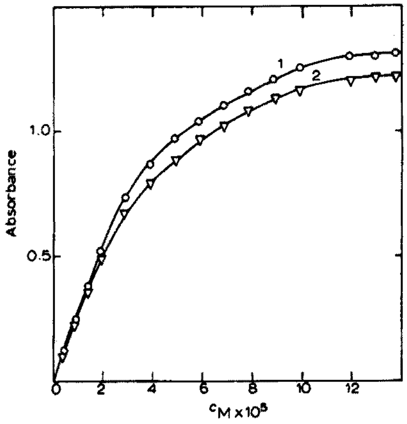


Fig. 3. pH dependence of absorbance of azonol A (1) and its scandium (2) and cobalt(II) (3) complexes at 610 nm. $c_L = 1.00 \cdot 10^{-4}\ M$; $c_{Sc} = c_{Co} = 2.00 \cdot 10^{-5}\ M$.

Fig. 4. Dependence of absorbance on the concentration of metal ion (c_M) at 610 nm. pH 1.10; $c_L = 1.00 \cdot 10^{-4}\ M$; (1) scandium; (2) cobalt(II).

Effect of time and temperature

The stability of the reagent was investigated in aqueous solution at 20° and 50° for 24 h. It may be seen from Table II that the stability of the aqueous reagent solution is quite satisfactory in usual temperature conditions and in the range of 1–10 h. The cobalt (II) and scandium complexes prepared in this time interval were also of reasonable stability.

TABLE II

STABILITY OF AQUEOUS REAGENT SOLUTION ($1.00 \cdot 10^{-4}\ M$)

Time (min)	*5*	*10*	*20*	*40*	*60*	*120*	*180*	*300*	*600*	*1440*
Absorbance[a]	0.935	0.921	0.918	0.915	0.911	0.910	0.909	0.905	0.901	0.874
(490 nm)[b]	0.920	0.912	0.906	0.900	0.895	0.889	0.815	0.814	0.911	0.780

[a] 20°.
[b] 50°.

Effect of foreign ions on the determination of cobalt(II) and scandium

The effects of 25 cations and 15 anions on the cobalt(II) and scandium determinations were investigated. The limiting value of the concentration of a foreign ion was taken as that which caused an error of ±5% in the determination of 0.5 µmole of cobalt(II) or scandium. The results obtained are summarized in Tables III and IV. For cobalt(II), interfering ions (in µmole) are: vanadium(V) (2), palladium(II) (3), copper(II) (3), scandium (3), zinc (4), thorium (10), nickel (10), oxalate (10), cyanide (15), iron(III) (20), iron (II) (4), yttrium (20), tin(II) (20), hafnium (50), mercury(II) (50), cadmium (50), manganese(II) (50), molybdenum(VI) (50), and lead(II) (50). The determination of scandium is affected by: bismuth (0.02), thorium (0.02), hafnium (0.05), iron(III) (0.05), zirconium (0.3), yttrium (0.3), lanthanum (0.5), vanadium(V) (2), fluoride (5), phosphate (5), arsenate (5), oxalate (10), tin(II) (20), lead(II) (50), and molybdenum(VI) (50). Other ions in amounts up to 50 µmole do not interfere.

TABLE III

DETERMINATION OF COBALT(II) IN THE PRESENCE OF FOREIGN IONS

Foreign ion	*Cobalt (II) found (µmole)*		
	a	b	c
—	0.500	0.500	0.500
Bi	0.498	0.505	0.514
Zr	0.496	0.506	0.580
Hf	0.497	0.507	0.550
Th	0.501	0.560	0.610
Fe(III)	0.501	0.505	0.880
Hg(II)	0.502	0.503	0.560
Al	0.500	0.502	0.480
Cd	0.503	0.510	0.550
Zn	0.510	0.720	0.870
Sc	0.520	0.605	0.920
U(VI)	0.505	0.506	0.487
La	0.507	0.520	0.580
Sn(II)	0.510	0.515	[e]
CN^-	0.508	0.480	0.420
PO_4^{3-}	0.498	0.486	0.507
Cl^-	0.502	0.500	0.497
Br^-	0.489	0.485	0.483
I^-	0.493	0.489	0.486
NO_3^-	0.505	0.500	0.498
ClO_4^-	0.501	0.505	0.504
Oxalate	0.498	0.495	[e]
Y	0.520	0.590	0.620
Ag	0.480	0.495	0.505
Mn(II)	0.487	0.485	0.560
Mo(VI)	0.490	0.495	0.570
V(V)	0.603	[d]	[d]
Mg	0.495	0.502	0.505
Ba	0.502	0.500	0.505
Sr	0.498	0.490	0.500
Ca	0.505	0.507	0.520
Pd(II)	0.520	0.580	0.710
Pb(II)	0.480	0.505	0.530
Cu(II)	0.520	0.610	0.935
Ni	0.515	0.580	0.870
Fe(II)	0.520	0.610	0.850
F^-	0.505	0.483	0.485
AsO_4^{3-}	0.491	0.483	0.475
AcO^-	0.496	0.505	0.508
Tartrate	0.491	0.485	0.478
Citrate	0.488	0.485	0.479
SCN^-	0.490	0.485	0.484
SO_4^{2-}	0.501	0.500	0.503

[a] 1 μmole of foreign ion present.
[b] 10 μmole of foreign ion present.
[c] 50 μmole of foreign ion present.
[d] Destruction of reagent because of oxidation.
[e] Destruction of reagent because of reduction.

TABLE IV

DETERMINATION OF SCANDIUM IN THE PRESENCE OF FOREIGN IONS

Foreign ion	*Scandium found (µmole)*		
	a	b	c
—	0.500	0.500	0.500
Bi	0.610	0.780	0.900
Zr	0.560	0.605	0.780
Hf	0.610	0.720	0.850
Th	0.612	0.740	0.880
Fe(II)	0.590	[d]	[d]
Hg(III)	0.504	0.490	0.515
Al	0.507	0.512	0.520
Cd	0.506	0.490	0.515
Zn	0.510	0.503	0.480
Co(II)	0.520	0.522	0.525
U(VI)	0.506	0.490	0.512
La	0.526	0.590	0.668
Sn(II)	0.512	0.518	[e]
EDTA	0.480	0.411	0.188
PO_4^{3-}	0.482	0.464	0.382
Cl^-	0.500	0.505	0.510
Br^-	0.506	0.510	0.517
I^-	0.498	0.491	0.488
NO_3^-	0.489	0.500	0.504
ClO_4^-	0.501	0.495	0.497
SO_4^{2-}	0.491	0.483	0.478
Y	0.550	0.580	0.750
Ag	0.505	0.502	0.490
Mn(II)	0.503	0.497	0.501
Mo(IV)	0.491	0.494	0.560
V(V)	0.605	[d]	[d]
Mg	0.498	0.503	0.495
Ba	0.508	0.506	0.489
Sr	0.500	0.488	0.501
Ca	0.505	0.509	0.480
Pd(II)	0.508	0.515	0.526
Pb(II)	0.510	0.512	0.520
Cu(II)	0.505	0.507	0.515
Ni	0.507	0.512	0.523
Fe(II)	0.505	0.510	0.521
F^-	0.480	0.450	0.335
AsO_4^{3-}	0.480	0.451	0.365
AcO^-	0.491	0.488	0.485
Tartrate	0.480	0.476	0.450
Citrate	0.485	0.478	0.463
Oxalate	0.486	0.488	[e]
SCN^-	0.494	0.491	0.487

[a] 1 μmole of foreign ion present.
[b] 10 μmole of foreign ion present.
[c] 50 μmole of foreign ion present.
[d] Destruction of reagent because of oxidation.
[e] Destruction of reagent because of reduction.

Precision data

These were obtained by multiple analyses of series of solutions containing 0.3 μmole of cobalt(II) or scandium. The precision of the absorbance measurement for cobalt(II) is ±1.5 (relative standard deviation), corresponding to 0.0045 μmole of cobalt (II); for scandium it is ±1.4% corresponding to 0.0041 μmole.

Structure of complexes

The stability constants of proton complexes of azonol A were determined in the acidity range from $H^\circ = -3$ (Hammett function) to pH 12.95 by visible spectrophotometry at 490 nm, 515 nm and 610 nm (see ref. 6). The values found are given in Table V.

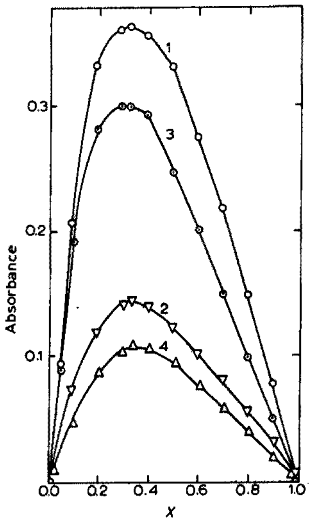
TABLE V

STABILITY CONSTANTS, MOLAR ABSORPTIVITIES AND ISOSBESTIC POINTS OF PROTON COMPLEXES

Complex	L^-	HL	H_2L^+	H_3L^{2+}
log K_n[a]	—	6.43 ± 0.02	2.30 ± 0.05	−0.87 ± 0.15
λ_{max}(nm)	450	490	620	520
$\varepsilon_{\lambda(max)} \cdot 10^{-4}$	1.04	0.92	1.28	1.10
λ_{isos}(nm)	410 540	413	525 430	563

[a] $K_n = [H_nL]\,[H_{n-1}L]^{-1}[H]^{-1}$

According to the color properties of individual proton complexes and the known acidity constants of pentane-2,4-dione[7] and antipyrine[8], it may be assumed that the value of K_1 corresponds to the protonization of the enolic oxygen of pentane-2,4-dione, the value of K_2 to the protonization of nitrogen attached to the methyl group of the py-



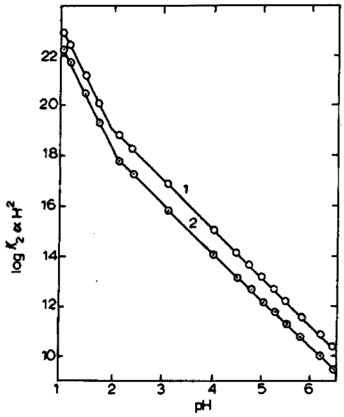


Fig. 5. Continuous variation in isomolar solutions; (1) and (2) scandium; (3) and (4) cobalt (II) 610 nm; $x = c_M/(c_L + c_M)$, $c_L + c_M = 8.00 \cdot 10^{-5}$ *M*. (1) and (3) pH 1.10; (2) and (4) pH 5.27.

Fig. 6. Dependence of log $K_{12}\alpha_H{}^2$ on pH. (1) scandium complex; (2) cobalt(II) complex.

razolone ring and the value of K_3 to the protonization of the azo nitrogen connected by a bridge bond with the carbonyl oxygen either of the pyrazolone ring or of pentane-2,4-dione. For these reasons, particles L^- and HL are yellow, H_2L^+ is blue and H_3L^{2+} is wine red.

The ratio of metal to ligand in the complexes formed was investigated by the method of continuous variation in isomolar solutions. The corrected curves are given in Fig. 5. A ratio of 1:2 was found in both cases; the same constant molar ratio of the complexes formed was found in the pH range 1–6. According to the structure of the reagent, a mononuclear composition of the complexes seems probable.

The composition and overall stability constants of the metal complexes were determined by the method of BUDESINSKY AND HAAS[9,10], the side reactions of the ligand with hydrogen ion being taken into consideration. The hydrolytic reactions of metal ions may be ignored within given conditions. The conditional stability con-

TABLE VI

CONDITIONAL STABILITY CONSTANTS AND OVERALL STABILITY CONSTANTS OF COBALT(II) AND SCANDIUM COMPLEXES

Complex composition	*pH*	A_1/A_2[a]	*log* K_{12}	*log* α_H[b]	*log* β[c]
CoH_4L_2	1.10	2.880	9.07	6.52	26.51
	1.25	2.900	9.06	6.27	26.60
	1.54	3.240	8.75	5.80	26.51
	1.82	3.302	8.65	5.28	26.48
CoH_2L_2	2.18	4.242	8.11	4.81	22.09
	2.46	3.250	8.74	4.22	22.10
	3.15	3.550	8.52	3.33	22.10
	4.05	2.750	9.22	2.40	22.12
	4.45	2.774	9.21	2.01	22.13
	4.77	2.682	9.32	1.64	22.14
	5.27	2.488	9.66	1.08	22.36
	5.52	2.750	9.22	0.98	22.22
	5.80	2.714	9.27	0.75	22.37
	6.20	2.928	9.02	0.43	22.28
	6.45	3.146	8.82	0.30	22.32
ScH_4L_2	1.10	2.400	9.87	6.52	27.31
	1.25	2.412	9.84	6.27	27.38
	1.54	2.530	9.57	5.80	27.33
	1.82	2.582	9.47	5.28	27.30
ScH_2L_2	2.18	2.782	9.18	4.81	23.16
	2.46	2.420	9.82	4.22	23.18
	3.15	2.292	10.21	3.33	23.17
	4.05	2.290	10.22	2.40	23.12
	4.45	2.300	10.19	2.01	23.11
	4.77	2.288	10.26	1.64	23.08
	5.27	2.242	10.39	1.08	23.09
	5.52	2.318	10.13	0.98	23.13
	5.80	2.356	10.00	0.75	23.10
	6.20	2.420	9.82	0.43	23.08
	6.45	2.484	9.66	0.30	23.17

[a] Absorbance proportions.

[b] Coefficient of side reactions of the ligand L with protons; $\alpha_H = \sum_0^N [H]^n K_0 K_1 K_2 \ldots K_n$, $K_0 = 1$.

[c] $\log \beta = \log K_{12}\alpha_H^2 + i$ pH; $i = 2, 4$ (see Fig. 6).

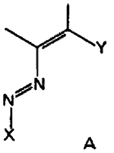
stants, K_{12}, were determined by the method of proportional absorbances[11]; their values are given in Table VI. The calculated dependence of log $K_{12}\alpha_H^2$ on pH is plotted graphically in Fig. 6. The slope of the curves indicates a complex composition MH_4L_2 in the pH range 1.10–2.20, and of MH_2L_2 in the range 2.20–6.40 (in both cases M = Co(II), Sc). The corresponding overall stability constants and molar absorptivities are given in Table VII.

TABLE VII

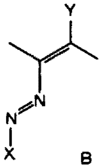
OVERALL STABILITY CONSTANTS AND MOLAR ABSORPTIVITIES OF COBALT(II) AND SCANDIUM COMPLEXES

Complex	*log β*	λ_{max}	$\varepsilon_{\lambda(max)} \cdot 10^{-4}$
CoH_2L_2	22.20 ± 0.03	490	1.26
CoH_4L_2	26.53 ± 0.02	525	2.56
ScH_2L_2	23.13 ± 0.08	525	2.42
ScH_4L_2	27.33 ± 0.01	525	2.73

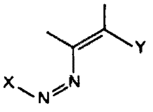
From the viewpoint of *cis–trans* isomerism, four different compounds A, B, C, D may be formed by the coupling of 4-antipyrinyldiazonium chloride with pentane-2,4-dione, where X denotes the pyrazolone ring and Y the enolic hydroxyl. Compounds



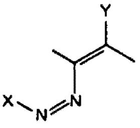
A



B



C



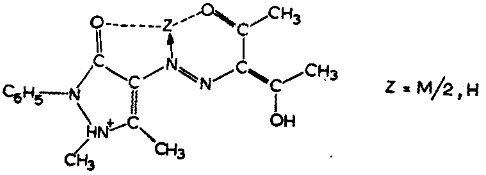
D

C and D are less probable for steric reasons. If compound B is formed, two types of metal chelates are possible. In the first, B appears as a bidentate ligand with oxygen donors from pentane-2,4-dione only and complexation is connected with the displacement of one proton; in the second, B is a tridentate ligand with two oxygen donors (one from the pyrazolone ring and the other from the pentane-2,4-dione) and one nitrogen donor of the azo group, and no proton displacement occurs. If compound A is formed, it appears as a tridentate ligand with the possibility of the formation of two different types of complexes. The first type is connected with a proton displacement reaction and the complexation occurs with oxygen of the enolic hydroxyl, oxygen of the pyrazolone ring and nitrogen of the azo group. The second type is sterically identical with the second type of complexes of compound B, except that the enolic hydroxyl is in the *trans* position so that the complexation of both oxygens of pentane-2,4-dione with the same metal ion is impossible.

The results of experimental investigations, showing that the compound A has the most probable structure corresponding to azonol A, may be summarized as follows:

1. no proton displacement reaction was observed during the complexation;
2. complexes of metal–ligand molar ratio of 1:2 are formed usually, which indicates that azonol A probably always appears as a tridentate ligand;
3. 3-phenylazo pentane-2,4-dione prepared by the same procedure gives yellow (pH 13–1) and violet ($H^\circ \leq -1$) solutions which show no significant complexation with metal ions;

4. the chromogenic similarity (see Figs. 1 and 2) of complexes of MH_4L_2 and H_3L^{2+} may be explained by a similar structure



Other properties of azonol A and its complexes

Complexes H_3L^{2+}, H_2L^+, MH_4L_2 and MH_2L_2 may be extracted into *n*-butanol and chloroform. The extraction depends strongly on the nature of the anion present in the aqueous phase. If the more usual monovalent anions are present, the ratio of extraction increases according to the series $ClO_4^- > NO_3^- > Cl^-$. No extraction takes place with benzene or carbon tetrachloride. For this reason, it may be assumed that the extraction proceeds with the complexes in the form of their electroneutral ion associates, *i.e.* $(H_2L)^+(ClO_4)^-$. Dependence of azonol A extraction on the type of anion may be used for photometric determination of some anions. Complexes HL and complexes of divalent metals of ML_2 (pH >6.5) may be extracted into chloroform or benzene because of their electroneutrality.

Azonol A may also be used as an indicator in compleximetric titrations of Bi, Zr, Hf, Sc, lanthanons, Zn, Hg(II), Cd, Pb(II), Fe(II) and Mn(II) because of its unusual chromogenic properties. Titrations of Th, Co(II), Cu(II), Ni, and Pd(II) give poor results, since the indicator complexes are too stable.

The formation of the azonol A–nickel complex shows an interesting time dependence which can be used for a very selective nickel determination.

A disadvantage of azonol A appears in its instability towards oxidizing and reducing agents. However, this may be of advantage for an additional determination if an easy elimination of reagent is necessary.

This work was aided by a grant from the National Research Council, Ottawa, Ont.; this help is greatly appreciated.

SUMMARY

3-(4-Antipyrinylazo)-2,4-pentanedione (azonol A) forms brick-red and wine-red complexes with Co(II), Pd(II), Ni, Fe(II), Cu(II), Zn, Cd, Hg(II), Pb(II), Mn(II), Sc, Y, lanthanons, Zr, Hf, Th and Bi, in the pH range of 1.00–10.00. The complexes usually have a metal:ligand ratio of 1:2, except for the thorium and bismuth complexes which are 1:3. Complexation with cobalt(II) at pH 1.10 in the presence of EDTA allows a selective determination of cobalt; of 25 cations studied, only 4-fold molar ratios of vanadium(V), 6-fold molar ratios of palladium(II), copper(II) and scandium and 8-fold molar ratios of zinc and iron(II) caused interference in the determination of 0.5 μmole of cobalt(II). Amongst 15 anions, 20-fold molar ratios of oxalate and 30-fold molar ratios of cyanide caused low results. Scandium can be determined at pH 1.10 in presence of cyanide; only bismuth, thorium, hafnium and iron(III) interfere seriously.

RÉSUMÉ

La 3-(4-antipyrinylazo)-2,4-pentanedione (azonol A) forme des complexes rouge brique et rouge vin avec Co(II), Pd(II), Ni, Fe(II), Cu(II), Zn, Cd, Hg(II), Pb(II), Mn(II), Sc, Y, La, Zr, Hf, Th et Bi à des pH compris entre 1.0 et 10.0. Le rapport métal:ligand est généralement de 1:2, sauf pour thorium et bismuth (1:3). Pour effectuer un dosage sélectif du cobalt, il est possible de le complexer par EDTA, au pH 1.1. Parmi les 25 cations étudiés, seuls vanadium(V), palladium(II), cuivre(II), scandium, zinc et fer(II) peuvent gêner le dosage de 0.5 µmole de cobalt. Les oxalates et les cyanures sont la cause de résultats trop faibles. Le scandium peut être dosé au pH 1.1, en présence de cyanure: seuls bismuth, thorium, hafnium et fer(III) gênent sérieusement.

ZUSAMMENFASSUNG

3-(4-Antipyrinylazo)-2,4-pentandion (Azonol A) bildet im pH-Bereich von 1–10 ziegelrote und weinrote Komplexe der Elemente Co(II), Pd(II), Ni, Fe(II), Cu(II), Zn, Cd, Hg(II), Pb(II), Mn(II), Sc, Y, Lanthaniden, Zr, Hf, Th und Bi. Die Komplexe besitzen im allgemeinen ein Metall–Liganden-Verhältnis von 1:2, ausser beim Thorium und Wismut, bei denen das Verhältnis 1:3 beträgt. Der Kobalt-Komplex ermöglicht beim pH 1.10 und in Gegenwart von ÄDTE die selektive Bestimmung des Kobalts. 25 Kationen wurden untersucht, jedoch störte die Bestimmung von 0.5 µmol Kobalt(II) nur das vierfache Molverhältnis von Vanadium(V), das sechsfache Molverhältnis von Palladium(II), Kupfer(II), Scandium und das achtfache Molverhältnis von Zink und Eisen(II). Bei 15 Anionen ergab ein 20faches Molverhältnis von Oxalat und ein 30faches Molverhältnis von Cyanid niedrigere Ergebnisse. Scandium kann bei einem pH von 1.10 in Gegenwart von Cyanid bestimmt werden. Nur Wismut, Thorium, Hafnium und Eisen(III) stören ernsthaft.

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ELECTROCHEMICAL CHARACTERISTICS OF 2-METHYL-1,4-NAPHTHOQUINONE (VITAMIN K_3)

A COULOMETRIC MICROMETHOD OF DETERMINATION

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The importance of 2-methyl-1,4-naphthoquinone (vitamin K_3, menadione) and its action in relation to blood coagulation processes is well known.

The increased use of this compound in polyvitamin preparations and the fact that its electrochemical characteristics have not been studied critically led us to this investigation.

FIESER AND FIESER[1] were the first to show that it is possible to reduce naphthoquinones at a dropping mercury electrode. ONTRUST AND WOSTMANN[2] determined menadione, using a solvent mixture of isopropanol–petroleum ether and a buffer composed of ammonia and ammonium chloride as supporting electrolyte. In this medium the reduction wave shows a maximum suppressed only by methylene blue. JONGKIND *et al.*[3] used a solvent mixture of benzene and methanol with 0.2 M lithium chloride and made alkaline with ammonia; they also employed methylene blue as a maximum suppressor. The alkaline media proposed by these authors are unsatisfactory because of the instability of vitamin K_3 at pH above 8. BURGER[4] employed 0.5 M potassium chloride as a supporting electrolyte but without buffering the medium.

The purpose of this work was to investigate the electrochemical characteristics of menadione and to develop a micro-coulometric method of determination of this compound. We were interested in several electroanalytical aspects and the investigations were carried out by different techniques such as d.c. polarography, coulometric titration, controlled potential coulometry, and cyclic voltammetry.

EXPERIMENTAL

Polarograms were recorded in the usual manner with a Leeds and Northrup Electrochemograph at 25° ±0.1°.

Cyclic voltammetry was performed with a hanging mercury drop electrode, at a voltage sweep of 20 mV per sec.

The controlled potential coulometry was carried out, with a potentiostat, in an H-cell with a mercury pool cathode and a platinum wire auxiliary electrode.

The coulometric titrations with electrogenerated cerium(IV) ion were performed in an H-type glass cell with a fine sintered glass disk in the cross arm. The solution

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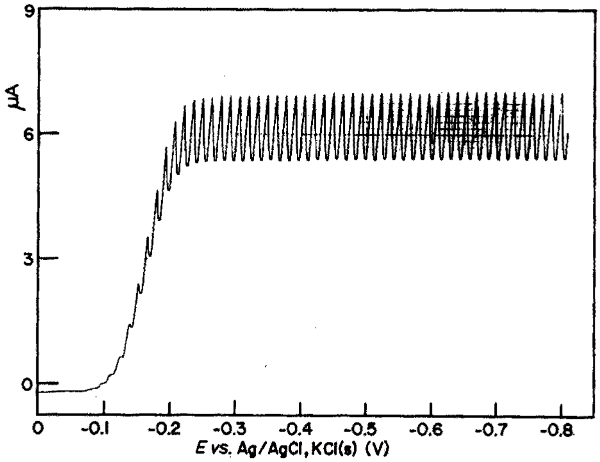


Fig. 1. Polarogram of 1 m*M* vitamin K_3 in an acetate buffer of pH = 5.9.

TABLE I

HALF-WAVE POTENTIALS OF VITAMIN K_3 AS A FUNCTION OF pH

pH	$E_{\frac{1}{2}}$ *vs. Ag/AgCl, KCl (s) (V)*
4.30	−0.040
4.75	−0.075
4.98	−0.085
5.35	−0.120
5.70	−0.132
5.90	−0.150
6.25	−0.175
8.00	−0.285

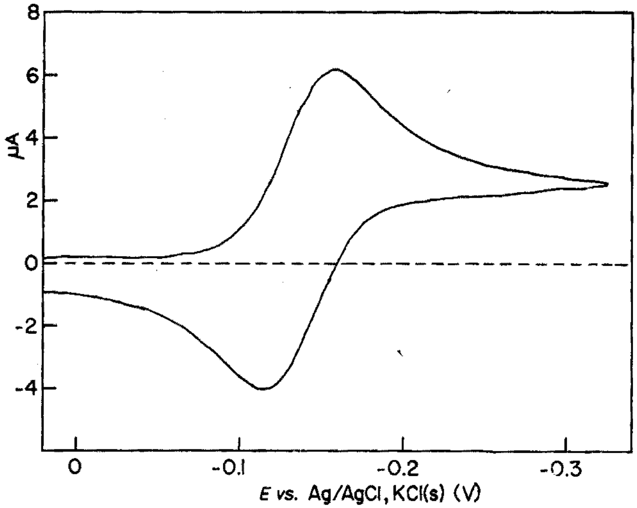


Fig. 2. Cyclic voltammetry of 1 m*M* vitamin K_3 in acetate buffer of pH = 5.9. Voltage sweep: 20 mV/sec. Hanging mercury drop electrode.

level in the auxiliary electrode compartment was kept above that in the working electrode compartment to avoid backflow of sample. The volume of the test solution was 75–100 cm^3 and rapid magnetic stirring was employed.

As discussed in detail elsewhere[5], the current efficiency for the oxidation of cerium(III) to cerium(IV) ion at a platinum anode approaches more closely to 100%, the greater the concentrations of both cerium(III) ion and sulfuric acid. However, because the solubility of cerium(III) sulfate is not very large, and decreases with increasing concentration of sulfuric acid, a compromise is necessary. An optimal compromise is 3 F sulfuric acid and 0.05 F $Ce_2(SO_4)_3 \cdot 8\ H_2O$, and this supporting electrolyte was used in all of the titrations. The same supporting electrolyte was used in the auxiliary electrode compartment.

A platinum foil generator anode with an area of 5 cm^2 (total of both sides) was used to provide a current-density of 2–3 mA/cm^2 in the optimal range. A coiled platinum wire served as auxiliary electrode and its area was not critical.

The electrolysis current was supplied from a conventional line-operated power supply. Since the current was only approximately constant (±1%), the Ether Ltd. integrator previously described[6] was used to measure precisely (±0.1%) the number of coulombs passed during the coulometric titrations.

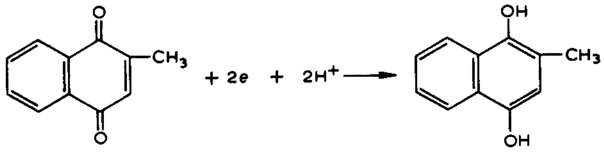
Potentiometric end-point detection with a platinum indicator electrode and an Ag/AgCl, KCl (s) reference electrode, was employed.

Standard solutions of vitamin K_3 (U.S.P. Standard) were freshly prepared in methanol.

DATA AND DISCUSSION

Because vitamin K_3 is very unstable in alkaline medium, an alkaline supporting electrolyte was avoided, and acetate–acetic acid and phosphate buffers of pH below 8 were employed.

In these two media, the 2-methyl-1,4-naphthoquinone shows a well shaped wave, whose limiting current is controlled by diffusion and is without a maximum. The reduction involves two electrons to produce the corresponding hydroquinone:



A typical polarogram is shown in Fig. 1.

The observed half-wave potentials in various buffers of different pH values are listed in Table I. The values are referred to the Ag/AgCl, KCl (s) reference electrode whose potential is +0.197 V *vs.* N.H.E.

The slope of the wave indicates that the 2-electron reduction is nearly but not perfectly reversible. Values of $E_{\frac{3}{4}}$—$E_{\frac{1}{4}}$ from many polarograms averaged 34±2 mV (even though correction for iR drop was considered), compared to the theoretical value of 28 mV.

When plotted against pH, the values of $E_{\frac{1}{2}}$ produce a straight line whose slope is 68 mV, which is 8.9 mV greater than the theoretical value. Extrapolated to pH 0, the straight line gives a value of +0.26 V *vs.* Ag/AgCl, KCl (s) which is close to the standard oxidation–reduction potential.

The near reversibility of the reaction is also demonstrated by the cyclic voltammogram in Fig. 2. The difference in potential between the cathodic and anodic peaks is 43 mV which is only 13.8 mV greater than the theoretical value of a 2-electron reaction. The quasi-reversibility of the system is further shown by the fact that the anodic half-wave potential of the hydroquinone (prepared by controlled potential reduction at a mercury cathode) is only a few millivolts more positive than the cathodic $E_{\frac{1}{2}}$.

The limiting current for the reduction of vitamin K_3 is diffusion-controlled and thus directly proportional to the concentration. In a buffer composed of 0.1 *M* sodium acetate and 0.08 *M* acetic acid, and 3–10 vol. % methanol (necessary to dissolve the vitamin originally), the observed value of $i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ was 3.88 ± 0.04 with a dropping electrode whose $m^{\frac{2}{3}}t^{\frac{1}{6}}$ value was 1.60.

The usual method of determining menadione is based on its preliminary reduction to the hydroquinone by zinc dust in acid medium, followed by titration with standard cerium(IV) solution[7]. This method is only suitable with relatively large samples (150 mg) and because of the low levels of this vitamin in pharmaceuticals, biological fluids, and foods, it is highly desirable to have a micromethod for its determination.

We have developed such a method based on preliminary reduction to the hy-

TABLE II

CERI-COULOMETRIC DETERMINATION OF 2-METHYL-1,4-NAPHTHOQUINONE AFTER REDUCTION BY METALLIC ZINC IN A MIXTURE OF ACETIC AND SULFURIC ACIDS

Taken (mg)	*Found (mg)*	*Difference (mg)*
0.300	0.297	−0.003
0.628	0.619	−0.009
1.000	1.010	+0.010
1.256	1.250	−0.006
1.500	1.520	+0.020
1.820	1.800	−0.020
2.50	2.49	−0.01
2.50	2.46	−0.04
3.00	3.00	0.00
3.03	3.00	−0.03
3.20	3.24	+0.04

TABLE III

CERI-COULOMETRIC DETERMINATION OF 2-METHYL-1,4-NAPHTHOQUINONE AFTER REDUCTION BY CONTROLLED POTENTIAL COULOMETRY AT −0.60 V *vs.* Ag/AgCl KCl (s)

Taken (mg)	*Found (mg)*	*Difference (mg)*
0.855	0.860	+0.004
0.855	0.848	−0.007
1.710	1.690	−0.020
3.42	3.39	−0.03

droquinone by controlled potential electrolysis, or by zinc, followed by coulometric titration with electrogenerated cerium(IV) ion.

Table II summarizes results obtained by coulometric titration with electrogenerated cerium(IV) ion after reduction by zinc metal in a mixture of 2 *M* acetic and 1 *M* sulfuric acid.

Table III summarizes results obtained by coulometric titration with electrogenerated ceric ion after reduction by controlled potential electrolysis at —0.60 V *vs.* Ag/AgCl KCl (s).

In all cases potentiometric end-point detection with a platinum indicator electrode was employed. The potential change at the end-point is large (about 150 mV per 1% titrated).

It should be easily possible to determine considerably less than the quantities of vitamin K_3 listed in Tables II and III simply by employing a smaller volume of supporting electrolyte in an appropriately smaller cell. This would be desirable, for example, after separating small amounts of 2-methyl-1,4-naphthoquinone by solvent extraction from foods and biological samples.

We are grateful to le Fonds National de la Recherche Scientifique (Belgium) and to the Scientific Committee of the NATO Organization which provided fellowships to one of us (G.J.P.).

SUMMARY

Electrochemical characteristics of 2-methyl-1,4-naphthoquinone (vitamin K_3) were studied by polarography, controlled potential coulometry, and cyclic voltammetry. A polarographic procedure in acetate and phosphate buffers and a microcoulometric method of determination of this compound with electrogenerated cerium(IV) ion are described.

RÉSUMÉ

Les caractéristiques électrochimiques de la 2-methyl-1,4-naphtoquinone ont été déterminées à l'aide de la polarographie, de la coulométrie à potentiel contrôlé et par voltamétrie cyclique. Les auteurs proposent une microméthode coulométrique de dosage à l'aide de l'ion cerium(IV) électrogénéré de même qu'une méthode polarographique de dosage en milieux acétique et phosphorique tamponnés.

ZUSAMMENFASSUNG

2-Methyl-1,4-naphthochinon (Vitamin K_3) wurde polarographisch, coulometrisch mit kontrolliertem Potential und mit der zyklischen Volametrie untersucht. Die mikrocoulometrische Bestimmung dieser Verbindung mit elektroerzeugtem Cer(IV)-Ionen wird beschrieben.

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ANION-EXCHANGE CHROMATOGRAPHY OF HYDROXY ACIDS WITH AUTOMATIC ANALYSIS OF THE ELUATE

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The separation of hydroxy acids by anion-exchange chromatography combined with automatic analysis of the eluate by three simultaneous methods has been described previously[1]. Chromic acid oxidation is applied as a non-specific method and gives responses with all the hydroxy acids studied. The second method is the carbazole reaction[2,3] which gives a very strong response with uronic and 5-hexulosonic acids. Aldobionic, isosaccharinic, metasaccharinic and some other hydroxy acids are also recorded in this channel (see Table I). Hydroxy acids which yield formaldehyde on oxidation with periodate are detected by the third method; the formaldehyde reacts with pentane-2,4-dione in the presence of ammonium ions[4]. The method is specific for acids which contain a primary hydroxyl group with either a neighbouring hydroxyl or carbonyl group. Although these methods have proved very useful in analyzing complicated mixtures of hydroxy acids[5,6], there are still some types of acids which cannot be distinguished from one another.

The aim of this work was to introduce a fourth channel into the analyzing system which should make it possible to obtain additional information concerning the identity of various hydroxy acids. In this channel the consumption of periodate is determined automatically by ultraviolet spectrophotometry.

CHROMATOGRAPHIC SEPARATIONS

The equipment was the same as that used previously[1,2]. The eluents were 0.08 M sodium acetate with acetic acid added to pH 5.9, 0.5 M acetic acid and 1 M acetic acid at 30°. The amounts of acids applied to the column were between 1 and 2 mg. The experimental details are given in the legends under Figs. 3 and 4.

Most of the acids studied were prepared in connection with previously published work from this laboratory or were from commercial sources. Altronic and 2,3-*erythro*-dihydroxybutyric acids were prepared by E. MARTINSSON and their preparation will be described in a forthcoming paper.

The volume distribution coefficients, D_v, were calculated as usual[7].

THE FOUR-CHANNEL ANALYZER

The principle of the four-channel analyzer is indicated in Fig. 1. The eluate is divided into five streams, one of which goes to a fraction collector, or if no additional identification is required, to the waste. If the eluent stream is less than that required

TABLE I

DISTRIBUTION COEFFICIENTS, PERIODATE CONSUMPTION AND RELATIVE RESPONSE INDICES OF HYDROXY ACIDS[a]

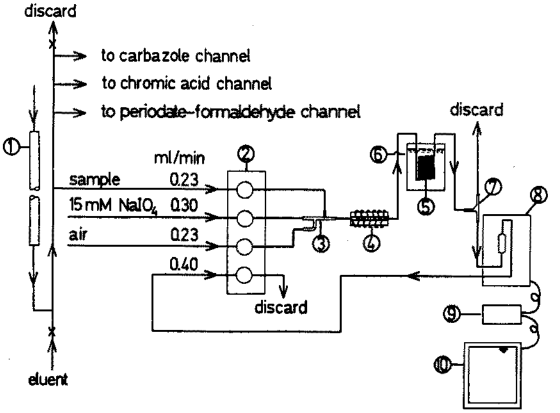
Acid	*D_v value*		*Mole periodate per mole acid*	*Periodate index*	*Formaldehyde index*	*Carbazole index*
	0.5 M HAc	*0.08 M NaAc*				
Erythronic	19.0		1.2	0.80	1.88	0.04
Threonic	19.2	10.9	1.7	0.90	1.72	0.03
Arabinonic	14.1	9.3	2.4	1.00	1.30	0
Lyxonic	19.4		2.2	0.97	1.53	0
Ribonic	9.1		1.7	1.05	1.30	0
Xylonic	15.6		2.5	1.01	1.38	0
Allonic	9.4		2.0	0.92	0.80	≃0.01
Altronic	11.7		2.1	0.90	0.65	≃0.01
Galactonic	11.3	8.0	2.2	0.95	0.87	≃0.01
Gluconic	12.5	7.6	2.0	1	1	≃0.01
Gulonic	13.5		2.4	1.01	1.11	≃0.01
Idonic	12.6	7.1	2.3	0.96	0.92	≃0.01
Mannonic	17.8	9.6	2.6	1.00	1.17	≃0.01
Talonic	6.2		2.1	1.11	1.06	≃0.01
6-Deoxy-mannonic	19.2	11.3	2.2	0.95	0	0
Melibionic	4.65	2.96	2.3	0.40	0	0.06
Lactobionic	5.10	3.46	1.5	0.30	0.50	0.07
α-D-Glucoisosaccharinic	6.01		0.7	0.50	1.80	0.07
β-D-Glucometasaccharinic	9.4		1.0	0.41	1.14	0.09
α-D-Glucosaccharinic	5.45		1.4	0.90	1.20	0
3,4-Dihydroxybutyric	3.37		0.9	0.70	1.42	0
2,3-*threo*-Dihydroxybutyric	16.7		1.0	0.77	0	0
2,3-*erythro*-Dihydroxybutyric	21.8		0.9	0.71	0	0
2,4-Dihydroxybutyric	14.5		0	0	0	0.04
Glycolic	18.7	15.0	0	0	0	0.10
Lactic	15.1	13.8	0	0	0	0.04
Glyoxylic		21.7	0.5	0.67	0.02	0.70

[a] The reported periodate consumption and the relative response indices refer to runs in acetic acid except for glyoxylic acid which was studied only in sodium acetate.

by the analyzing system, the eluate stream is diluted with eluent. The other four streams are passed to the analyzer by a peristaltic pump and analyzed automatically by (*a*) chromic acid oxidation, (*b*) color reaction with carbazole, (*c*) periodate oxidation and subsequent determination of formaldehyde, and (*d*) periodate oxidation with subsequent determination of the periodate consumption.

The method used in the periodate consumption channel is illustrated in Fig. 1. By a peristaltic pump an aqueous solution of sodium periodate is segmented by an air stream and mixed with the sample solution and then passed to a thermostatted vertical reaction coil. After deaeration in a T-fitting, the main part of the solution is pumped through a flow cell and the UV absorption is measured at 247 nm with a double-beam spectrophotometer. A variable beam attenuator (Beckman No. 104186) is used as a reference. The signal is expanded by a factor of five and recorded continuously.

To obtain a stable baseline the absorbance of the reagent solution should not be too high, and for this reason a moderate periodate concentration had to be chosen. On the other hand, a periodate concentration which is too low would result in excessively slow reaction rates. A 15 m*M* sodium metaperiodate solution (8.5 m*M* after mixing with the sample solution) was found satisfactory. The baseline was adjusted to 40% transmittance with the attenuator. Under these conditions a stable baseline was recorded. To obtain the desired sensitivity under the applied conditions, the reaction temperature was kept at 70°. The total hold-up time in this channel was the same as in the other analyses. The time in the mixing coil was 45 sec and that in the reaction coil 6 min. Under these conditions ethylene glycol was oxidized quantitatively, whereas with the polyhydroxy acids the consumption of periodate was less than the theoretical amount calculated from the number of vicinal hydroxyl groups. The pH of the solution after its passage through the mixing coil was dependent upon the applied eluent. With 1 *M* acetic acid, 0.5 *M* acetic acid and 0.08 *M* sodium acetate (pH adjusted to 5.9 with acetic acid) the pH was 2.6, 2.75 and 5.8, respectively.



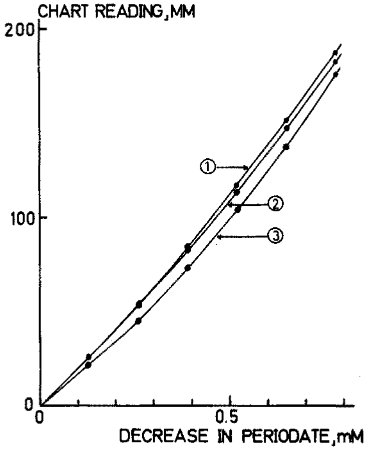


Fig. 1. Equipment and working conditions applied in the periodate consumption channel. (1) Ion-exchange column; (2) peristaltic pump (Technicon); (3) glass fitting (Technicon H3); (4) mixing coil, Teflon tube, inner diam. 0.8 mm, length 1.2 m; (5) reaction coil, Teflon tube, inner diam. 0.7 mm, length 12 m; (6) heating bath 70°; (7) T-fitting for deaeration (Technicon C1); (8) spectrophotometer (Beckman DB-G); (9) scale expander (Beckman 73490); (10) recorder (Beckman 100502).

Fig. 2. Calibration curves showing the chart reading as a function of the decrease in periodate concentration when 0.08 *M* sodium acetate, pH 5.9 (1), 0.5 *M* acetic acid (2) and 1 *M* acetic acid (3) are used as eluents.

The choice of wavelength was based on determinations of the absorbance spectra in the media applied and on calibration experiments with ethylene glycol in the monitor. In pure water the single absorbance maximum for sodium metaperiodate was recorded at 222 nm, whereas in 0.2 *M* acetic acid and 0.032 *M* sodium acetate the position of the maximum, recorded against the solvents as a reference, was displaced to 235 nm. At this wavelength iodate exhibits a significant absorbance which becomes less important at a somewhat higher wavelength, however.

In the calibration experiments, solutions of ethylene glycol in the applied eluents were oxidized with periodate in the monitor and the decrease in absorbance was measured at different wavelengths. The strongest response was recorded at 247 nm and this wavelength was used in all experiments described in this paper. As can be seen from Fig. 2, the calibration curves show some deviation from linearity. Moreover, the response depends upon the applied eluents. This does not interfere with the application of the method for quantitative analyses.

The periodate consumption of the eluted acids (mole per mole of acid) was calculated as $C_{max} \cdot w/a \cdot f$, where C_{max} is the maximum decrease in the periodate concentration (m*M*) obtained from the peak height and the calibration curve, *w* the band width (ml) at half the band height, *a* the amount of acid (μmoles) applied to the column, and *f* the fraction of the eluate passed through the periodate consumption channel.

In analyses of unknown mixtures, it is recommended that response indices be applied. The response indices are defined as the areas of the elution curves recorded in the more specific channels (*b*, *c* and *d*) divided by that recorded in the chromic acid channel. The absolute values of the response indices are affected by changes of tubings in the peristaltic pump. In the present paper the response indices in the periodate consumption and in the periodate–formaldehyde channels have therefore been calculated relative to those obtained with gluconic acid. Likewise, the carbazole response index has been divided by that obtained with galacturonic acid. These relative response indices are less affected by unavoidable fluctuations of the conditions in the analyzer.

RESULTS AND DISCUSSION

Typical chromatograms recorded with the four-channel analyzer after elution with sodium acetate and acetic acid are reproduced in Figs. 3 and 4. Compounds which

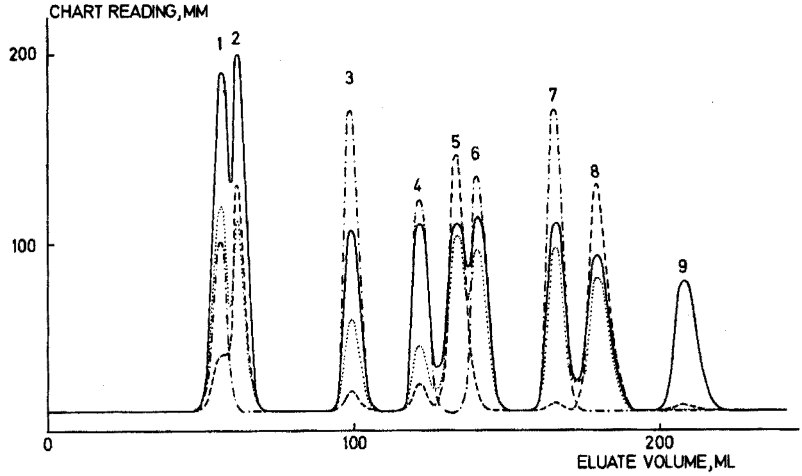


Fig. 3. Separation of lactobionic (1), 2-O-(α-D-galactopyranosyluronic acid)-L-rhamnose (2), α-D-glucoisosaccharinic (3), β-D-glucometasaccharinic (4), D-galacturonic (5), D-arabinonic (6), D-threonic (7), D-glucuronic (8) and lactic (9) acids. (———) Chromic acid channel, (– – – – –) carbazole channel, (·—·—·—·—) periodate–formaldehyde channel, (.....) periodate consumption channel. Eluent: 0.08 *M* sodium acetate; pH 5.9; flow rate: 5.2 ml cm^{-2} min^{-1}; resin bed: 4 700 mm, Dowex 1-X8; 13–18 μm.

give serious overlapping are included in both runs to illustrate the ability of the analyzer to distinguish between various types of hydroxy acids even under unfavourable chromatographic conditions. By determination of the areas of the elution curves recorded in different channels a fairly accurate determination can be made even of compounds which overlap seriously. In repeated runs of well separated compounds, the areas were readily reproducible until the tubings in the peristaltic pump were exhausted. In duplicate runs, the deviation from the mean was 3% or less.

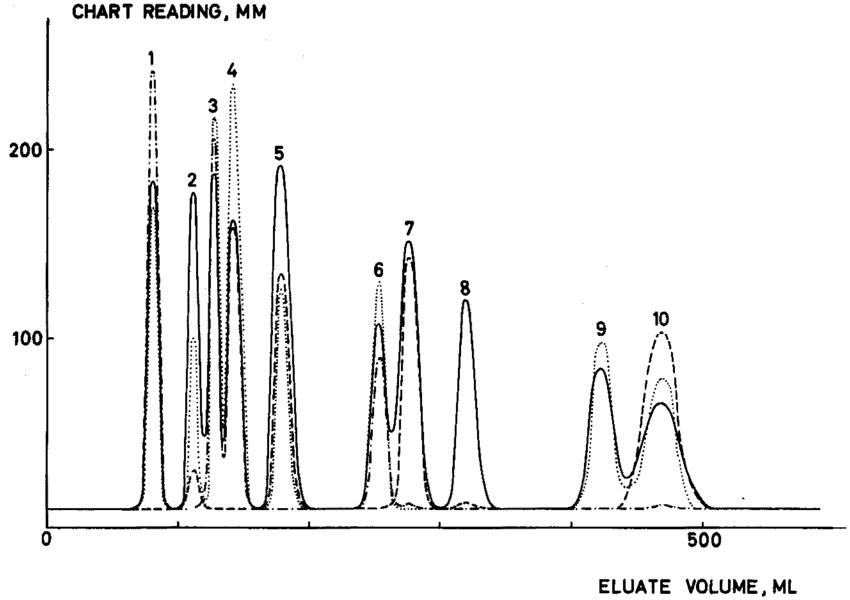


Fig. 4. Separation of 3,4-dihydroxybutyric (1), melibionic (2), α-D-glucosaccharinic (3), talonic (4), 2-O-(α-D-galactopyranosyluronic acid)-L-rhamnose (5), galactonic (6), 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid)-D-xylose (7), 2,4-dihydroxybutyric (8), rhamnonic (9) and D-galacturonic (10) acids. The denotations for the channels are the same as for Fig. 3. Eluent: 0.5 *M* acetic acid; flow rate: 4.4 ml cm^{-2} min^{-1}; resin bed: 6 × 760 mm, Dowex 1-X8, 24–27 μm.

The most important features of the multichannel analyzer are that it can give valuable information about the identity of the separated acids, as well as information about their purity, and about the presence of trace components hidden under curves recorded for major compounds in less specific channels.

The results obtained in runs with single compounds and various mixtures studied in the present work are summarized in Tables I and II. The reactions in the carbazole and periodate–formaldehyde channels for various types of acids have been discussed in previous papers[1,2] and the following discussion is mainly confined to the periodate consumption channel.

As expected, the monohydroxy acids and 2,4-dihydroxybutyric acid gave no response in this channel. Glyoxylic acid is known to react with periodate[8] and as can be seen from Table I, it gave a fairly strong response in the periodate consumption channel but only a weak response in the periodate–formaldehyde channel. All other acids listed in Table I contained vicinal hydroxyl groups and, as expected, these gave a positive reaction. In the three-channel analyzer, the two isomeric 2,3-dihydroxybuty-

TABLE II

DISTRIBUTION COEFFICIENTS, PERIODATE CONSUMPTION AND RELATIVE RESPONSE INDICES OF ALDOBIOURONIC, HEXURONIC AND HEXULOSONIC ACIDS

Acid	*D_v value*			*Mole periodate per mole acid*	*Periodate index*	*Formaldehyde index*	*Carbazole index*
	0.5 M HAc	*1 M HAc*	*0.08 M NaAc*				
2-O-(α-D-Galactopyranosyluronic acid)-L-rhamnose	8.4		4.16	2.4	0.54	<0.01	0.49
4-O-(α-D-Galactopyranosyluronic acid)-D-xylose	12.0			2.0	0.48	<0.01	0.54
6-O-(β-D-Glucopyranosyluronic acid)-D-galactose	15.5			2.2	0.46	<0.01	0.47
2-O-(4-O-Methyl-α-D-glucopyranosyluronic acid)-D-xylose	13.2			0	0	0	0.57
Cellobiouronic acid	26.0		6.0	1.4	0.25	<0.01	0.51
Alluronic		17.1		2.4	0.94	0.04	0.85
Galacturonic		11.0	9.4	2.3	0.90	0.01	1
Glucuronic		22.4	12.8	2.0	0.81	<0.01	0.65
Guluronic		12.3		2.1	1.00	0.04	0.50
Mannuronic		18.6	14.2	2.1	0.86	0.04	0.70
Taluronic		14.2		2.3	0.91	0.01	0.94
4-O-Methyl-D-glucuronic		18.0	8.0	1.1	0.35	<0.01	0.80
arabino-5-Hexulosonic		13.2		1.7	0.67	0.20	1.27
lyxo-5-Hexulosonic		15.4		1.9	0.56	0.27	0.80
ribo-5-Hexulosonic		28.2	17.4	1.5	0.65	0.26	1.30
xylo-4-Hexulosonic		22.3		2.1	0.83	0.90	0.11

ric and 6-deoxyaldonic acids are recorded only in the non-specific chromic acid channel, but as expected, these acids give a strong response in the periodate consumption channel and can therefore easily be distinguished from many other types of acids.

It is interesting to note that under the applied working conditions, the periodate consumption recorded with various diastereomers differs significantly. The values obtained under standardized conditions give hints about the identity of the separated compounds. As an example it can be mentioned that threonic acid is oxidized more rapidly than erythronic acid indicating that similarities exist between the rate of cleavage of various bonds within the aldonic acid and alditol series[9].

On the assumption that only vicinal diols are oxidized (no overoxidation), the theoretical periodate consumptions per mole of isosaccharinic, metasaccharinic and saccharinic acids are 2, 2 and 3 moles, respectively, and the amounts of formaldehyde liberated are 2, 1 and 1 mole, respectively. The deviation from the theoretical periodate consumption can be explained by the short reaction time used. The isosaccharinic acids, which have two α-glycol (CH_2OH–CH(OH)–) groupings, deviate more from the theoretical consumption than do metasaccharinic acids, with one α-glycol and one vicinal *erythro* function, and saccharinic acids, with one α-glycol and two vicinal *erythro* sites. This confirms the observations made by HUTSON AND WEIGEL[10], that the vicinal *erythro* functions are cleaved more easily than are the α-glycol functions.

Of the two aldobionic acids investigated, 6-O-α-D-galactopyranosyl-D-gluconic acid (melibionic) and 4-O-β-D-galactopyranosyl-D-gluconic acid (lactobionic), only the latter acid gave a response in the formaldehyde channel. As expected, melibionic acid consumed more periodate than did lactobionic acid.

Studies with cyclic 1,2-diols[11,12] and methyl aldohexopyranosides[13,14] have shown that *cis*-diols are oxidized more readily than *trans*-diols. The results presented in Table II indicate that the hexuronic acids follow the same rule. The largest difference recorded is that between 4-O-methylglucuronic acid and the unmethylated hexuronic acids. The 5-hexulosonic acids, which can be distinguished from the hexuronic acids by the formaldehyde indices, consume less periodate than the uronic acids. The relative periodate consumption recorded for gluconic, glucuronic and 5-hexulosonic acid is in agreement with earlier observations by SPRINSON AND CHARGAFF[8]. *xylo*-4-Hexulosonic acid, which can be identified by its formaldehyde and carbazole indices, consumes as much periodate as the hexuronic acids.

Of the five aldobiouronic acids studied (Table II) all give about the same carbazole indices. By the periodate indices 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid)-D-xylose and cellobiouronic acids can be distinguished from one another and from the other three aldobiouronic acids. HONEYMAN AND SHAW[15] have shown that the large aglycons decrease the rate of periodate oxidation at the 2,3-glycol site. An analogous effect of the xylose moiety, the 4-methoxy group and the fact that only a *trans*-glycol is accessible for periodate in the xylose moiety, explain the inertness of 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid)-D-xylose under the conditions used in the periodate channel. In a separate experiment with this acid, it was shown that at room temperature and with the same periodate concentration, it consumed one mole of periodate per mole acid in 20 h.

The financial support of the Swedish Council for Applied Research is gratefully acknowledged.

SUMMARY

An automatic method is described for the analysis of complex mixtures of monoprotic hydroxy acids. The acids are separated by anion-exchange chromatography and the eluate is analyzed in a four-channel analyzer by (*a*) chromic acid oxidation, (*b*) the carbazole reaction, and by periodate oxidation with subsequent determination of (*c*) the formation of formaldehyde and (*d*) the periodate consumption.

RÉSUMÉ

Une méthode automatique est décrite pour l'analyse de mélanges complexes d'acides organiques. On effectue une séparation par chromatographie avec échangeur d'anions. L'éluat est analysé: (*a*) par oxydation à l'acide chromique; (*b*) par la réaction au carbazole; et oxydation au periodate avec détermination (*c*) du formaldéhyde formé et (*d*) de la consommation en periodate.

ZUSAMMENFASSUNG

Es wird eine automatische Methode zur Analyse komplexer Mischungen monoprotonischer Hydroxy-Säuren beschrieben. Die Säuren werden mit Hilfe der Anionenaustauscherchromatographie getrennt und das Eluat auf folgende Weise mit Hilfe einer 4-Kanal-Analysators untersucht: (a) Oxydation mit Chromsäure, (b)

Durchführung der Carbazol-Reaktion und nach Oxydation mit Perjodat die Bestimmung, (c) der Bildung des Formaldehyds und (d) des Perjodatverbrauchs.

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METHYLENEIMINODIACETIC ACID DERIVATIVES OF SOME 7-HYDROXYCOUMARINS AS ANALYTICAL REAGENTS

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An interesting study of the fluorescent reactions of 7-hydroxy-4-methylcoumarin methyleneiminodiacetic acid with various metal ions was described by EGGERS some years ago[1]. Almost simultaneously, WILKINS[2] proposed this compound, under the name calcein blue, as an indicator for direct titrations of alkaline earth metals with EDTA, and for the determination of various other metals by addition of excess of EDTA, and back-titration with copper(II) solution; determinations of metal mixtures by compleximetric titrations were also discussed[3]. The fluorescence of the compound and its metal complexes differs sharply with pH. In the pH range 4–10, the indicator shows a bright blue fluorescence which is immediately quenched by copper ion, and very slowly by the palladium ion. Above pH 12, the free indicator does not fluoresce but its complexes with alkaline earth metals show the fluorescence of the free indicator in its acidic form. DIEHL[4] has also reported briefly on the preparation of fluorescent calcein blue derivatives.

These studies prompted an investigation of various derivatives of 7-hydroxycoumarinmethyleneiminodiacetic acid in an attempt to broaden the applicability of this type of reagent, since the parent compound has an unusually high stability to ultraviolet irradiation and shows its maximum fluorescence at the uncommonly long wavelength of 445 nm.

EXPERIMENTAL

Preparation of reagents

7-Hydroxycoumarin and its various derivatives (see Table I) were generally prepared by the PECHMANN reaction[5]; the 3-carboxylic acid ethyl ester derivative was prepared by the method of KNOEVENAGEL[6]. In some cases the modifications suggested by SESHADRI *et al.*[7,8] were introduced in order to improve yields. For the preparation of 3-acetoxy-7-hydroxycoumarin the method of BALAIAH *et al.*[9] was found the most satisfactory. Full details of the preparations of these derivatives are described elsewhere[10]. In general, few difficulties were encountered in obtaining the pure coumarin derivatives, which were characterised by melting points, elemental analyses and thin-layer chromatopraphy.

The methyleneiminodiacetic acid derivatives of the hydroxycoumarins were prepared by Mannich-type condensation of the relevant coumarin with iminodiacetic acid and formaldehyde. In order to establish the optimal conditions for the condensation, since few details of such condensations have been published in the literature, the

TABLE I

7-HYDROXYCOUMARIN DERIVATIVES STUDIED

Complexone of	*Fluorescent colour*	*Mol. wt.*		*N content (%)*		*Excitation peak (nm)*	*Emission peak (nm)*
		Theory	*Found*	*Theory*	*Found*		
7-Hydroxycoumarin	Blue[a]	307	308	4·55	4·1	340, 390	445
4-Methyl-7-hydroxycoumarin	Blue	321	323	4·4	4·5	340, 385	441
5-Methyl-7-hydroxycoumarin	Yellow green	321	317	4·4	4·6	340, 385	442
8-Methyl-7-hydroxycoumarin	Yellow green	321	322	4·4	4·2	340, 390	444
3-Carboxy-7-hydroxycoumarin	Blue	351	347	4·0	4·0	342	450
4-Carboxy-7-hydroxycouramin	Yellow	351	354	4·0	4·0	375	525
6-Carboxy-7-hydroxycoumarin	Blue	351	354	4·0	4·4	340, 380	450
3-Carboxy-7-hydroxycoumarin ethyl ester	Blue	379	379	3·7	3·3	405	460
4-Carboxy-7-hydroxycouramin ethyl ester	Yellow	379	382	3·7	3·5	375	530
4-Methyl-6-carboxy-7-hydroxycoumarin	Blue	365	363	3·8	3·4	335	460
3-Acetoxy-7-hydroxycoumarin	Blue	349	347	4·0	3·7	383	495
4-Phenyl-7-hydroxycoumarin	Pale Blue	383	389	3·7	3·4	295, 370	490
7-Hydroxycoumarin-4-acetic acid	Yellow	365	363	3·8	4·6	325, 400	465
6,7-Dihydroxycoumarin	Green blue	(low yield)		4·3	3·6	390	470
4-Methyl-6,7-dihydroxycoumarin	Green blue	337	333	4·2	3·1	382	455

[a] An intense fluorescence appeared.

preparation of 4-methyl-7-hydroxycoumarin complexone (calcein blue) was examined in detail; better yields were obtained in glacial acetic acid, as described by PŘIBIL AND KÖRBL[11], than were available in acetate–acetic acid[12], aqueous acetic acid[1], neutral or alkaline media. This method was, therefore, used for the preparation of all the iminodiacetic acid derivatives.

Procedure. The relevant hydroxycoumarin (0.02 mole) and iminodiacetic acid (0.02 mole) were dissolved in 25 ml of glacial acetic acid by warming in a 100-ml flask. The solution was cooled to room temperature and 2 ml of 37 % formaldehyde solution was added. The flask was stoppered and the mixture was stirred (magnetic stirrer) for 12 h. The mixture was then heated at 60–70° on an oil bath for a further 8–12 h, with continuous stirring. The mixture was then cooled and the white solid was filtered off. The filtrate was rejected and the residue was suspended in distilled water in order to remove unreacted formaldehyde and iminodiacetic acid. The crude complexone was filtered off and washed well with warm distilled water and ethanol. The crude product was purified by dissolution in 0.2 *M* sodium carbonate solution, filtration and reprecipitation by addition of 1 *M* hydrochloric acid. The complexone was then filtered off, washed repeatedly with distilled water and warm ethanol, and dried at 75–80° *in vacuo*.

When the parent coumarins contained an 8-methyl group, the solid material obtained after the initial reaction period showed no fluorescence properties. However, when the filtrate was reduced to a third of its initial volume under vacuum and poured into an excess of ethanol, a yellow precipitate was formed; this was dissolved in 0.2 *M* sodium acetate, reprecipitated by addition of hydrochloric acid and then washed as described above. The final products showed the desired fluorescent properties, though the yields were rather poor.

Various modifications of the above procedure were tested in attempts to prepare 6-chloro-7-hydroxycoumarin complexone, but none of these was successful although the parent coumarin was readily synthesized. 4-Methyl-7-hydroxy-8-carboxycoumarin complexone could not be separated from its parent coumarin by the above method and two spots were always obtained in thin-layer chromatography.

Characterization of the coumarins and their complexone derivatives

Thin-layer chromatography. The purity of the coumarins was checked by thin-layer chromatography on silica gel[13]; of the solvent systems suggested by SUNDT AND SACCARDI[13], *n*-hexane–ethyl acetate (85:15) was found to be the most convenient, although all were satisfactory.

For the TLC of the complexone derivatives, a solvent mixture containing ethanol, glacial acetic acid and water (80:20:20) was found most satisfactory for the separation of the complexone from its parent coumarin which moved with the solvent front; with this mixture there was, however, very little difference in the R_F values of the various derivatives, all of which were about 0.7. All the derivatives mentioned in Table I gave single fluorescent spots under ultraviolet light.

Molecular weight determinations. Molecular weights were determined by fluorimetric titration with 0.01 M copper(II) chloride solution which had been standardized iodimetrically in the conventional manner[14] and against EDTA solution with fast sulphon black as indicator[15]. It was assumed that a 1:1 complex was formed between the complexone and copper(II), an assumption justified by all later experience. For the titration, 10.0 ml of 0.01 M complexone solution in 0.2 M sodium acetate were mixed with 20 ml of acetate buffer pH 7 and titrated with the copper(II) solution. The results reported in Table I are the average of 3 or 4 titrations of each reagent.

Nuclear magnetic resonance. N.M.R. studies were carried out in order to permit definite assignment of the methyleneiminodiacetic group. These studies have been described previously[16]. In all cases, the complexone group could be assigned to the 8-position, or, where the 8-position was already occupied, to the 6-position.

Fluorescence spectra. The excitation and emission spectra of the reagents prepared were recorded on a Farrand spectrofluorimeter; 10^{-7} M solutions of the reagents were measured at pH 7. The main peaks are shown in Table I.

ANALYTICAL REACTIONS OF THE COUMARIN COMPLEXONES

In general, the complexones did not differ significantly in their behaviour with metal ions. As was expected[1], no reactions occurred with Ca, Ba, Sr or Mg below pH 10. Quenching of fluorescence occurred to a greater or lesser extent with Cu^{2+}, Ni^{2+}, Co^{2+}, Ce^{4+}, Bi^{3+}, Fe^{3+}, Pd^{2+} and Hg^{2+}, the fluorescence being restored by addition of an excess of EDTA as indicated previously for 4-methyl-7-hydroxycoumarin complexone[1,2].

With 4-carboxy-7-hydroxycoumarin complexone and 7-hydroxy-8-methylcoumarin complexone, an apparent enhancement of the fluorescence was observed with Al^{3+}, Fe^{3+}, Cd^{2+}, In^{3+} and Ga^{3+}, but fluorimetric examination showed that the emission spectra were unchanged by the reaction so that no fluorimetric determination of these ions was possible. 4-Methyl-7,8-dihydroxycoumarin complexone (4-methyldaphnetin complexone) showed no colour or fluorescent reactions with any of the ions tested. Many of the reagents listed showed a quenching reaction with vanadium(V) at pH *ca.* 2; the fluorescence was not restored on addition of EDTA, indicating that a strong complex was formed. However, the interesting feature of this reaction was that the complex could be extracted into pentanol to give a pinkish colour which could be utilized spectrophotometrically.

Application as fluorescent indicators

As in the case of 4-methyl-7-hydroxycoumarin complexone (calcein blue)[1,2], the main analytical application for these reagents will be as fluorescent indicators for the titration of copper(II) with EDTA solutions. It can be seen from Table I that the reagents fall into three groups, the fluorescence of the different groups being bright blue, yellowish green and green, respectively. Most of the compounds in each group were examined for their indicator properties over the pH range 2–10. At pH 2, the quenching of the fluorescence at the end-points of titrations of buffered 0.05 *M* copper(II) solutions with 0.1 *M* EDTA was very indistinct; at pH 4, end-points were sharp but the fluorescence appearing on addition of excess of EDTA was not very intense. Much more intense fluorescence was observed over the pH range 5–10, where very sharp end-points were obtained. From the point of view of fluorescence intensity, especially at the low pH values, the 3-carboxy-7-hydroxycoumarin derivative was the best indicator. Reverse titrations of EDTA with copper(II) solutions were also satisfactory, except at pH 10, where a certain amount of residual fluorescence was evident after the end-point had been reached. In these titrations at pH 7, there was no interference from calcium(II), barium(II), strontium(II) or magnesium(II), but iron(III), cobalt(II), nickel(II), vanadium(V), palladium(II), bismuth(III) and manganese(II) were found to interfere because of their slow quenching of the fluorescence of the indicator. The slow reaction with the indicators made direct titrations of these metals with EDTA impracticable, but the addition of an excess of EDTA and back-titration with copper(II) solution provided satisfactory methods.

All the indicators tested gave satisfactory end-points with 10^{-2} *M* solutions in buffered media at pH 7, but the end-points were indistinct with 10^{-3} *M* solutions except in the case of the highly fluorescent 3-carboxy-7-hydroxycoumarin derivative.

Procedure. To 10.0 ml of the copper solution were added 10 ml of acetate buffer pH 7 and 4–5 drops of a 0.01% (w/v) solution of the indicator (dissolved in 1–2 ml of 0.05 *M* sodium acetate and then diluted with water). The mixture was then titrated with an appropriate EDTA solution to the appearance of fluorescence under ultraviolet light.

A few of the indicators were also tested for the titration of calcium with EDTA at pH 12–13, the end-point being indicated by the quenching of the fluorescence of the calcium–reagent complex[2]. Satisfactory end-points were obtained, particularly in the presence of rhodamine B as a fluorescent screening agent[17].

Application as fluorescent reagents

With several of the complexones fluorimetric determinations of copper(II) by quenching of the fluorescence of the complexone proved feasible. With the 7-hydroxycoumarin derivative, there was a linear relationship between fluorescence intensity and copper concentration in the range c.6–6 μg in buffered media at pH 7, when 10 ml of 10^{-5} *M* reagent solution were added and the solution was diluted to 50 ml.

When 3-carboxy-7-hydroxycoumarin complexone was used, the fluorescence intensity of the reagent solutions showed a linear dependence on reagent concentration down to 10^{-8} *M*. At pH 7, 0.06–1.2 μg of copper(II) in a final volume of 50 ml could be determined by addition of 16 ml of 10^{-6} *M* reagent solution; in this case the mixtures were allowed to stand for 1 h before measurement.

With both these reagents, the fluorescence was quenched by the addition of an equimolar amount of copper(II) to the reagent solution, only a very slight and constant fluorescence remaining when an excess of copper(II) had been added. This is further proof of the 1:1 composition of the complexes formed.

DISCUSSION

The reactivities of the compounds prepared with metal ions showed only slight differences despite the variety of substituent groups and their positioning on the coumarin system. Whether the methyl group was in the 4-, 5-, or 8-position scarcely affected the reactivity of the molecule except that the 8-methyl derivative (with the methyleneiminodiacetic acid in the 6-position) appeared to form less stable complexes; the intensities of the yellow-green fluorescence of the 5- and 8-methyl derivatives were approximately the same, both being more intense than that of the blue fluorescence of the 4-methyl derivative. The 4,8-dimethyl derivative, which could be prepared only in low yield, behaved very similarly to the 8-methyl derivative.

3-Carboxy-7-hydroxycoumarin complexone fluoresced most strongly of all the derivatives prepared; both the 4- and 6-carboxy derivatives showed less intense fluorescence but the 6-carboxy derivative had the peculiarity that nickel and cobalt did not form complexes with it, although in most respects its reactions were similar to those of the 4-methyl-7-hydroxycoumarin complexone. The ethyl esters of these acids reacted similarly to the parent acids but their fluorescence was relatively weak as were the fluorescence intensities of the 4-acetic acid, 3-acetoxy and, particularly the 4-phenyl derivatives. The aesculetin and 4-methylaesculetin complexones fluoresced rather weakly.

It is obvious from this study that the reactivity of this type of complexone is hardly influenced by the nature or position of substituent groups in the molecule; what is affected is the fluorescence intensity, and hence the sensitivity of the reactions in which these complexing agents participate. Thus, though no real improvement in selectivity has been obtained, the properties of the compound, 3-carboxy-7-hydroxycoumarin complexone, constitute a significant improvement over existing metallofluorescent indicators derived from coumarin. The unusual behaviour of vanadium(V) towards these coumarin complexones mentioned earlier is being studied further, and will be described at a later date.

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SUMMARY

Fifteen derivatives of 7-hydroxycoumarin methyleneiminodiacetic acid were prepared and examined for their analytical reactions in an attempt to improve the selectivity and sensitivity of the calcein blue type of reagent. However, most of the derivatives behaved similarly in their reactions with metal ions. The 3-carboxy-7-hydroxycoumarin complexone fluoresced most intensely and is recommended as an indicator for the titration of copper(II) with EDTA solutions; end-points are satisfactory even with 10^{-3} *M* solutions. Other metals can be determined by addition of EDTA and back-titration with copper(II) solution. Determinations of 0.06–6 μg of copper by quenching of fluorescence are suggested.

RÉSUMÉ

On a préparé et examiné 15 dérivés de l'acide hydroxy-7-coumarine méthylèneiminodiacétique dans le but d'améliorer sélectivité et sensibilité de réactifs du type bleu calcéine. La plupart de ces dérivés se comportent de manière similaire avec les ions métalliques. La carboxy-3-hydroxy-7-coumarine complexone donne une fluorescence plus intense; elle est recommandée comme indicateur pour le titrage du cuivre(II) au moyen d'EDTA. Les virages sont nets même avec des solutions 10^{-3} *M*. D'autres métaux peuvent être dosés par addition d'EDTA et titrage en retour par une solution du cuivre(II). On propose des dosages de cuivre (0.06 μg à 6 μg) par fluorimétrie d'extinction.

ZUSAMMENFASSUNG

Fünfzehn Derivate der 7-Hydroxycumarin-methyleniminodiessigsäure wurden dargestellt und auf ihre analytischen Reaktionen geprüft als Versuch, die Selektivität und Empfindlichkeit der Reagenzien vom Calceinblau-Typ zu verbessern. Allerdings verhalten sich die meisten der Derivate bei ihren Reaktionen mit Metallionen ähnlich. Das 3-Carboxy-7-hydroxycumarin-Komplexon fluoresziert sehr intensiv und wird als Indikator für die Titration von Kupfer(II) mit ÄDTA-Lösungen empfohlen; die Endpunkte sind selbst bei 10^{-3} *M* Lösungen zufriedenstellend. Andere Metalle können durch Zugabe von ÄDTA und Rücktitration mit Kupfer(II)-Lösung bestimmt werden. Fluorimetrische Bestimmungen von 0.06 bis 6 μg Kupfer unter Ausnutzung des Fluoreszenz-Löscheffektes werden vorgeschlagen.

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STUDIES WITH DITHIZONE

PART XXI. A NOVEL BICYCLIC OXIDATION PRODUCT OF DITHIZONE

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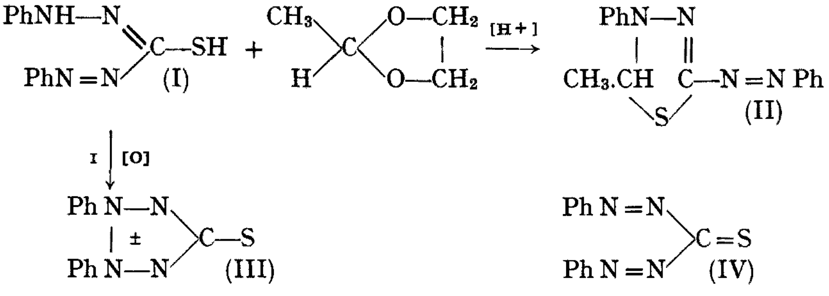
During a study of acid dissociation constants of substituted dithizones in water–dioxane mixtures, MAHNOT[1] noted a rapid change of colour in solutions more acid than 0.1 *M*. The initially green solution turned purple and the bands characteristic of dithizone (I; H_2Dz) at *ca.* 620 and *ca.* 440 nm were replaced by a single peak at *ca.* 530 nm. On a preparative scale two compounds were isolated from the reaction mixture, one red and the other purple in colour.

The red compound was shown to be 2-methyl-3-phenyl-5-phenylazo-1,3,4-thiadiazoline (II) formed by the condensation of (I) with acetaldehyde liberated hydrolytically from small amounts of 2-methyldioxalane present in the sample of dioxane used[2,3]. The "purple compound", m.p. 180–2°, has the molecular formula $C_{13}H_{10}N_4S$ corresponding to the loss of 2 atoms of hydrogen from one molecule of dithizone. It is therefore isomeric with the sydnone (III; anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide) which can be prepared from dithizone using a wide variety of oxidising agents[4–6]. It can be prepared more conveniently by heating a solution of diphenylthiocarbazide, $C_6H_5NH.NH.CS.NH.NHC_6H_5$, or of dithizone (I) or of the sydnone (III) in glacial acetic acid[1]. By the last two of these reactions OGILVIE AND CORWIN[5] had prepared "a beautiful reddish bronze crystalline compound" of empirical formula $C_{13}H_{10}N_4S$ which they referred to as the "isomeric dehydrodithizone" and for which they suggested (IV) as a possible structure. We have confirmed the identity of our "purple compound" with OGILVIE AND CORWIN's "isomeric dehydrodithizone' by elemental analysis, mixed melting point and visible and infrared spectra. We could not, however, reproduce all details reported of its behaviour on reduction and re-oxidation



1. H_2O_2/NH_4OH; $Fe(CN)_6^{3-}$; MnO_2; $C_5H_{11}ONO$; $PhICl_2$; I_2/H_2O

TABLE I

THE ABSORPTION SPECTRA OF THE "PURPLE COMPOUND" IN DIFFERENT SOLVENTS

Solvent	*Dielectric constant*	λ_{max}	λ_{min}	λ_{max}
CCl_4	2.20	314 (16.7)[a]	386 (0.80)	515 (3.88)
C_6H_6	2.28	316 (17.4)	390 (0.97)	518 (5.07)
$CHCl_3$	4.81	316 (24.8)	394 (1.76)	524 (7.50)
CH_2Cl_2	9.10	315 (16.3)	392 (1.01)	524 (4.24)
CH_3COCH_3	20.7	327 (12.0)	398 (0.92)	534 (5.79)
C_2H_5OH	24.3	314 (23.6)	394 (1.81)	536 (9.03)

[a] Molecular extinction coefficients given in parentheses as $10^3\ \varepsilon$.

(ref. 5, p. 5027) and incline to the belief that this may be due to differences in experimental conditions or to impurities in CORWIN's sample.

The absorption spectrum of the purple compound varies somewhat with the solvent used (Table I). Such physical solvent effects can depend on the type of absorption band and on the nature of the solute and solvent[7], but in the very dilute solutions (*ca.* $10^{-5}M$) used, adventitious traces of acids or bases may have complicated the issue. Figure 1 shows the absorption spectrum of a $2.702 \cdot 10^{-5}\ M$ solution of the purple compound in chloroform (curve *a*), and in chloroform pre-saturated with dry hydrogen chloride or ammonia (curves *b* or *c* respectively). Clearly, ammonia has only a small effect whereas the peak at 524 nm is shifted bathochromically to 680 nm in the acidic medium and there is an increase in absorbancy and a colour change to green. Simultaneously the peak at 316 nm shifts hypsochromically to *ca.* 310 nm with a decrease in absorbancy, and a shoulder appears at *ca.* 410 nm. The spectra of the green solutions

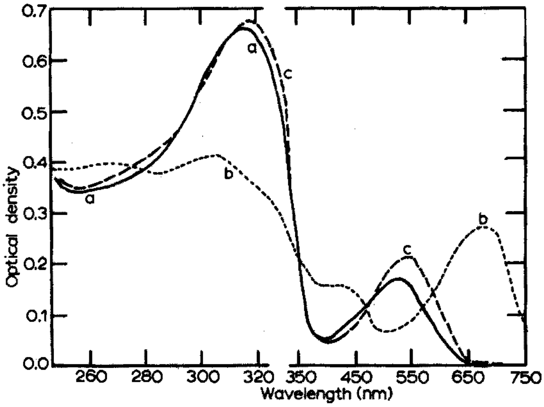


Fig. 1. The absorption spectrum of the purple compound ($2.702 \cdot 10^{-5}M$). Curve *a* in chloroform; curve *b* in chloroform saturated with dry hydrogen chloride; curve *c* in chloroform saturated with dry ammonia.

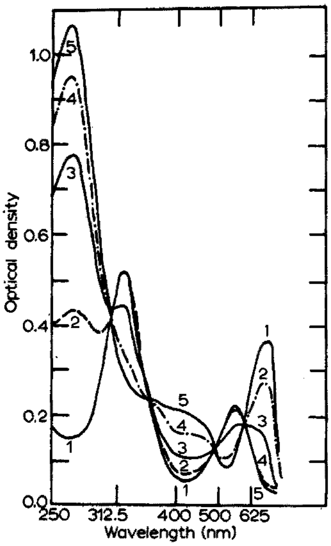


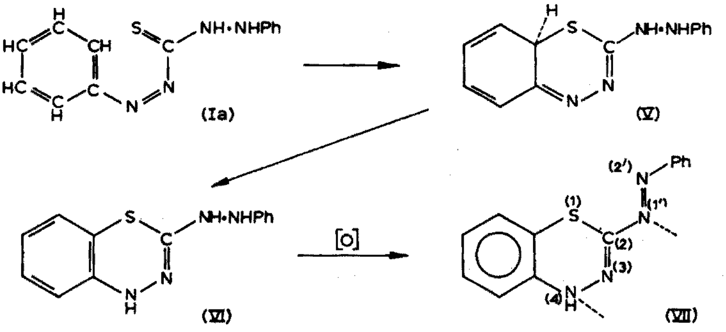
Fig. 2. The absorption spectrum of the purple compound in 20% (v/v) ethanol–water containing different concentrations of hydrochloric acid. Curves 1, 2, 3, 4, 5 correspond to 0.0, 2.01, 4.02, 5.03 and 5.75 *M* hydrochloric acid.

obtained in 20% (v/v) ethanol–water containing different concentrations of acid are shown in Fig. 2. The progressive development of the pronounced peak at 262 nm and the isosbestic points at 300, 375, 488 and 595 nm suggest equilibrium between the purple compound and its conjugate acid. The colours faded with time and no attempt was made to measure the acid dissociation constant.

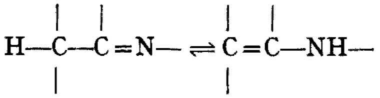
Although insoluble in aqueous alkali the purple compound dissolved readily in an aqueous–alcoholic solution of caustic potash to give a blue solution, the peaks at 524 and 316 nm shifting to 610 and 320 nm with a small increase and decrease respectively in absorbancy. The blue solutions became colourless on keeping, but if reacidified at an early stage the original spectrum (Fig. 2, curve 1) was restored. The presence of a feebly acidic hydrogen was confirmed by the infrared spectrum (KBr disk) which showed a strong band at 3270 cm^{-1} (>N–H stretch).

Deuteration, by exchange brought about by keeping a solution of the purple compound in deuteromethanol, CH_3OD, for several weeks (following a procedure used by BELLAMY AND GUTHRIE for the deuteration of aldehyde phenylhydrazones[8]), or by acidifying the blue solution of the anion in CH_3OD by adding thionyl chloride, gave a product in which the >NH band was replaced by one at 2400 cm^{-1}. This is within the recognised range for >N–D stretching and the ratio of frequencies $3271/2400 = 1.37$ agrees well with that predicted, *viz.* $\sqrt{2/1} = 1.41$. Other features of the infrared spectrum could be ascribed to mono- and di-substituted benzene rings[1,6]. The n.m.r. spectrum did not illuminate the structural problem but the presence of a single :NH group was confirmed by the preparation of a well crystallized, orange-red *mono-acetyl derivative* (m.p. 156°). Its infrared spectra showed no peak at 3271 cm^{-1} from >NH groups but a new peak at 1700 cm^{-1} from the carbonyl group of the tertiary amide.

The presence of an :NH group clearly eliminates the possibility of the purple compound being the thiacarbadiazone (IV) and a possible structure is that of a benzthiadiazole, the present compound (VII), 3-phenylazobenzo-1,3,4(4H)thiadiazole being apparently the first representative of this novel heterocyclic ring system. An examination of molecular models shows that in one conformation of the thioketonic isomer of dithizone (Ia), there is a conjugated system of double bonds that brings the sulphur atom into a favourable position for cyclisation (Ia → V) with the *ortho*-position



of one of the phenyl residues. Tautomerism of a hydrogen atom in the triad system



$$H—C—C=N— \rightleftharpoons C=C—NH—$$

would yield the hydrazo compound (VI) which is readily oxidised (*v. infra*) to the purple azo compound (VII).

Reduction of (VII) by ammonium hydrosulphide gave a colourless compound (m.p. 126–8° dec.), which could not be obtained pure, since it became purple and regenerated (VII), whenever it came in contact with air or alcohol. PREUND AND KUH[9] have described the reduction of 3-phenyl-5-phenylazo-1,3,4-thiadiazole-2-one (or 2-thione) to the corresponding 5-hydrazo compounds with the same reducing agent, and noted their ready reoxidation to the parent azo compounds. More vigorous reduction of (VII) with tin(II) chloride gave a colourless amine, probably 3-amino-benzo-1,3,4-(4H)thiadiazole, which was not further investigated.

These observations conflict with those of OGILVIE AND CORWIN, who stated[5] that their purple compound was slowly reduced by ammonium hydrosulphide to an acidic material (m.p. 135–140° dec.), which "displayed an activity towards heavy materials similar to that of dithizone".

The structure (VII) for the purple compound was fully confirmed by X-ray crystallography[10] which demonstrated the *anti*-conformation of the phenyl and heterocyclic rings with respect to the –N:N– double bond. The molecule is approximately planar, no atom deviating by more than 0.25 Å from the mean plane. A feature of special interest is that the shortest intermolecular contact is of length 3.08 Å between N(4) and N(1) of adjacent molecules. This is close to the average for an NH···N hydrogen bond[11]. The possibility of such association in solution was examined by recording the infrared spectrum of a saturated solution of the purple compound in carbon tetrachloride under conditions of high resolution. Two prominent bands occurred in the $\rangle$N–H region, namely a sharp peak at 3430 cm^{-1} due obviously to the "free" $\rangle$N–H stretching vibration and a broader absorption band at 3280 cm^{-1} which falls in the hydrogen-bond region. It has been reported[12] that "intra-molecular hydrogen-bond frequencies are unaffected by dilution whereas the dilution of an inter-molecularly hydrogen-bonded compound in a non-polar solvent (other variables kept constant) causes a reduction of the inter-molecular hydrogen-bonding". In agreement with this prediction, the infrared spectrum of a dilute solution of (VII) in carbon tetrachloride showed a strong peak at 3430 cm^{-1} whereas that at 3280 cm^{-1} had almost vanished.

EXPERIMENTAL

Preparation of the purple compound (VII)

(a) From dithizone. Repurified dithizone (3.5 g) was heated under reflux with glacial acetic acid (50 ml). During 30 min the reagent went into solution and the colour changed from green to purple. The product, cooled in an ice–salt mixture, was adjusted to pH 5 with 6 *M* sodium hydroxide and extracted with benzene (5 × 50 ml). Removal of the solvent left crude material (2.4 g) which was purified chromatographically on alumina, with 1% methanol in benzene (v/v) as eluting agent. A bright red fore-run preceded the main fraction of the desired compound and a dark band remained at the origin. The purple eluate was taken to dryness and the residue was recrystallized from aqueous alcohol as shining dark-blue needles with a brilliant bronze reflex. M.p. 180/182° dec. Yield 1.7 g; 50%. (Found: C, 61.6; H, 3.9^5; N, 22.0; S, 12.4%. M by vapour pressure osmometry in chloroform, 246. Calcd. for $C_{13}H_{10}N_4S$: C, 61.4; H, 4.0; N, 22.0; S, 12.6%; M = 254.3.)

(b) From the sydnone (III). Sydnone (0.4 g) prepared by oxidising dithizone with hydrogen peroxide in the presence of ammonia[6] was heated under reflux with glacial acetic acid (5 ml). The crude product (0.28 g; 70%) obtained by dilution with water and extraction with chloroform was purified chromatographically. A brownish fore-run with no well defined spectra preceded the purple band (21%); unreacted sydnone (32%) was obtained by eluting the slow moving yellow band with chloroform.

(c) From diphenylthiocarbazide. Freshly recrystallised diphenylthiocarbazide (1.5 g) was heated under reflux with glacial acetic acid (15 ml) for 30 min. The crude product (0.53 g; 53%) isolated as before was treated with the minimum volume of chloroform which dissolved the purple compound (0.38 g) and left a white solid residue (0.15 g; m.p. 200–201 dec.) from ethanol which was identified as β-phenylthiosemicarbazide by comparison of its infrared spectrum and mixed m.p. with that of an authentic specimen.

Deuteration of the purple compound

Method A. Magnesium methoxide, prepared from 3 g of AnalaR magnesium turnings and absolute methanol (30 ml) was dried *in vacuo* and shaken with 99.97% D_2O (9 ml) in an apparatus flushed with dry nitrogen. Deuteromethanol so formed[13] was distilled (4.2 ml) under reduced pressure onto the purple compound (0.25 g) and the *ca.* 1% solution was kept for 40 days under nitrogen. After removal of the solvent *in vacuo* the infrared spectrum of the deuterated product was recorded in a KBr disk.

Method B. A deep blue colour developed when a solution of the purple compound in CH_3OD was treated with a concentrated solution of NaOD (prepared by dissolving metallic sodium in 99.97% D_2O). This solution was immediately acidified by adding a few drops of thionyl chloride. The solvent was removed *in vacuo* and the deuterated product thoroughly dried before measuring its spectrum in a KBr disk with a Grubb-Parsons GS-4 spectrometer.

All the above operations were carried out in a glove-box flushed with dry nitrogen.

N-acetyl derivative of (VII). When a solution of (VII) in acetic anhydride was heated with a droplet of concentrated sulphuric acid, the colour changed from deep purple to reddish brown. Careful addition of water precipitated the *acetyl derivative* which crystallized from aqueous ethanol as orange red needles, m.p. 156° (found: C, 60.3; H, 4.0; N, 18.5%; $C_{15}H_{12}N_4OS$ requires C, 60.7; H, 4.1; N, 18.2%).

SUMMARY

The purple compound $C_{13}H_{10}N_4S$ produced by the oxidation of dithizone has been shown to be a novel bicyclic compound of structure 3-phenylazobenzo-1,3,4 (4H)-thiadiazole. The absorption spectrum of its green conjugate acid and blue anion and the infrared spectrum of the parent compound and its deuteration product are reported. The association through hydrogen-bonding indicated in the solid by X-ray crystallography has been confirmed by infrared measurements of solutions in carbon tetrachloride.

RÉSUMÉ

On démontre que le composé pourpre $C_{13}H_{10}N_4S$ produit par oxydation de la dithizone est un nouveau composé bicyclique de structure 3-phénylazo-benzo-1,3,4(4H)-thiadiazole. On donne le spectre d'absorption de son acide conjugué vert et de l'anion bleu, le spectre infra-rouge du composé parent, ainsi que son produit "deutéré". Les résultats obtenus par cristallographie aux rayons-X confirment ceux des mesures dans l'infra-rouge pour les solutions dans le tétrachlorure de carbone.

ZUSAMMENFASSUNG

Es konnte gezeigt werden, dass die purpurne Verbindung $C_{13}H_{10}N_4S$, die bei der Oxidation von Dithizon gebildet wird, eine neue bicyklische Verbindung mit der Struktur 3-Phenylazo-benzo-1,3,4(4H)-thiadiazol ist. Das Absorptionsspektrum seiner grünen konjugierten Säure und seines blauen Anions und das Infrarotspektrum der Ausgangsverbindung und seines deuterierten Produkts wird angegeben. Die Assoziation durch Wassestoffbrückenbindung, welche sich im Festkörper auch kristallographisch zeigt, konnte durch Infrarotmessungen in Tetrachlorkohlenstoff bestätigt werden.

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IDENTIFICATION AND DETERMINATION OF IMPURITIES IN SALICYLANILIDE

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Salicylanilide is a white, crystalline solid which has found extensive use as a fungicide[1-3] and bacteriostat[4]. In recent years there has been considerable interest in this product as a starting material for the production of halogenated salicylanilides[5,6]. Laboratory, pilot plant, and production studies for its synthesis required a knowledge of the impurities present, a method of assay, and methods for the determination of impurities. A review of the literature shows a complete lack of information on this subject.

Salicylanilide is generally produced by the reaction of salicylic acid and aniline in the presence of phosphorus trichloride[7,8]. In addition to the starting materials, four impurities were isolated and identified in salicylanilide. An assay method and methods of analysis for impurities are described in this paper.

EXPERIMENTAL

Apparatus and reagents

Spectrophotometric measurements were made on a Cary 15 recording spectrophotometer. A Cary model 16 spectrophotometer was used for measurements at a single wavelength. Silica cells of 1.00 cm path length were used for all ultraviolet spectrophotometric measurements.

A Precision Scientific Company, catalogue No. 67013, autoclave was employed for hydrolysis studies. Continuous flow electrophoresis separations were made on a Beckman Spinco model CP continuous flow electrophoresis cell.

Ion-exchange separations were made on Dowex 2-X8, acetate form, 200–400 mesh resin. Preparation of resin, chromatographic columns, and gradient elution equipment have already been described[9].

Diagnostic thin-layer chromatographic separations were made on 0.25-mm silica gel GF_{254} thin-layer plates (E. Merck AG, Darmstadt, Germany). Preparative separations employed 1.0-mm plates of the same silica gel GF_{254} prepared in the laboratory.

A.C.S. methanol was used without further purification. Salicylic acid, methyl salicylate, and aniline of 99% or better purity were used without further purification. 4-Hydroxybenzanilide was prepared by condensing 4-hydroxybenzoic acid and aniline in the presence of phosphorus trichloride. Salicylsalicylanilide was prepared by condensing salicylsalicylic acid with aniline in the presence of phosphorus trichloride. The product was recrystallized from toluene followed by 70% ethanol (m.p. 160–161°).

Commercial salicylanilide of 99% purity was recrystallized from toluene twice, 50% methanol–toluene and chlorobenzene in that order. The chlorobenzene solution was heated with activated charcoal. The sample was air-dried and put through a No. 30 sieve. Last traces of solvent were removed by placing in a vacuum desiccator overnight. Analysis of the material by the freezing point method indicated a purity of 99.8 mole percent with a maximum freezing point of 135.9°.

ISOLATION AND IDENTIFICATION OF IMPURITIES

4-Hydroxybenzanilide

This impurity was isolated by preparative thin-layer chromatography on 1.0-mm silica GF_{254} plates, with methanol (5% v/v) in chloroform as the developing solvent. After the band had been located under ultraviolet radiation at 254 nm, it was scraped from the plate. Desorption from the silica gel was accomplished with methanol. Final purification was carried out by ion-exchange separation on a 13 × 300 mm bed of Dowex 2-X8, acetate form, 200–400 mesh resin, by means of a 0.2% (v/v) acetic acid–methanol gradient elution[9]. The compound was found in the 100–200 ml volume of eluate. Hydrolysis of the purified material for 2 h at 125° and 15 psi pressure yielded nearly quantitative amounts of aniline and 4-hydroxybenzoic acid as indicated by ultraviolet spectrophotometry. There was no evidence for salicylic acid. Infrared spectrometric comparison with a standard proved it to be identical. Elemental analysis gave the following values: 72.8% C, 5.06% H, 6.54% N (theor. 73.2% C, 5.16% H, 6.57% N).

4-Hydroxybenzanilide p-*hydroxybenzoate*

Isolation and purification of this impurity was achieved in a manner similar to that used for 4-hydroxybenzanilide. Hydrolysis of this compound under the conditions previously described yielded almost quantitative amounts of 4-hydroxybenzoic acid (two moles) and aniline. Again no salicylic acid was present. Infrared spectrometric examination gave spectra consistent with the proposed structure. The ester linkage was supported by the band at 1730 cm^{-1} and the anilide carbonyl group gave the band at 1650 cm^{-1}. Ebulliometric molecular weight determination gave a value of 330 (theor. 333). Elemental analysis showed 70.2% C, 4.75% H, and 3.82% N (theor. 72.1% C, 4.50% H and 4.20% N).

ar-*Phosphonosalicylanilide*

This material was received as an acetone-insoluble impurity. Further purification was accomplished in two ways. It was shaken between water and chloroform. The phosphonosalicylanilide, which is sparingly soluble in water and chloroform, was filtered off and dried. In the second purification procedure, a 0.5% sample was prepared in 0.01% sodium bicarbonate solution. This was placed on the continuous flow electrophoresis cell, with aqueous 2% (v/v) acetic acid as the electrolyte. The separation was carried out at 640 V and 36 mA. The quality of the products as indicated by quantitative ultraviolet measurements was identical.

The ultraviolet spectrum of this impurity was nearly identical to that of salicylanilide but of lower absorptivity. In basic solution, it gave the usual shift in wavelength of maximum absorbance characteristic of aromatic hydroxyl. Exchange on Dowex 2-X8 resin showed that there was a considerable difference in acidity when the impurity was compared with salicylanilide. The latter compound could be removed from the resin with dilute acetic acid–methanol solution, while the impurity could not be removed with glacial acetic acid. Hydrolysis of the compound by refluxing with 0.1 *N* sodium hydroxide solution failed to cause any change, while the hydrolysis conditions previously described yielded aniline and a salicylic acid-like moiety.

Examination of the salicylic acid-like hydrolysis product by continuous flow electrophoresis indicated that it had a greater mobility than the phosphonosalicylanilide. Infrared spectrometric examination supported the phosphonosalicylic acid structure.

Elemental analysis gave 53.2% C, 4.76% H, 4.52% N, 10.3% P (theor. for *ar*-phosphonosalicylanilide 53.2% C, 4.10% H, 4.78% N, 10.6% P).

Salicylsalicylanilide

A sample of production-grade salicylanilide was recrystallized from toluene. The salicylanilide crystals were filtered off and the mother liquor was evaporated to half its volume. After removal of additional crystals, the residue was recrystallized twice from carbon tetrachloride. This resulted in the removal of more salicylanilide. After evaporation of the carbon tetrachloride, the residue was recrystallized twice from 70% ethanol. This yielded a white solid that melted at 156–157° compared with 160–161° for a standard of salicylsalicylanilide. Infrared spectrometric comparison proved it to be identical. Exchange on Dowex 2-X8, acetate-form resin, yielded equimolar amounts of methyl salicylate and salicylic acid. The standard also underwent quantitative alcoholysis in the same manner. Ebulliometric molecular weight determination gave a value of 318 (theor. 333).

METHODS OF ANALYSIS

Salicylanilide assay

Weigh a 0.1-g sample to the nearest 0.1 mg into a 250-ml volumetric flask. Add four drops of aqueous 20% (w/v) sodium hydroxide and dilute to volume with methanol. Transfer a 10-ml aliquot to a 200-ml volumetric flask and dilute to volume with methanol. Measure the absorbance at 338 nm in a 1.00-cm cell with methanol as the reference solvent. Calculate the salicylanilide concentration by comparison with a standard.

Salicylsalicylanilide and aniline

Dissolve a 0.1-g sample of salicylanilide in 10 ml of methanol. Pass the solution through a 13 × 150 mm bed of Dowex 2-X8, acetate-form, resin. Rinse the column with four 10-ml portions of methanol. Collect all the eluate in a 100-ml volumetric flask and dilute to volume with methanol. Scan the solution from 250–340 nm on a recording ultraviolet spectrophotometer. Add one drop of concentrated hydrochloric acid solution and rescan. The decrease in absorbance at 285 nm is a measure of the aniline concentration, since aniline hydrochloride has negligible absorption at this wavelength. The absorbance at 306 nm of the acidified solution is a measure of the methyl salicylate concentration resulting from alcoholysis of salicylsalicylanilide. The sensitivity for each component is 0.1%.

Salicylic acid and ar-*phosphonosalicylanilide*

Dissolve 0.5 g of salicylanilide in 75 ml of chloroform. Extract with two 25-ml portions of aqueous 0.01% sodium bicarbonate solution. Wash the combined sodium bicarbonate extracts with 10 ml of chloroform. Scan the sodium bicarbonate solution from 240 nm to 380 nm. The absorbance at 344 nm is due to phosphonosalicylanilide. From the phosphonosalicylanilide standard spectra, correct the absorbance at 296 nm and calculate the salicylic acid concentration. The sensitivity for these two components is 0.05%.

RESULTS AND DISCUSSION

Identification of the impurity, phosphonosalicylanilide, proved to be one of the most difficult parts of this work. Preliminary examination of this material by ultraviolet spectrophotometry and elemental analysis gave a spectrum nearly identical to that of salicylanilide and a significant concentration of phosphorus. A comparison of the spectra for salicylanilide and phosphonosalicylanilide is given in Fig. 1. This spectrophotometric similarity made it appear that the impurity was merely a mixture of salicylanilide and an inorganic phosphorus compound. However, further examination on Dowex 2-X8 resin in the acetate form, indicated exchange characteristics indicative of a strong acid. When the impurity was separated by continuous flow electrophoresis, the species with an ultraviolet absorption spectrum characteristic of salicylanilide also contained 10.3% phosphorus.

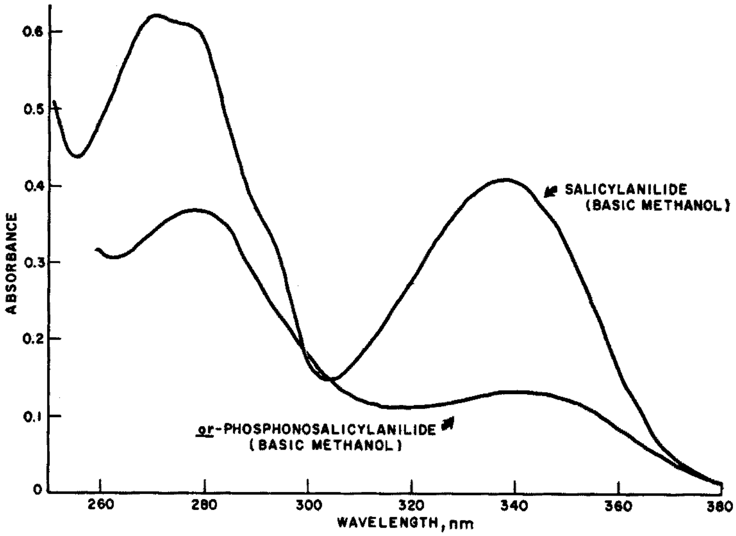
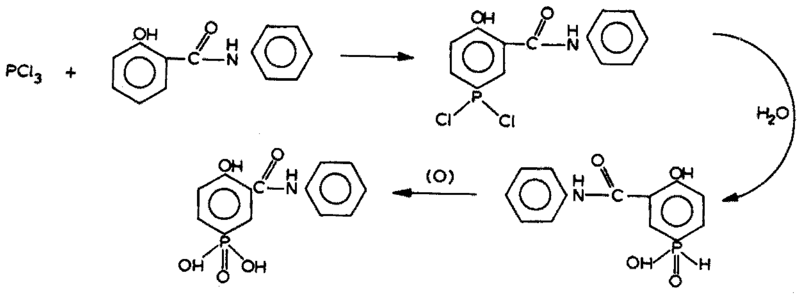


Fig. 1. Ultraviolet absorption spectra of salicylanilide and *ar*-phosphonosalicylanilide in basic methanol.

The formation of phosphonosalicylanilide is suspected to occur according to the following scheme.



ar-Phosphonosalicylanilide

The initial reaction is very likely a Friedel–Craft reaction to form the corresponding phosphonous dichloride[10,11]. This is followed by hydrolysis to form the phosphinic acid[12]. Partial oxidation[13] of the phosphinic acid then occurs to form the phosphonosalicylanilide.

Phosphonosalicylanilide generally will not be found in salicylanilide if the product has been satisfactorily washed. This washing must be made with alkaline solutions to be effective. Therefore, this impurity will usually be found in wash and process liquors. If some does occur in the product, it will be extracted into the 0.01% sodium bicarbonate layer. This layer will also contain salicylic acid. Since residual salicylanilide can be quantitatively washed from the sodium carbonate layer with two portions of chloroform, what appears to be non-extractable salicylanilide will in actuality be phosphonosalicylanilide. The salicylic acid concentration must then be corrected for interference from phosphonosalicylanilide.

In the assay of salicylanilide by direct ultraviolet spectrophotometric measurement, salicylsalicylanilide will interfere and, therefore, must be corrected for. Salicylic acid and aniline have no ultraviolet absorption at 338 nm. Phosphonosalicylanilide which is not normally found in the final product would give interference at the wavelength used for the assay measurement. Spectral data for salicylanilide and impurities are tabulated in Table I.

Salicylanilide prepared from the mother liquor residue of salicylic acid was found to contain two sizable impurities which had not been previously observed. This grade

TABLE I

SPECTRAL DATA FOR SALICYLANILIDE AND IMPURITIES

Compound	*Neutral methanol*		*Basic methanol*	
	Wavelength (nm)	*Absorptivity*	*Wavelength (nm)*	*Absorptivity*
Salicylanilide	268	54.96	338	42.8
Salicylsalicylanilide			337	36.16
Aniline	285	16.04	285	16.04
Salicylic acid	304	28.90	297	27.76
Methyl salicylate	306	27.86	333	30.29
ar-Phosphonosalicylanilide			344	10.19
4-Hydroxybenzanilide	273	99.50	306	137.9
4-Hydroxybenzanilide *p*-hydroxybenzoate	270	108.3	307	121.8

of salicylic acid contains 1–5% 4-hydroxybenzoic acid. By a combination of preparative thin-layer and ion-exchange chromatography, these two impurities were isolated. They were identified as 4-hydroxybenzanilide and the *p*-hydroxybenzoate of 4-hydroxybenzanilide. U.S.P. salicylic acid generally contains 100 p.p.m. or less of *p*-hydroxybenzoic acid. Therefore, salicylanilide prepared from this grade of salicylic acid will contain negligible amounts of these two impurities. However, the presence of these two impurities will cause only slight interference in the salicylanilide assay since their ultraviolet absorbance at 338 nm in basic methanol is very weak.

The qualitative presence or absence of impurities in salicylanilide can be determined by thin-layer chromatorgraphy. By proper choice of developing solvents, the impurities can be resolved. The same plate can be placed in successive developing solvents after short drying periods. If the plate indicates no impurities at or near the origin after chloroform development, the presence of those compounds with low R_F values can be immediately discounted; R_F values for salicylanilide and its impurities are given in Table II.

TABLE II

R_F VALUES FOR SALICYLANILIDE AND IMPURITIES ON A SILICA GEL GF_{254} THIN-LAYER CHROMATOGRAPHY PLATE

Compound	*R_F value*		
	Chloroform	*Chloroform/ methanol, 19/1*	*Benzene/dioxane/ acetic acid, 90/25/4*
Salicylanilide	0.69	0.88	0.96
Salicylsalicylanilide	0.72	0.89	0.96
Aniline	0.50	0.83	0.96
4-Hydroxybenzanilide	0.02	0.58	0.81
4-Hydroxybenzanilide *p*-hydroxybenzoate	0.02	0.73	0.88
Salicylic acid	0.0–0.03	0.0–0.20	0.63
ar-Phosphonosalicylanilide	0.0	0.0	0.0

Salicylsalicylanilide was found to undergo alcoholysis yielding quantitative amounts of methyl salicylate and salicylanilide when passed through Dowex 2 ion-exchange resin in the acetate form, in methanol solution. This is analogous to the alcoholysis found for salicylsalicylic acid[14]. The salicylanilide moiety of the salicylsalicylanilide remains on the resin while the methyl salicylate is found in the eluate.

Since aniline and methyl salicylate are both found in the eluate, the concentration of each component could be determined by solving simultaneous equations based on their ultraviolet absorption spectra. However, when a methanol solution of aniline is acidified, the ultraviolet absorption at 285 nm is reduced to zero. This reduction in absorbance can be used as a measure of the aniline concentration. Methyl salicylate exhibits no change in its ultraviolet spectra in going from neutral to acidic methanol.

The author is indebted to R. A. NYQUIST for infrared examinations of impurities and E. S. PARSEY for preparation of salicylsalicylanilide.

SUMMARY

In studies on the production of salicylanilide an assay method for salicylanilide itself and methods for the identification and determination of impurities were required. In addition to the starting materials (aniline and salicylic acid) four impurities were isolated and identified: salicylsalicylanilide, *ar*-phosphonosalicylanilide, 4-hydroxybenzanilide, and the *p*-hydroxybenzoate of 4-hydroxybenzanilide. Salicylanilide was assayed by direct ultraviolet spectrophotometry in basic methanol solution. Salicylic acid and phosphonosalicylanilide were extracted from a salicylanilide–chloroform solution with dilute sodium bicarbonate solution. Aniline and salicylsalicylanilide were determined by passing a methanolic solution of salicylanilide through Dowex 2, acetate-form, resin. Aniline, and methyl salicylate resulting from alcoholysis of salicylsalicylanilide, were contained in the eluate. All impurity concentrations were determined by ultraviolet spectrophotometry.

RÉSUMÉ

Une recherche est effectuée pour identifier et doser les impurités d'une salicylanilide. En plus des matières premières, on a pu isoler et identifier quatre substances; la salicylanilide, la phosphonosalicylanilide, l'hydroxy-4-benzanilide et le *p*-hydroxybenzoate d'hydroxy-4-benzanilide. La salicylanilide est testée par spectrophotométrie directe dans l'ultra-violet, en solution méthanol basique. Les impuretés sont séparées soit par extraction, soit à l'aide de résine Dowex-2 et dosées par spectrophotométrie dans l'ultra-violet.

ZUSAMMENFASSUNG

Bei Untersuchungen zur Herstellung von Salicylanilid waren zur Festlegung der optimalen Reaktionsbedingungen Methoden zur Identifizierung und Bestimmung von Verunreinigungen erforderlich. Zusätzlich zu den Ausgangsmaterialien konnten 4 Verunreinigungen identifiziert werden: Salicyl, Salicylanilid, ar-Phosphonosalicylanilid, 4-Hydrobenzanilid und *p*-Hydroxobenzoat des 4-Hydroxybenzanilid. Das Salicylanilid wurde durch direkte ultraviolette Spektralphotometrie in der methanolischen Ausgangslösung bestimmt. Salicylsäure und Phosphonosalicylanilid wurden aus einer Salicylanilid–Chloroform-Lösung mit verdünnter Natriumhydrogencarbonatlösung extrahiert. Anilin und Salicylsalicylanilid wurden mit Hilfe von Dowex 2 in seiner Acetatform bestimmt, und zwar über die durch Alkoholyse des Salicylsalicylanilids im Eluat enthaltenen Stoffe Anilin und Methylsalicylat. Die Konzentrationen aller Verunreinigungen wurden mit der u.v.-Spektralphotometrie bestimmt.

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X-RAY FLUORESCENCE ANALYSIS OF NICKEL–IRON THIN FILMS WITH STANDARDS PREPARED BY THE PYROLYSIS OF METAL ORGANIC COMPOUNDS

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The analysis of thin films represents one of the major challenges in the field of analytical chemistry. The total material available for analysis is usually in the microgram range, and non-destructive determinations are often needed. In addition, there is the requirement for easily accessible and reliable standards.

This paper describes a rapid method of preparing and analyzing thin-film standards for X-ray fluorescence and similar applications. It will focus on the application of these standards to the non-destructive analysis of thin films of nickel and iron.

The procedure consists of applying a mixture of metal organic compounds, in which the metal content corresponds to the final proportions desired, to an appropriate substrate and then firing the specimens in a hydrogen atmosphere to obtain thin films. These standards are then used directly to analyze samples made by any of the various methods of thin-film preparation. The various techniques used to calibrate the standards have been described[1-3] but the proposed method of standard preparation is a novel addition to the scope of the technique.

EXPERIMENTAL

Preparation of Ni–Fe thin-film standards

Materials. Nickel tetradecanoate (myristate) and iron dodecanoate (laurate) were prepared by the precipitation process[4]. Corning Pyrex #7059 glass slides (1 in × 1 in × 0.048 in) were used.

Procedure. The nickel and iron organic compounds were mixed in such a manner that their metal content was in the desired ratio. The mixture thus prepared was diluted twofold on a weight basis with mineral spirits as a solvent. This mixture was gently heated and stirred until a true solution was obtained.

The glass slide to be used as a substrate was washed with detergent, distilled water, Chromerge and distilled water, in that order. It was then dipped into a 5% hydrofluoric acid solution for 30 sec, again rinsed with distilled water, then dried in a stream of filtered argon and placed on a 300° hot plate for 30 sec. The clean and dried glass slide was placed on a photoresist spinner and 4 or 5 drops of iron–nickel organic solution were deposited in the center of the slide. The specimen was then spun at 3000 r.p.m. for 5 sec. The slide was transferred to a hot plate maintained at 150° for 30 sec and then into a tube furnace (designed for hydrogen firing) at 550°. The hydrogen flow rate in the furnace was held at 5 l min^{-1}. The specimen was fired for exactly 15 min. The application of the metal organic compounds and the subsequent drying and firing of the specimen was repeated at least five times to obtain a film thickness of *ca.* 1500 Å.

Ni–Fe film analysis

Apparatus. A Norelco Vacuum Universal Four-Position X-ray Spectrograph with inverted optics was used with a Philips FA 60 tungsten target X-ray tube, and Spex Industries X-ray solution cells.

Procedure. Nickel–iron thin-film standards prepared by the pyrolysis technique were compared with nickel–iron thin-film samples prepared by vacuum evaporation. No special holder was required for the slides. They were simply placed in the holder supplied by the manufacturer of the X-ray equipment. X-Ray operating conditions are listed in Table I. Comparison took the form of a linear calibration curve that plotted the X-ray intensity ratios of Ni Kα/Fe Kα *versus* the weight ratio of Ni/Fe in each case. The sample and standard films were then dissolved in warm 10% nitric acid; the solutions were diluted to 10 ml with the same solvent, and then compared against solution standards whose nickel and iron concentrations were in the same range as those of the films. Comparisons took the form of linear calibration curves that plotted nickel and iron concentrations *versus* the X-ray intensities of Ni Kα and Fe Kα for each solution. The weight ratios were then calculated from the total iron and nickel contents of the solutions. The concentration of nitric acid in standards, samples and blank solutions was maintained at 10% by volume. In the case of the undissolved film comparison, a blank slide of similar dimensions and thickness was used for background correction.

TABLE I

OPERATING CONDITIONS FOR THE NORELCO VACUUM X-RAY SPECTROGRAPH

X-ray tube:	W Target FA-60. 50 kV, 40 mA for solutions. 30 kV, 20 mA for films.
Detector:	Flow proportional counter operated at 1600 V d.c.
Crystal:	LiF.
Collimator:	5 mil.
P.H.A.:	Integral circuit.
X-ray path:	Helium.
Sample cell:	Solution cells, supplied by Spex Industries, #3515. Specimen holder for films supplied with X-ray spectrograph.
Wavelength Ni:	48.65°, 2 θ
Wavelength Fe:	57.52°, 2 θ
Minimum number of total counts collected:	32,000.

RESULTS AND DISCUSSION

Six thin films prepared by the pyrolysis technique were used as standards. Three films prepared by vacuum evaporation served as the samples. Table II presents the theoretical Ni/Fe weight ratios of the metal–organic solutions used to prepare the standard thin films, and the Ni/Fe weight ratios of these films as determined by the solution technique. Table III presents the Ni/Fe weight ratios of the submitted sample films prepared by vacuum evaporation as determined by direct comparison with the standards prepared by pyrolysis and with solution standards after the samples had been dissolved. In all the above cases satisfactory agreement is indicated.

TABLE II

THEORETICAL Ni/Fe WEIGHT RATIOS OF METAL–ORGANIC SOLUTIONS USED TO PREPARE PYROLYSIS-PRODUCED STANDARD THIN FILMS AND Ni/Fe WEIGHT RATIOS AS DETERMINED BY SOLUTION TECHNIQUES

Standard	*Theoretical*	*Determined*
1	4.00	3.93
2	1.90	1.91
3	1.26	1.25
4	0.84	0.84
5	0.31	0.34
6	1.00	1.00

TABLE III

Ni/Fe WEIGHT RATIOS DETERMINED FOR SUBMITTED SAMPLES PREPARED BY VACUUM EVAPORATION

Sample	*With pyrolysis-prepared film standards*	*With solution standards*
1	0.74	0.78
2	0.78	0.78
3	0.77	0.80

In order to determine the relative precision of the method, a single pyrolysis-produced film was run ten times directly and then as a solution. In both cases the relative precision was about 1.0%. It is concluded, therefore, that Ni–Fe thin-film standards produced by this pyrolysis technique are applicable to the non-destructive analysis of Ni–Fe thin films.

The compounds used for preparing the thin films were metal soaps of high-molecular-weight fatty acids. The metal organic compounds decompose in a hydrogen atmosphere leaving behind the metals as their residues. Firing in air has been found to lead to the formation of an oxide suggesting the possibility of producing oxide standards for analytical purposes by the same technique. The deposit of thin metal films on beryllium substrates by this pyrolysis technique has been shown to be useful for the determination of mass absorption coefficients[5].

One problem associated with the proposed method of standard preparation is the possible formation of carbon, carbide and oxide impurities in these types of metallic films. In attempting to prepare films of metals other than the Ni–Fe type, it may be advantageous, but not absolutely necessary, to insert an internal standard into the matrix to compensate for the possible adverse effects of impurities present.

It is significant that the ratio of metals contained in the mixture of soaps is virtually unchanged in the final deposited metallic films. This fact eliminates the need for the trial and error adjustments of metal ratios as well as other parameters in the solution in order to obtain the desired metal ratio in the final film. In this respect the film preparation is very advantageous in comparison to electro-plating or vapor deposition.

The authors gratefully acknowledge the contributions of Mrs. M. SEXTON, Mr. O. HAINES, and Mr. N. SCHIRALLI to the experimental work.

SUMMARY

A rapid method of preparing Ni–Fe thin-film standards for X-ray fluorescence and similar applications is described. The procedure consists of applying a mixture of metal organic compounds to an appropriate substrate followed by firing the specimen in a reducing atmosphere. Standards prepared in this manner are used to perform non-destructive X-ray fluorescence analysis of thin-film samples. Relative precision at the 1.0% level is attained.

RÉSUMÉ

On décrit une méthode rapide de préparation de films minces d'étalons Ni–Fe pour la fluorescence aux rayons-X et pour des applications similaires. Elle consiste à appliquer un mélange de composés organo-métalliques sur un substrat approprié, avec passage au feu dans une atmosphère réductrice. Les étalons préparés de cette manière sont utilisés pour l'analyse non destructive par fluorescence aux rayons-X d'échantillons en film mince. On atteint une précision relative de 1.0%.

ZUSAMMENFASSUNG

Es wird eine schnelle Methode zur Herstellung dünner Ni–Fe-Filme als Standard für die Röntgenfluoreszenz und ähnlicher Anwendungen beschrieben. Das Verfahren beruht auf der Verwendung einer geeigneten Mischung metallorganischer Verbindungen und anschliessender Verbrennung dieser Proben in reduzierender Atmosphäre. Auf diese Weise hergestellte Standards eigneten sich zur zerstörungsfreien röntgenfluoreszenzanalytischen Bestimmung dünner Filme. Es wurde eine relative Genauigkeit von etwa 1% erreicht.

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THE ELECTROCHEMICAL REDUCTION OF SOME PALLADIUM(II)-PYRIDINE COMPLEXES

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Pyridine was first used by WILLIS[1] in the polarographic determination of palladium. Later, PANTANI found that the methylpyridines were also suitable and showed, by coulometric measurements, that the complexes are reduced to the metal[2]. DOUGLAS AND MAGEE[3] have presented a method for the determination of palladium and rhodium with pyridine, while the methylpyridines have recently been used in the determination of palladium, rhodium and osmium[4].

The reduction of the pyridine complex has recently been re-investigated by PARRY AND OLDHAM[5]. Their results indicated that the reduction was irreversible, in contrast to earlier reports.

This paper discusses some of the reduction characteristics of the pyridine, 2-methyl, 3-methyl and 4-methylpyridine complexes of palladium. In particular, the capabilities of polarography and chronopotentiometry for the determination of palladium with pyridine bases are discussed.

EXPERIMENTAL

Equipment

A Davis Differential A1660 cathode-ray polarograph was used in this investigation. The single-cell technique was used throughout and the instrument was calibrated by injecting a small current into the input sockets and measuring the deflection produced. The dropping mercury electrode had an m value of 0.50 mg sec^{-1}. Chronopotentiograms were obtained with a Beckman Electroscan 30. A Beckman platinum electrode, type 39007, was also used as a working electrode in the chronopotentiometric experiments.

The cell used in the chronopotentiometric experiments with the mercury electrode (area 1.53 cm^2) is shown in Fig. 1. Transition times were determined by the method of DELAHAY AND BERZINS[6]. Transition times in this paper are the average of at least three separate values.

Experiments were carried out at a temperature of 28 ± 1°.

A 10^{-2} M stock solution of palladium chloride, $8.69 \cdot 10^{-3}$ M in hydrochloric acid was used. Pyridines were purified by refluxing over molecular sieves before distillation. Analar potassium chloride served as supporting electrolyte.

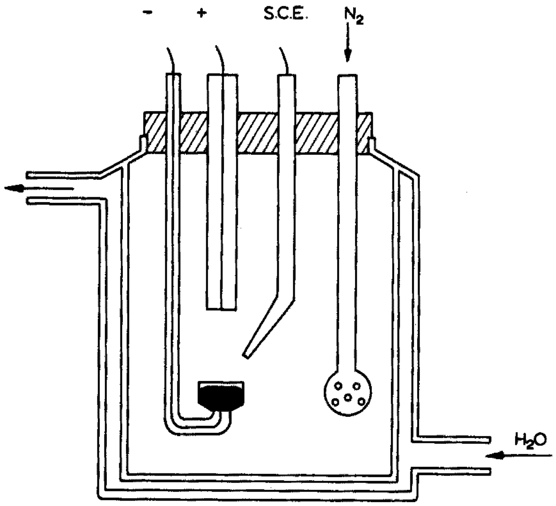

Fig. 1. The chronopotentiometric cell.

RESULTS AND DISCUSSION

Polarographic studies

The pyridine and 3-methylpyridine systems. The reduction waves of the complexes showed well shaped single peaks. Data are given in Fig. 2. In both systems the complex $PdPy_2Cl_2$ precipitated at low ligand concentrations, resulting in a lowering of the peak height.

The 2-methylpyridine system. At a ligand concentration of 0.2 *M* only one reduction wave was apparent. At lower concentrations two waves were observed, the second wave being more pronounced at lower ligand concentrations and at lower metal concentrations (Fig. 3). The lack of any relationship between the peak heights of these waves rules out the possibility of a stepwise reduction, as does the marked decrease of

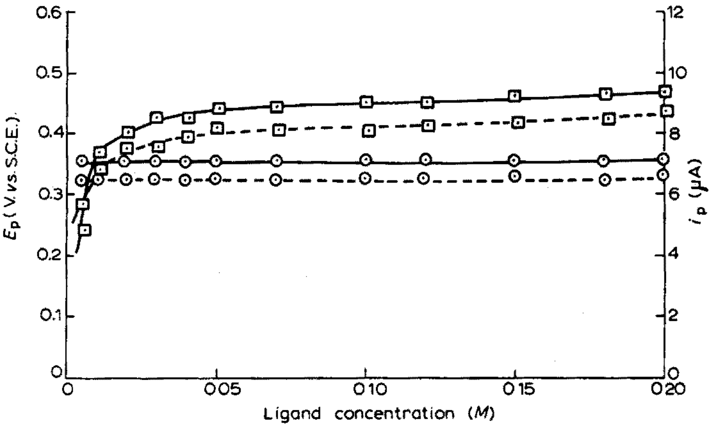

Fig. 2. The pyridine and 3-methylpyridine systems. $[Pd^{2+}] = 10.34 \cdot 10^{-4}$ *M*; [KCl] = 0.1 *M*. (——) Pyridine; (– – – –) 3-methylpyridine. ⊙ refers to E_p axis; ⊡ refers to i_p axis.

peak height of the first wave with ligand concentration (Fig. 3). No precipitation of the pyridine-chloro complex at ligand concentrations higher than 0.02 *M* was observed.

PANTANI[2] observed two steps in his investigation, and reported that the first step becomes more evident at higher chloride concentrations. He also observed that this phenomenon almost completely disappeared in nitrate or sulphate media.

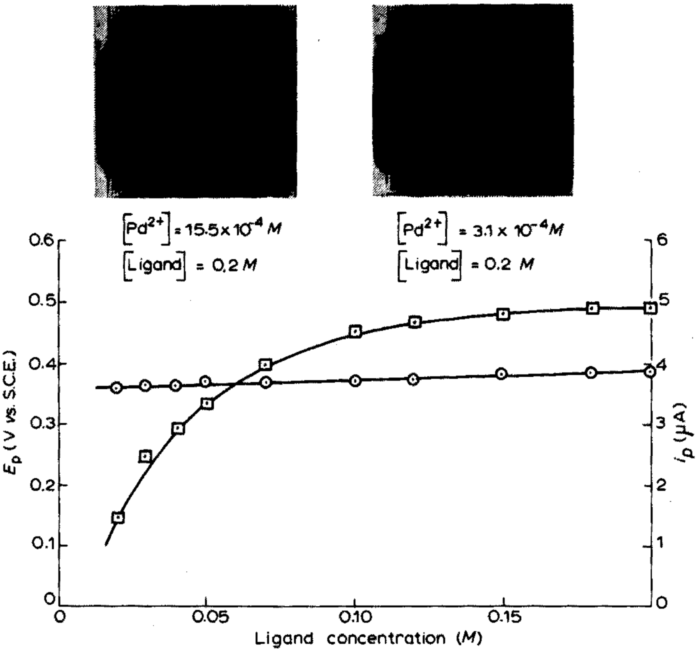

Fig. 3. The 2-methylpyridine system. $[Pd^{2+}] = 10.34 \cdot 10^{-4}$ *M* (except where indicated otherwise); [KCl] = 0.1 *M*. ⊙ refers to E_p axis and ⊡ to i_p axis.

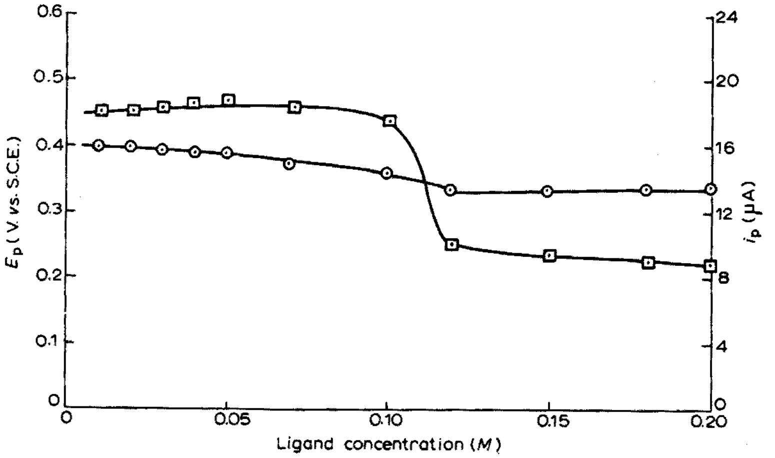

Fig. 4. The 4-methylpyridine system. $[Pd^{+2}] = 10.34 \cdot 10^{-4}$ *M*; [KCl] = 0.1 *M*. ⊙ refers to E_p axis and ⊡ to i_p axis.

The present experiments confirmed that excess of chloride eliminated the second reduction wave. This, coupled with the steric effect associated with a methyl group in the 2-position, indicates that the species producing the first reduction wave probably contains coordinated chloride, *e.g.* $[Pdpy_3Cl]^+$.

The 4-methylpyridine system. The 4-methylpyridine complex exhibited an anomalous reduction wave at lower ligand concentrations, the height of which was almost twice the height of the normal reduction wave (Fig. 4). This anomaly was also observed by PANTANI in conventional polarography.

Chronopotentiometric studies

In experiments with the mercury electrode, it was observed that the mercury surface had to be cleaned before reproducible reductions could be obtained. During temperature equilibration and deoxygenation of the test solution, a scum of mercury(II) oxide formed on the surface of the mercury electrode. The scum was removed by electrolysis with a current of 1 mA.

After the electrode surface had been cleaned, it was observed for all the systems that the initial transition times were anomalously large. This phenomenon also occurred if electrolysis was carried out after a rest period (*e.g.* 30 min). The increase of the transition times can be accounted for by assuming that pyridine is adsorbed on the mercury surface. Desorption then occurs on the application of a potential across the cell. Pyridine is known to adsorb on mercury[7].

Chronopotentiometric reduction waves for the systems are shown in Fig. 5. The products $i\tau^{\frac{1}{2}}$ for the systems were measured at various current densities (Table I) and found to be independent of the current density through the cell. It is concluded that either the complexes in question are directly reduced, or that dissociation of the complexes before reduction is so rapid that no kinetic effects are observed[6].

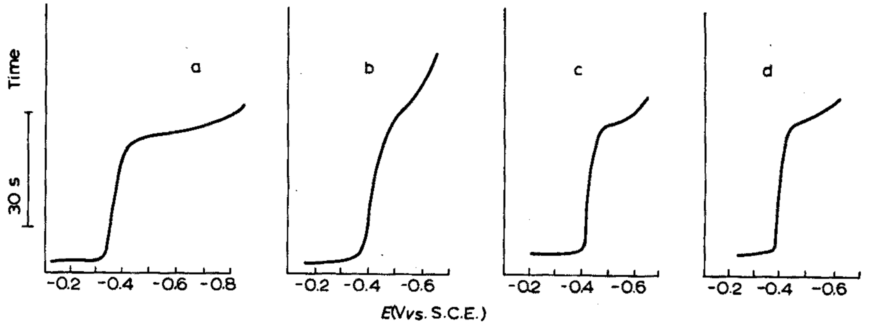

Fig. 5. Chronopotentiograms at the mercury electrode. $[Pd^{2+}] = 10.01 \cdot 10^{-4}$ *M*; [ligand] = 0.2 *M*; [KCl] = 0.1 *M*. (a) Pyridine, 0.1 mA; (b) 2-methylpyridine, 0.1 mA; (c) 3-methylpyridine, 0.1 mA; (d) 4-methylpyridine, 0.1 mA.

Reductions were irreversible in every case although methyl substitution decreased the irreversibility somewhat. The log plot analysis of the chronopotentiometric waves (Fig. 6) resulted in αn_a values of 1.17, 1.21, 1.48 and 1.52 for the pyridine, 2-methyl, 3-methyl and 4-methylpyridine complexes, respectively, indicating a value of two for n_a, the number of electrons involved in the rate-determining step. The value of 0.58 for α for the pyridine complex compares with a value of 0.63 reported by PARRY

TABLE I

$i\tau^{1/2}$ PRODUCTS FOR THE VARIOUS PALLADIUM–PYRIDINE SYSTEMS

($10.01 \cdot 10^{-4}$ *M* Pd^{2+}; 0.1 *M* KCl; 0.2 *M* ligand)

Current (mA)	τ *(sec)*	$i\tau^{1/2}$ *(mA sec$^{1/2}$)*	*Current (mA)*	τ *(sec)*	$i\tau^{1/2}$ *(mA sec$^{1/2}$)*
Pyridine system			*3-Methylpyridine system*		
0.20	9.8	0.63	0.20	8.8	0.59
0.18	12.7	0.64	0.18	10.6	0.59
0.16	16.2	0.64	0.16	13.0	0.58
0.14	21.7	0.65	0.14	16.3	0.57
0.12	29.0	0.65	0.12	21.3	0.55
0.10	40.1	0.63	0.10	33.4	0.58
2-Methylpyridine system			*4-Methylpyridine system*[a]		
0.20	8.7	0.59	0.20	9.3 (7.8)	0.61 (0.56)
0.18	9.7	0.56	0.18	11.9 (10.5)	0.62 (0.58)
0.16	12.3	0.56	0.16	14.4 (14.6)	0.61 (0.61)
0.14	15.0	0.54	0.14	17.6 (17.2)	0.59 (0.58)
0.12	21.2	0.55	0.12	24.2 (24.6)	0.59 (0.60)
0.10	30.7	0.55	0.10	33.7 (30.1)	0.58 (0.55)

[a] Numbers in brackets refer to 0.05 *M* ligand concentration.

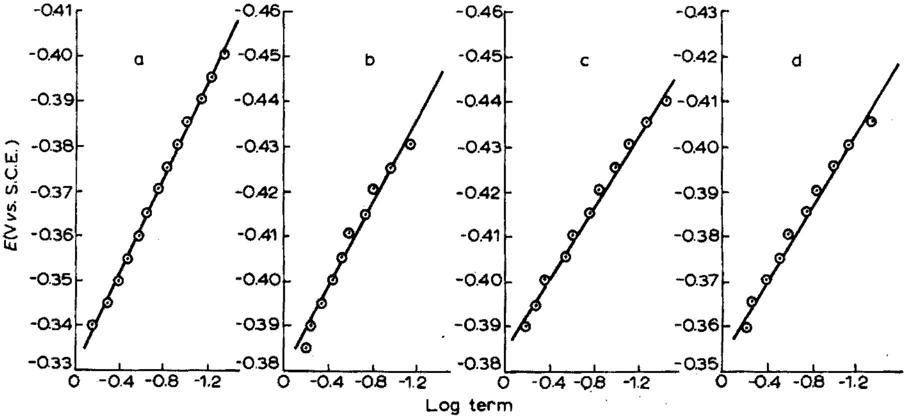

Fig. 6. Chronopotentiometric log plots of the pyridine (a), 2-methyl (b), 3-methyl (c), and 4-methylpyridine (d) systems.

AND OLDHAM[5]. Diffusion coefficients were calculated from the SAND equation[8] (Table II).

Special attention was paid to the 2-methyl and 4-methylpyridine systems. No evidence was found for the existence of two reducible species containing 2-methylpyridine, probably owing to the closeness of the polarographic reduction peaks of the species (*ca.* 0.1 V). No anomalous reduction waves were obtained with the 4-methylpyridine system at lower ligand concentrations (Table I).

The reduction of the complexes at the platinum electrode was also investigated. Reduction waves occurred at more negative potentials and were poorly shaped with the point of inflection ill-defined; with $10.01 \cdot 10^{-4}$ *M* palladium(II) and 0.2 *M* ligand in 0.1 *M* potassium chloride, at a current of 0.20 mA, reduction started at −017, −0.77, and −0.73 V (*vs.* S.C.E.) for the pyridine, 3-methylpyridine and 4-methylpyridine complexes, respectively. A positive potential drift also occurred in the systems after palladium deposition had commenced, being most pronounced with the 4-methylpyridine system. The 2-methylpyridine system gave an extremely ill-defined reduc-

TABLE II

DIFFUSION COEFFICIENTS CALCULATED FROM THE SAND EQUATION

(0.2 *M* ligand; 0.1 *M* KCl)

Complex	*D* ($cm^2\ sec^{-1}$)
Pyridine	$5.8 \cdot 10^{-6}$
2-Methylpyridine	$4.5 \cdot 10^{-6}$
3-Methylpyridine	$4.8 \cdot 10^{-6}$
4-Methylpyridine	$5.2 \cdot 10^{-6}$

TABLE III

VARIATION OF $i\tau^{\frac{1}{2}}$ WITH CURRENT DENSITY FOR THE PYRIDINE, 3-METHYL AND 4-METHYLPYRIDINE COMPLEXES AT THE PLATINUM ELECTRODE

($10.01 \cdot 10^{-4}$ *M* Pd, 0.1 *M* KCl, 0.2 *M* ligand)

Current (mA)	$i\tau^{\frac{1}{2}}$ *for pyridine complex*	$i\tau^{\frac{1}{2}}$ *for 3-methylpyridine complex*	$i\tau^{\frac{1}{2}}$ *for 4-methylpyridine complex*
0.21	1.65	1.49	1.50
0.23	1.64	1.52	1.44
0.25	1.53	1.40	1.37
0.27	1.73	1.42	1.44
0.29	1.72	1.47	1.46

TABLE IV

RESULTS OF THE PALLADIUM–PYRIDINE SYSTEM AT VARIOUS PALLADIUM CONCENTRATIONS AT THE PLATINUM ELECTRODE

(0.1 *M* KCl, 0.2 *M* pyridine)

Palladium concentration ($\cdot 10^{-4}$ *M*)	*Current (mA)*	$i\tau^{\frac{1}{2}}$ (*mA* $sec^{\frac{1}{2}}$)
8.01	0.24	1.23
	0.25	1.14
	0.26	1.26
6.01	0.20	1.04
	0.21	0.96
	0.22	0.98
3.00	0.17	0.53
	0.18	0.53
	0.19	0.50
1.00	0.14	0.15
	0.15	0.18
	0.16	0.19

tion wave, whose transition time could not be measured. Owing to the shape of the reduction waves, a different procedure was adopted in measuring transition times. A tangent was drawn at the point of inflection and τ was measured at the point where the tangent and the reduction wave diverged.

Results for the pyridine, 3-methylpyridine and 4-methylpyridine systems are recorded in Table III. The pyridine system was also investigated at various metal concentrations (Table IV). Although $i\tau^{1/2}$ was proportional to metal concentration in the range investigated, the values obtained at any one metal concentration showed considerable variations in contrast to the results obtained with the mercury electrode (Table V). For analytical purposed, therefore, a mercury electrode is to be preferred.

TABLE V

RESULTS FOR THE PALLADIUM–PYRIDINE AND PALLADIUM–4-METHYLPYRIDINE SYSTEMS AT VARIOUS PALLADIUM CONCENTRATIONS AT THE MERCURY ELECTRODE

(0.1 M KCl, 0.2 M ligand)

Palladium concentration $(\cdot 10^4 M)$	*Current (mA)*	$i\tau^{1/2}$ *(mA sec*$^{1/2}$*) for py* [a]	$i\tau^{1/2}$ *(mA sec*$^{1/2}$*) for 4-Mepy* [a]
15.01	0.10–0.20	0.875 ± 0.01	0.96 ± 0.02
8.01	0.10–0.20	0.50 ± 0.01	0.525 ± 0.015
6.01	0.10–0.20	0.355 ± 0.005	0.365 ± 0.025
3.00	0.10–0.20	0.175 ± 0.005	0.195 ± 0.015

[a] Average of 6 results at currents increasing in 0.02 mA steps.

The results indicated that, for the system in question, the polarographic method of analysis is superior in several respects. At low metal concentrations (*ca.* 10^{-4} M) the chronopotentiograms became distorted, leading to inaccuracies in the measurement of transition times. In contrast, polarography can be applied to concentrations down to about 10^{-6} M. LINGANE[9] attributes the distortion to the fact that chronopotentiometry is more sensitive to the rates of the various steps involved in the reduction. Thus chronopotentiometry is an excellent tool for the study of reaction kinetics. In addition, the non-additivity of chronopotentiometric transition times contrasts sharply with the additivity of polarographic diffusion currents, and complicates the chronopotentiometric analysis of mixtures.

SUMMARY

The reduction of the palladium(II) complexes of pyridine, 2-methyl, 3-methyl and 4-methylpiridine has been studied. The reductions were irreversible in all cases, with no evidence of any dissociation of the complexes before reduction. Adsorption of the ligands at the mercury cathode was observed chronopotentiometrically. A comparison is made of the analytical capabilities of polarography and chronopotentiometry for the systems investigated.

RÉSUMÉ

On a examiné la réduction des complexes du palladium(II) de la pyridine, de la méthyl-2, de la méthyl-3 et de la méthyl-4-pyridine. Les réductions sont irréversibles dans tous les cas, sans aucune preuve de dissociation des complexes avant réduction. On a observé chronopotentiométriquement l'adsorption des ligands à la cathode de mercure. On compare les possibilités d'analyse par polarographie et par chronopotentiométrie pour les systèmes étudiés.

ZUSAMMENFASSUNG

Es wurde die Reduktion der Palladium(II)-Komplexe mit Pyridin, 2-Methyl, 3-Methyl und 4-Methyl-Pyridin untersucht. Die Reduktionen waren in allen Fällen irreversibel ohne Hinweis auf irgendeine Dissoziation der Komplexe vor der Reduktion. Chronopotentiometrisch wurde die Absorption der Liganden an der Quecksilberkathode beobachtet. Die untersuchten Systeme wurden auf ihre analytische Eignung für die Polarographie und Chronopotentiometrie verglichen.

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PRECISE DETERMINATION OF OXYGEN AND SILICON IN CHONDRITIC METEORITES BY 14-MeV NEUTRON ACTIVATION WITH A SINGLE TRANSFER SYSTEM

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The significance of the chondritic meteorites to the study of solar system elemental abundances has recently been reviewed[1]. The chondrites fall into well defined chemical and petrological classes, with characteristic oxygen and silicon abundances[2]. Every meteorite fall is unique, and museum curators are reluctant to distribute large samples. There is a considerable advantage, therefore, in the use of non-destructive techniques, and especially those that require only small amounts of material.

The non-destructive analysis of meteorites for silicon and oxygen by 14-MeV neutron activation is rapid and accurate[2,3]. In these single transfer methods, samples and comparator standards were irradiated separately and counted sequentially, and corrections made for variations in neutron flux by means of the output of a neutron monitor. More recently, assemblies have become available which allow the irradiation of the sample and comparator standard simultaneously. Uniform exposure to the neutron beam is achieved by biaxial rotation. Oxygen and silicon have been analysed in a suite of standard USGS rocks with a biaxially rotating target assembly and a dual transfer system[4,5]. Results on 2.5–3 g splits of well mixed rock powders were reproducible to ±0.25% oxygen and ±0.12% silicon (mean standard deviation). In this application sample and standard were counted simultaneously on separate detectors. Differences in the geometry of the two irradiation positions and the efficiency of the two detectors were compensated by a four-cycle irradiation sequence. Each irradiation position and detector combination was used for both sample and standard, and the resulting counts were pooled for the abundance calculations. Stable beam conditions are essential for the compensation to be valid. Reproducibility for a single determination cannot be estimated, as each individual value is the mean of four irradiation-counting cycles.

A dual transfer–biaxial rotator system for the 14-MeV neutron activation of oxygen has been reported which avoids the problems associated with the dual detector system[6]. Sample and standard were irradiated simultaneously, but were counted sequentially. The γ-ray energy region between 4.8 and 8.0 MeV was registered by a multiscaler, so that precise timing of the sample and standard counting sequence was achieved. The precision of the ratio of activities of two pure benzoic standards agreed with that expected hypothetically from the counting statistics. The sequential counting system gives considerably poorer counting statistics than a single irradiation–transfer system under identical conditions, and the simpler irradiation assembly of the single system allows the sample to be more favorably positioned in the neutron beam.

The disadvantages of the dual transfer–biaxial rotator system for large samples are greatly outweighed by the precision achieved under optimum conditions. For meteorites, the available sample is generally small and the loss in precision from poorer counting statistics is more serious. There are definite advantages, therefore, in the use of the single transfer system, though improvement in precision is needed.

An evaluation of sources of random error was made. In the analysis for oxygen precise timing was important, and errors could arise from fluctations in beam intensity if the integrated neutron dose only was recorded. These considerations were met by adapting the multiscaler approach to the single transfer system. The output of the boron trifluoride neutron monitor and the induced activity were recorded on the same multiscaler pass. By mathematically treating each channel recording the relative neutron flux as an individual irradiation, changes in beam intensity could be precisely compensated.

Requirements for precise silicon analyses were rather different. Improvements were made to the statistical treatment of the γ-ray photopeak evaluation and refinements were introduced to the method of analyser live-time correction as applied to short-lived radionuclides.

NUCLEAR DATA

Analyses were made by means of 14.7-MeV neutrons produced by the reaction ^{3}H (d,n) ^{4}He.

Irradiation of oxygen and silicon with these essentially monoenergetic fast neutrons induces several reactions which are summarized in Table I. The most sensitive reaction for oxygen is that leading to the production of 7.35-sec ^{16}N, whose energetic γ-rays are highly specific for this radionuclide. The most convenient indicator nuclide for silicon is 2.3-min ^{28}Al, produced by an (n,p) reaction on the abundant ^{28}Si isotope. The 1.78-MeV γ-ray of ^{28}Al is not as unequivocal as the high-energy ^{16}N photons, but for several minutes after a short 14-MeV neutron

TABLE I

14-MeV NEUTRON REACTIONS ON OXYGEN AND SILICON

Element	*Reaction*	*Isotope abundance (%)*	*Cross section (mb)*	*Half life*	*Gamma energy (MeV)*	*Branching ratio (%)*
Oxygen	$^{16}O(n,p)^{16}N$	99.8	33	7.35 sec.	6.13	68
					7.12	5
	$^{16}O(n,2n)^{15}O$		0.5	2 min	0.511	100
	$^{17}O(n,p)^{17}N$	0.037	112	4.1 sec	—	—
	$^{18}O(n,\alpha)^{15}C$	0.20	11	2.3 sec	5.3	—
Silicon	$^{28}Si(n,p)^{28}Al$	92.2	250	2.3 min	1.78	100
	$^{29}Si(n,p)^{29}Al$	4.7	100	6.6 min	1.28	94
					2.43	6
	$^{30}Si(n,\alpha)^{27}Mg$	3.1	45–185	9.5 min	0.84	69
					1.07	30.4
					0.18	0.6

irradiation, it is the most prominent photopeak in the spectrum of a silicate rock or stony meteorite.

Sources of interference in 14-MeV neutron activation analysis have been discussed by MATHUR AND OLDHAM[7], who classified interferences into two types. Type I are reaction interferences, where the indicator radionuclide is produced from elements other than that sought. Instrumental, or Type II, interferences arise from activities whose γ-rays are unresolvable by NaI(Tl) scintillation spectrometry. Possible interferences in the determination of oxygen and silicon are outlined in Table II.

TABLE II

INTERFERENCE REACTIONS IN THE DETERMINATION OF OXYGEN AND SILICON

	Reaction	*Isotope abundance (%)*	*Cross section (mb)*	*Half life*	*Gamma energy (MeV)*	*Branching ratio (%)*
Oxygen						
Type I interference	$^{19}F(n,\alpha)^{16}N$	100	23			
Type II interference	$^{11}B(n,p)^{11}Be$	80	3	13.6 sec	6.81 7.99	4 2
Silicon						
Type I interference	$^{27}Al(n,\gamma)^{28}Al$	100	0.5			
	$^{31}P(n,\alpha)^{28}Al$	100	140			
Type II interference	$^{56}Fe(n,p)^{56}Mn$	91.7	115	2.58 h	1.81	29

The interference of fluorine can be serious, as this element produces ^{16}N activity equivalent to about 0.6 of its weight of oxygen. An empirical determination of this interference[4] shows that 0.1% fluorine is equivalent to 0.0415% oxygen. The low (n,p) cross section for ^{11}B and the low branching ratio of the high-energy γ-rays of ^{11}Be mitigate against interference from this element, and boron-to-oxygen ratios up to 100 can be tolerated[2].

Interference to the silicon determination from the (n,γ) reaction on aluminum is insignificant for 14-MeV neutrons. There is some moderation of neutrons from shielding and empirical determinations of this interference[8] indicate that 5% aluminum is equivalent to 0.01% silicon. Phosphorus in the specimen can interfere and 1% phosphorus pentoxide gives an activity equivalent to 0.21% silicon[5]. The Type II interference from iron can be neglected for rocks low in this element, but for chondrites a small correction must be applied. Calculations show that 1% iron is equivalent to 0.0033% silicon.

EXPERIMENTAL

Apparatus

Deuterons were accelerated by a Cockcroft-Walton generator (Kaman Nuclear, Colorado Springs, Model A-1250). Titanium targets containing 5-Ci ^{3}H were used for the production of 14-MeV neutrons. To ensure stable conditions, the combined atomic and molecular deuterium beam was limited to 300–600 μA, and the accelerating potential to 140 keV. The beam was defocussed for more uniform target depletion and to improve the correlation between the sample neutron dose and the count recorded by the monitor[9].

At the time of these analyses, the target had been bombarded for 100–150 mA min^{-1}, and was rather depleted. The neutron yield was about one third of that obtained from a new target and the sensitivities are typical rather than optimal.

The relative neutron flux was determined by means of a low-geometry boron (40% ^{10}B) trifluoride tube. The stability of the neutron monitor has a marked effect on precision, and χ^2-tests were carried out on the BF_3 detector system with a Pu–Be source before each series of determinations. The high voltage plateau, bias voltage and time constant curves were checked periodically. After amplification and pulse shaping the output of the neutron monitor was remotely recorded on a 6-decade scaler. For multiscaling applications, the neutron monitor was connected to a single-channel analyser, which provided suitable output pulses of uniform amplitude.

The details of the pneumatic sample transfer system and sequential programming circuit have been previously described[10]. Irradiated samples were counted in a 4×4″ well-type NaI(Tl) detector, and the output was amplified by a double-delay line amplifier. Spectra were recorded on a Nuclear Data ND 2201 4096-channel analyser. For multiscaling, a pulse train of uniform height was obtained using the scaler output of a single-channel analyser.

Preparation of samples

Powders were prepared from four different interior portions of the Allende, Mexico, chondrite[11,12]. Aliquots of 0.4–0.5 g were heat-sealed[13] in 11/64-in internal diameter polyethylene vials. These were reproducibly located within 2 dram polyethylene snap top "pill packs" which were also heat-sealed ("rabbits").

The details of the source of the Allende specimens, and the weights of powder packed into each rabbit are summarized in Table III.

TABLE III

SAMPLING DETAILS OF ALLENDE SPECIMENS

Specimen number	*Specimen weight (g)*	*Rabbit number*	*Sample weight (g)*
S-5211a[a]	5.68	1845	0.4511
		1846	0.5113
		1847	0.4755
S-5211b[a]	6.20	1848	0.4710
S-5207a[b,c]	4.06	1849	0.4234
S-5207b[b,c]	3.17	1850	0.4694

[a] Donated by C. B. MOORE.
[b] Donated by R. S. CLARKE, JR.
[c] U.S. National Museum specimen number USNM 3510.

Preparation of standards

Oxygen standards were prepared from primary standard-grade potassium dichromate (Mallinckrodt Chemical Works) which was dried to constant weight at 110°. The loss in weight was 0.04%.

Silicon standards were initially prepared from Specpure silica (Johnson-Matthey), ignited[14] to constant weight at 600°. The weight loss was 1.71%. These standards were not entirely satisfactory and a primary standard was prepared from a piece of pure optical lens quartz, designated L-1. Comparator standards were packaged for irradiation in the same way as the samples.

Both oxygen and silicon standards were normalized to the pure quartz reference. The stoichiometry for the potassium dichromate agreed with the L-1 standard to within 0.4 rel. %, but the silicon abundance in *Specpure* silica was low by 1.9 rel. %. A determination of the oxygen in *Specpure* silica, normalized to L-1 quartz, yielded a result which was 2.3 rel. % higher than the stoichiometric value. *Specpure* silica is very finely divided and of large surface area; polymerized water may be present and may not be entirely removed even at 600°. The oxygen and silicon analyses of *Specpure* silica give a total of 100.39%, indicating good internal consistency for the intercomparison of the three standards.

Determination of oxygen

At the beginning of each irradiation cycle, the amplified output of the boron trifluoride neutron monitor was connected through a single-channel analyser to the multiscaler input of the ND 2201 analyser. The dwell time of the multiscaler was set at 0.4 sec. The multiscaler pass was initiated and the irradiation cycle begun. The rabbit was irradiated for 15 sec during which time it was spun about its axis by a dry nitrogen jet. At the end of the irradiation, the rabbit was transferred back to the counting station. During the interval taken for the return of the sample, the multiscaler input was switched to the output of the detector assembly. A single-channel analyser integrated the energy region between 4.5 and 8.0 MeV.

The multiscaler pass continued for 90 sec after irradiation, to follow the decay to zero. The contents of the analyser memory were read out on to punched tape. The tapes were batch-processed on an IBM tape-to-card converter and the analytical data reduced by a computer.

In each series of analyses three samples and three potassium dichromate standards were irradiated in the sequence–standard, sample, sample, standard; the order was arranged so that a particular sample was not always irradiated between the same two standards.

Determination of silicon

The amplified output of the detector assembly was connected directly to an analogue-to-digital converter of the ND 2201 analyser. The discriminators and zero level were adjusted to analyse only the region about the ^{28}Al photopeak, and a conversion gain for 512 channels was used so that analyser dead time was only 1–2%.

The actual elapsed counting period was kept constant, and was accurately timed by means of a crystal-controlled time base. The live time was recorded in the first channel of the analyser memory.

Irradiation and delay times were preset at 60 sec each. The rabbit was loaded into the pneumatic system and the automatic irradiation cycle initiated. After a preset delay time, the deuteron beam was turned on. The integrated relative neutron dose, measured by the boron trifluoride detector was recorded on a six-decade scaler, gated by the timing circuit controlling the neutron generator. The same circuit regulated the dry nitrogen jet which spun the rabbit.

The actual length of the irradiation period was recorded by a electromechanical clock.

At the end of the irradiation, the rabbit was returned to the counting position. After the preset delay to allow ^{16}N activity to decay, the time base was enabled, starting the 300-sec counting period.

The recorded spectrum and elapsed live time were read out on to punched paper tape, and converted to punched cards for computer processing. Irradiation and delay times, and the integrated boron trifluoride count, were manually recorded and transferred to computer cards.

Calculation of results

Oxygen. A computer program OXYCALC was used for data reduction. Details of weight and type of material in each irradiation capsule, together with an index number indicating whether the rabbit was a sample, standard or blank, were read in first. These were referenced for use in the calculation by the rabbit number.

Each multiscaler record was inspected for the start and end of the BF_3 count. Each channel in this period was treated as an individual neutron irradiation. The growth factor, G, was given by

$$G = (1 - e^{-\lambda \Delta T})$$

where λ is the ^{16}N decay constant and ΔT is the multiscaler dwell time. The decay during each subsequent channel was constant and was described by a decay factor, D, such that

$$D = (e^{-\lambda \Delta T})$$

The ^{16}N activity induced during any time interval represented by a single channel, J, containing a BF_3 count $B(J)$, was proportional to $G \cdot B(J)$. The observed ^{16}N activity was corrected for flux variations in the following way. The term $G \cdot B(1)$ represented the integrated induced activity $I(1)$, at the end of the first dwell time period. At the end of the second dwell time interval, the integrated activity, $I(2)$, was represented by $D \cdot I(1) + G \cdot B(2)$. In the general case

$$I(J) = (D \cdot I(J-1) + G \cdot B(J))$$

The operation of the neutron beam was not synchronized with the multiscaler and irradiation did not last for the whole time period in the first and last channels. The calculation averaged the neutron dose over the whole dwell time for these two channels, but for short dwell times the error introduced was trivial.

At the end of the irradiation record, the beginning of the ^{16}N γ-count was sought. The multiscaler was running during the transfer of the activated rabbit, and one or two of the initial channels usually contained anomalously low counts. The channel containing the highest number of γ-ray counts was therefore taken as the true beginning of the ^{16}N count. The first 40 channels of the γ-count were corrected for decay to the midpoint of the channel representing the start of the ^{16}N decay curve, and a weighted summation made. The expected integrated activity calculated from the relative neutron dose was similarly corrected, and the weighted sum of the actual ^{16}N γ-counts was normalized to this number. An empirical correction was made for the activity of the empty rabbit.

Silicon. Abundances were derived with the COMSTAR program. Spectra were read in and corrected for the instrumental background. The area of the photopeak was evaluated by the method outlined by STERLINSKI[15], whose eqn. (7) was rewritten in the form

$$S_n = n \cdot a_0 + \sum_{i=1}^{n} (n-2i+0.5)\,(a_{+1}+a_{-1})$$

where n is the number of channels integrated, channel 0 being the middle channel of the photopeak; a_{+i}, a_{-i} are the counts in the ith channels above and below the midlle channel respectively. The computer program selected the center of the peak, and performed the integration for increasing values of n. The variance, V_{sn}, was calculated from:

$$V_{sn} = n^2 a_0 + \sum_{i=1}^{n} (n-2i+0.5)^2\,(a_{+i}+a_{-i})$$

and the value of S_n with the minimum relative variance selected for the abundance calculation. The integrated peak area was normalized for BF_3 integrated count and irrradiation, decay and live times.

The integration method can compare standard and sample spectral shapes to detect non-linearities in the sample spectrum underneath the photopeak. A linear regression was fitted to the ratio of sample to standard peak areas, with the integration width as the independent variable. The slope of the line was tested for significance by means of null hypothesis model. Significant slopes were not found, indicating a straight base line beneath the photopeak.

Sample and standard comparison

Results for oxygen and silicon were calculated according to three comparison models.

Dual standards. The activity of the sample was normalized to the mean of the activities of the nearest preceding and following standards. This method was preferred when analyses were made under conditions of serious beam instability.

Linear regression. A least-squares fit was made to the normalized activities of the standards in any series of irradiations, with run number as the independent variable. Conditions where the beam was decaying appreciably but smoothly were suitable for treatment by this model. It could be further sophisticated by fitting a polynomial to the data, rather than restricting the fit to a linear regression.

Comparison factor. The mean of the normalized activities of the comparator standards was used for the calculation of the sample abundances. Clearly, if the standard activities are sufficiently reproducible there is considerable statistical advantage to this approach. Provided that the generator and monitoring systems were operating in a stable manner, this method of calculation was superior to the other two models.

RESULTS AND DISCUSSION

The results of analyses of the Allende chondrite for oxygen are given in Table IV. The errors quoted are standard deviations for a single determination calculated from the replicate analyses and are *not* derived from counting statistics. For oxygen, the mean relative deviation for a single determination, derived from counting statistics, is about 2%. Table IV shows that the comparison factor method yields more precise replicates than the dual standard or linear regression methods. The mean relative deviation for a single determination calculated by the comparison factor model is 2.0% and agrees well with that determined from counting statistics. Random errors from other sources are therefore very small. The reproducibility of the replicate analyses for oxygen in each Allende sample approaches that obtained with a refined biaxial rotator system by LUNDGREN AND NARGOLWALLA[6] for the comparison of pure benzoic acid and oxalic acid standards.

TABLE IV

14-MeV NEUTRON ACTIVATION ANALYSES OF OXYGEN IN THE ALLENDE CHONDRITE

Sample number	*Rabbit number*	*Number of analyses*	*Dual standard*	*Linear regression*	*Comparison factor*
S-5211a	1845	6	36.3 ± 1.3	36.4 ± 1.3	36.2 ± 0.7
	1846	6	35.3 ± 1.6	34.9 ± 1.4	34.9 ± 1.0
	1847	6	35.7 ± 1.1	35.7 ± 0.7	35.6 ± 0.4
S-5211b	1848	6	36.4 ± 1.5	36.2 ± 1.1	36.2 ± 1.2
S-5207a	1849	6	35.6 ± 0.8	35.7 ± 0.9	35.7 ± 1.0
S-5207b	1850	6	36.8 ± 0.8	36.9 ± 0.5	36.9 ± 0.5

TABLE V

14-MeV NEUTRON ACTIVATION ANALYSES OF SILICON IN THE ALLENDE CHONDRITE

Specimen number	*Rabbit number*	*Number of analyses*	*Dual standard*	*Linear regression*	*Comparison factor*
S-5211a	1845	6	16.05 ± 0.22	15.98 ± 0.15	15.98 ± 0.14
	1846	6	15.49 ± 0.17	15.47 ± 0.13	15.48 ± 0.13
	1847	6	15.64 ± 0.14	15.66 ± 0.14	15.66 ± 0.14
S-5211b	1848	7	16.36 ± 0.35	16.38 ± 0.26	16.39 ± 0.24
S-5207a	1849	7	15.93 ± 0.27	15.87 ± 0.20	15.89 ± 0.11
S-5207b	1850	7	16.28 ± 0.24	16.26 ± 0.14	16.26 ± 0.11

The results for silicon in the Allende chondrite are listed in Table V. Errors are standard deviations for single determination calculated from the replicate determinations on each sample. Again the best precision was obtained by the comparison factor method, where the mean relative deviation for all the samples was 0.9%. The relative standard deviation expected from counting statistics is 0.4–0.5%, indicating a small contribution from random errors elsewhere in the analytical system. Some of the variation is probably due to the higher background in the 1.78-MeV region, and to small interferences from other 14-MeV neutron irradiation products.

The preceding discussion has been confined to the variation of replicate analyses for the same sample. These will now be compared with the errors between

TABLE VI

MEAN OXYGEN AND SILICON ABUNDANCES IN THE ALLENDE CHONDRITE

Sample number	*Number of samples*	*Abundance (%)*					
		Dual standard		*Linear regression*		*Comparison factor*	
		Oxygen	*Silicon*	*Oxygen*	*Silicon*	*Oxygen*	*Silicon*
S-5211a	3	35.8 ± 0.5	15.73 ± 0.29	35.7 ± 0.8	15.70 ± 0.26	35.6 ± 0.7	15.70 ± 0.2
S-5211	4	35.9 ± 0.5	15.89 ± 0.40	35.8 ± 0.7	15.87 ± 0.40	35.7 ± 0.6	15.88 ± 0.4
S-5207	2	36.2 ± 1.2	16.11 ± 0.35	36.3 ± 1.2	16.07 ± 0.39	36.3 ± 1.2	16.08 ± 0.3
Mean		36.0 ± 0.6	15.96 ± 0.35	36.0 ± 0.7	15.94 ± 0.35	35.9 ± 0.7	15.94 ± 0.3
Fluorine correction		0.001	—	0.001	—	0.001	—
Phosphorus correction		—	0.05	—	0.05	—	0.05
Iron correction		—	0.08	—	0.08	—	0.08
Corrected S-5211		35.9	15.76	35.8	15.74	35.7	15.75
Corrected S-5207		36.2	15.98	36.3	15.94	36.3	15.95
Corrected mean		36.0	15.83	36.0	15.81	35.9	15.81

different samples, which are summarized for both elements in Table VI. Standard deviations are calculated from the mean values for each sample. In the case of S-5207 where only two samples were analysed, the quoted error is simply the difference between the two values.

The variation between samples is considerably larger than would be expected for a homogeneously ground, well-mixed powder. A large variation between different pieces is reasonable, as the Allende chondrite does contain sporadically distributed

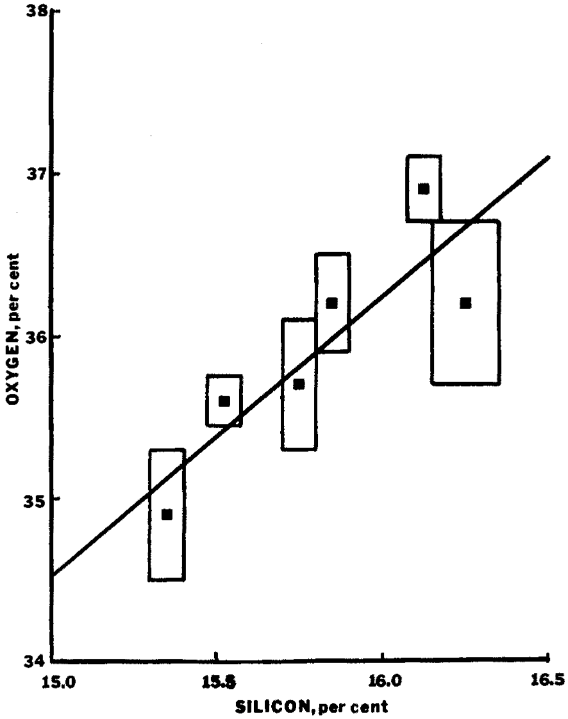

Fig. 1. Correlation of oxygen and silicon abundances in six samples of the Allende chondrite.

TABLE VII

OXYGEN AND SILICON IN TWO USGS STANDARD ROCKS

Standard rock	*Rabbit number*	*Number of analyses*	*Dual standard*		*Linear regression*		*Comparison factor*	
			Oxygen	*Silicon*	*Oxygen*	*Silicon*	*Oxygen*	*Silicon*
AGV-1	1821	6	47.9 ± 1.2	27.77 ± 0.62	48.1 ± 1.0	27.71 ± 0.66	48.3 ± 0.9	27.79 ± 0.75
	1822	6	47.7 ± 1.0	28.19 ± 0.45	47.8 ± 0.6	28.04 ± 0.46	47.8 ± 0.5	28.19 ± 0.54
	1823	6	47.4 ± 1.3	27.76 ± 0.37	47.6 ± 0.8	27.75 ± 0.42	47.6 ± 1.2	27.78 ± 0.56
Mean			47.7 ± 0.24	27.91 ± 0.25	47.8 ± 0.27	27.83 ± 0.18	47.9 ± 0.36	27.92 ± 0.23
Fluorine correction			0.02	—	0.02	—	0.02	—
Phosphorus correction			—	0.10	—	0.10	—	0.10
Iron correction			—	0.02	—	0.02	—	0.02
Corrected mean			47.7	27.79	47.8	27.71	47.9	27.80
BCR-1	1824	6	45.7 ± 0.9	26.11 ± 0.50	45.8 ± 0.8	26.11 ± 0.44	45.8 ± 0.9	26.17 ± 0.67
	1825	6	45.8 ± 0.5	25.48 ± 0.28	45.7 ± 0.4	25.51 ± 0.22	45.6 ± 0.4	25.53 ± 0.36
	1826	6	46.0 ± 0.7	25.69 ± 0.56	46.0 ± 0.7	25.75 ± 0.45	45.9 ± 0.5	25.74 ± 0.66
Mean			45.8 ± 0.15	25.75 ± 0.33	45.8 ± 0.16	25.79 ± 0.30	45.8 ± 0.14	25.81 ± 0.31
Fluorine correction			0.02	—	0.02	—	0.02	—
Phosphorus correction			—	0.07	—	0.07	—	0.07
Iron correction				0.03	—	0.03	—	0.03
Corrected mean			45.8	25.63	45.8	25.69	45.8	25.71

inclusions of widely varying compositions[2]. Three of the samples, however, were aliquots of the same powder (S-5211a), but their standard deviation is very close to that for six samples of four different pieces. Apparently, homogeneous mixing of a sample containing silicates of differing composition, sulphides and some free metal is not a trivial problem.

Silicon and oxygen are largely in the same phases in chondrites. Table VI indicates that their abundances are correlated. This is clearly seen in Fig. 1, where the mean abundance for each sample is plotted. Error boxes represent the standard deviations of the means and the regression line was calculated from the unweighted means with silicon as the independent variable. The correlation coefficient, $r=0.86$, indicates a highly significant correlation between these two elements.

The large variation between samples and the correlation between silicon and oxygen observed in the case of the Allende chondrite is in contrast to the results for well mixed rock powders. Results for the USGS standard andesite, AGV-1 (split 110, position 21) and standard basalt, BCR-1 (split 1, position 8) are shown in Table VII. These analyses indicate the high precision which can be obtained with well mixed powders. For both elements the deviation of the mean of three aliquots is significantly lower than the deviations of the individual replicates for each powder. The silicon analyses were made under conditions of severe beam instability, and illustrate the reproducibility of the mean of six analyses even under less than ideal circumstances. These silicon results again show how the dual standard model gives better precision for individual replicate runs when the beam is unstable. Although the analyses for the two standard rocks should not be taken as definitive, it is interesting to compare oxygen and silicon abundances reported here with those of other workers. These are summarized in Table VIII.

The silicon abundances reported here for Allende agree reasonably well with the chemical analysis made at the Smithsonian Institution by CLARKE *et al.*[12]. The specimens S-5207 were obtained from this Institution, and the mean value found for these (Table VI) agrees very well with the chemical results. Agreement is less satisfactory with the silicon abundances reported by KING *et al.*[11]. The spectrophotometric value falls within the range of abundances found in the present work, but the spectrographic results are significantly lower.

The agreement between the direct oxygen analysis in Allende and that determined from the full major element analysis is reasonable. The presence of sulphides, free metal and unusual mineral phases introduces some uncertainty when major elements are reported as oxides and may partly account for the difference observed. The agreement is better with the S-5207 results than with the mean of all samples.

Agreement between silicon analyses of andesite AGV-1 and basalt BCR-1 is acceptable particularly when the wide range of values making up FLANAGAN's[16] average is considered. The oxygen values reported here are higher than values calculated from total major element analyses by 0.3–0.6% oxygen. Strangely enough, the other 14-MeV neutron activation results[4] are *lower* than the chemical values by 0.4–1.0 absolute % oxygen. VOLBORTH AND VINCENT[4] discussed the problems of accurate direct oxygen determination and stressed the role of "minus" water (H_2O-), *i.e.* the water released by heating to 110°. Analyses for H_2O- summarized by FLANAGAN[16] range from 0.8 to 1.3% in AGV-1 and from 0.3 to 1.0% in BCR-1. These differences are of the same order as the discrepancies in the oxygen analyses. It is clear that in a

TABLE VIII

COMPARISON OF OXYGEN AND SILICON RESULTS FOR THE ALLENDE CHONDRITE AND TWO USGS STANDARD ROCKS

Method	*Abundance (%)*					
	Allende		*AGV-1*		*BCR-1*	
	Oxygen	*Silicon*	*Oxygen*	*Silicon*	*Oxygen*	*Silicon*
Compilation[a]	—	—	47.3	27.58	45.5	25.47
Spectrographic[b]	—	14.49	—	—	—	
Spectrophotometric[b]	—	15.59	—	—	—	
Chemical[c]	36.9	16.00	—	—	—	
14-MeV neutron activation[d]	—	—	46.9	27.85	44.5	25.43
14-MeV neutron activation[e]	36.0	15.83	47.7	27.79	45.8	25.63
14-MeV neutron activation[f]	36.0	15.81	47.8	27.71	45.8	25.69
14-MeV neutron activation[g]	35.9	15.81	47.9	27.80	45.8	25.71

[a] FLANAGAN[16]; oxygen calculated from total analysis.
[b] KING *et al.*[11].
[c] CLARKE *et al.*[12].
[d] VOLBORTH AND VINCENT[4] for oxygen; VINCENT AND VOLBORTH[5] for silicon.
[e] This work, dual standard model.
[f] This work, linear regression model.
[g] This work, comparison factor model.

definitive study of oxygen in standard rocks, determination of H_2O- and drying of samples at 110° before irradiation is essential.

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SUMMARY

Improved methods for the determination of oxygen and silicon by 14-MeV neutron activation are described. A single-transfer system is employed to attain a precision approaching that of biaxial rotator systems. Analyses of six samples of the Allende chondrite are given and a correlation is found between oxygen and silicon abundances.

RÉSUMÉ

On décrit des méthodes pour le dosage de l'oxygène et du silicium par activation neutronique 14-MeV. Un système "transfer simple" est utilisé pour arriver à une précision voisine de celle des systèmes "rotateur biaxial". Les résultats d'analyse de 6 échantillons sont donnés.

ZUSAMMENFASSUNG

Es werden verbesserte Methoden zur Bestimmung von Sauerstoff und Silicium mit Hilfe der 14-MeV-Neutronenaktivierung beschrieben. Um eine Genauigkeit zu erreichen, die derjenigen des Biaxial–Rotator-Systems entspricht, wurde ein Single-Transfer-System verwendet. Die Analysen von 6 Proben von chondritischen Meteoriten werden angegeben. Eine Zusammenhang zwischen den Sauerstoff- und Siliciumüberschüssen wird gefunden.

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COLORIMETRIC DETERMINATION OF SOME AROMATIC COMPOUNDS WITH A FORMALDEHYDE–SULPHURIC ACID REAGENT*

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Small amounts of aromatic compounds, especially hydrocarbons, ethers and other comparatively unreactive molecules, are generally difficult to determine. Pure physical methods, such as those based on direct measurement of absorption in the ultraviolet or infrared, are often insensitive and non-specific. The use of gas chromatography demands also a moderately expensive apparatus. In the present work, the possibilities of a simple colorimetric method have been investigated. An aldehyde–acid reagent has been employed, namely, formaldehyde–sulphuric acid, sometimes termed the Marquis reagent. LEROSEN *et al.*[1] quoted it in 1952 as a streak reagent in chromatography for aromatic compounds; these authors and FEIGL[2] gave a list of the colours yielded with some 60 benzenoid and heterocyclic aromatic compounds. The application of this reagent to the colorimetric determination of anisole was examined in an earlier work[3]. The only later quantitative application to aromatic hydrocarbons or ethers appears to be that of RAJZMANN[4] for biphenyl; her reagent contained iron(III) as oxidising agent, however.

EXPERIMENTAL

Reagents

Sulphuric acid (96%), glacial acetic acid and 37% aqueous formaldehyde solution, all analytical grade (Merck).

Aromatic compounds (hydrocarbons, ethers, sulphonic acids and some others), purified by distillation and/or crystallisation. The purities were checked where possible by gas or thin-layer chromatography.

Reagent solutions of formaldehyde and of the aromatic compounds were prepared in glacial acetic acid.

Procedures

For the determinations, 1 ml of a solution of the aromatic compound in acetic acid was mixed with 1 ml of a solution of formaldehyde in acetic acid; concentrated sulphuric acid was then added with vigorous stirring (2 ml to mixtures containing hydrocarbons and 3 ml to those containing ethers). The resulting solutions were placed in a bath at 100° for the desired reaction time of 20 or 25 min. Reaction was then arrested by removing the tubes to ice water and light absorbances were measured either

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directly in the test tubes used for the reaction or after the contents had been transferred to cuvettes. A basically similar procedure was used in studies of the spectra of various reaction mixtures. A procedure employing a different order of mixing is mentioned later.

The spectra were studied with the Unicam SP 600 and SP 800 instruments. Quantitative measurements were carried out with the Electrosynthèse or Lange colorimeters, equipped with filters.

RESULTS

Colour was usually still developing after the reaction time of 20–25 min but this had slowed up so much that longer times brought only little extra gain; an error of up to 1 min in the time caused negligible error in the values.

As found in the anisole determination, increase in concentration of formaldehyde first raised the absorbance and then suppressed colour development. This influence was especially marked with mesitylene and Fig. 1 shows the steep curves obtained.

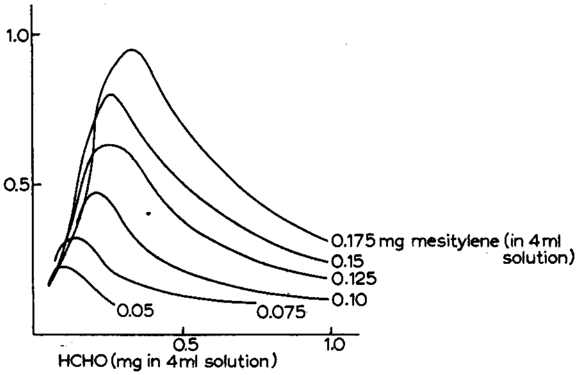


Fig. 1. Influence of formaldehyde concentration on colour derived from various mesitylene amounts.

Development of colour for durene also was moderately susceptible to the concentration of this reagent component. For each aromatic compound, the optimum amount of formaldehyde for colour development increased very approximately linearly with the amount of the compound. The mole ratios formaldehyde/compound for highest colour production are listed in Table I. They vary over a factor of more than ten. Any relation to constitution may be partly masked by the different reaction conditions used; but little is evident except that the ratio is lowest for compounds with several substituents. Unoccupied positions possibly consume extra formaldehyde so that more is needed to attain full colour intensity. Reasons for the inhibiting effect of excess of formaldehyde are obscure. Increased water content from the larger amounts of aqueous formalin solution is not responsible; this was established by controls in which the water amounts were varied at constant formaldehyde concentration.

A compromise formaldehyde concentration had thus to be chosen for each compound. In view of this and of the fact that reaction was not complete or that following reactions leading to colour decay were taking place, it was hardly expected that the Beer–Lambert law would be in force. In fact, straight lines relating absorbance and

TABLE I

MOLE RATIO FORMALDEHYDE : COMPOUND FOR OPTIMUM COLOUR INTENSITY

Compound	*% H_2SO_4 in solution*	*Reaction temp. (°)*	*Reaction time (min)*	*Ratio*
Durene	50	100	25	6
Anisole	10	50	60	7
Mesitylene	50	100	25	8
Diphenyl ether	60	100	20	20
Cumene	50	100	25	25
Benzyl acetate	60	100	20	50
Benzyl alcohol	60	100	20	60
Dibenzyl ether	60	100	20	80–100 (40–50 per nucleus)
Ethylbenzene	50	100	25	80

TABLE II

REACTION CONDITIONS FOR QUANTITATIVE COLORIMETRIC DETERMINATION

Compound	*% H_2SO_4 in mixture*	*[HCHO] (mg/ml)*	*Reaction temp. (°)*	*Reaction time (min)*	*λ[a] (nm)*	*Beer–Lambert law within limits (mg/ml)*
Durene	50	0.1	100	25	400	0.05–0.20
Mesitylene	50	0.07	100	25	400	0.075–0.15
Cumene	50	0.3	100	25	460	0.025–0.175
Ethylbenzene	50	0.9	100	25		0.05–0.175
Dibenzyl ether	60	3.0	100	20	425	0.02–0.2
Diphenyl ether	60	0.06	100	20	515	0.15–0.3
Anisole	10	1.4	50	60	522	up to 0.6

[a] Filters used.

concentration of aromatic compound were found within moderately wide limits. Table II gives an idea of these limits and of the sensitivity of the method.

Influence of changed order of mixing

This was tested on dibenzyl and diphenyl ethers. Ether solution in acetic acid (1 ml) was mixed with 3 ml of a sulphuric acid–acetic acid reagent; after various time intervals, the formaldehyde–acetic acid reagent (1 ml) was added. Colour development was then carried out in the usual way by heating at 100° for 20 min. After cooling in ice water, the absorbances were measured; results are shown in Table III. The pretreatment significantly inhibits subsequent colour development. This inhibition increases with increase in sulphuric acid concentration and is virtually complete after 1 min. It is presumably due to sulphonation of the reactive nuclear positions. The speed of the sulphonation is remarkable.

To test this assumption of sulphonation, colour development of the following series was investigated:

1. toluene: aldehyde and then sulphuric acid added (usual order of mixing);
2. *o*-toluenesulphonic acid (amount equivalent to the toluene amount in 1): aldehyde and then sulphuric acid added as in 1;
3. *p*-toluenesulphonic acid: as 2;

TABLE III

LIGHT ABSORBANCES AFTER PRETREATMENT WITH SULPHURIC ACID

[H_2SO_4] (%)	*Time of contact of ether and sulphuric acid before adding formaldehyde reagent and heating*						
	0[a]	*10 sec*	*1 min*	*5 min*	*10 min*	*20 min*	*30 min*
Dibenzyl ether							
58	1.215	1.04	0.57	0.45	0.45	0.45	0.415
72	1.215	0.70	0.41	0.38	0.375	0.365	0.365
96	1.215	0.36	0.265	0.24	0.24	0.24	0.24
Diphenyl ether							
58	1.155	1.06	0.90	0.87	0.845	0.84	0.82
72	1.155	1.00	0.65	0.575	0.56	0.555	0.555
96	1.155	0.91	0.10	0.10	0.10	0.10	0.10

[a] Value with the usual order of mixing.

TABLE IV

COLOUR FORMATION OF TOLUENESULPHONIC ACIDS

(200 μg of toluene (or equivalent amount of sulphonic acid) in 1 ml of acetic acid; 3.0 mg HCHO in 1 ml of acetic acid; 3 ml of 96% H_2SO_4)

Mixture	*Absorbance after time (min)*						
	5	*10*	*20*	*40*	*60*	*80*	*120*
1	0.755	0.805	0.85	0.89	0.91	0.935	0.99
2	0.11	0.20	0.33	0.595	0.72	0.775	1.01
3	0.065	0.08	0.09	0.12	0.13	0.175	0.215
4	0.06	0.065	0.07	0.12	0.125	0.13	0.15

4. toluene: 96% sulphuric acid added and left for 5 min; then the formaldehyde–acetic acid added to bring to the same final concentrations as in 1.

The results are shown in Table IV. *p*-Toluenesulphonic acid and toluene pretreated with sulphuric acid show closely similar colour development; toluene and the *o*-sulphonic acid attained similar absorbances after *ca.* 2 h. Evidently the position *para* to the methyl group participates predominantly or entirely in colour production. The slower colour development with *o*-toluenesulphonic acid is probably a consequence of deactivation of the nucleus by the sulphonic acid group.

DISCUSSION

Some comments may be made about the possible nature of the reaction and of the colour-yielding species in the reaction mixtures.

All the compounds studied except durene possess the necessary free *p*-position to an existing substituent or to existing substituents. The more active nucleus of durene may make it an exception or a methyl group may migrate (JACOBSEN rearrangement[5]). It is of interest that the formaldehyde/aromatic compound ratio for best colour development has its lowest value for durene.

Benzyl alcohol, benzyl acetate, dibenzyl ether, benzene and diphenylmethane all yield with formaldehyde–sulphuric acid the same absorption spectrum with a maximum at *ca.* 420 nm; the absorbances are essentially the same for equivalent amounts of the first three. These first three also give solutions with this same absorption maximum when treated with sulphuric acid of concentrations from 58 to 96%, in absence of formaldehyde. This agrees with the hypothesis that the colour-producing species is a carbonium ion C_6H_5–CH_2^+ or a homologue such as C_6H_5–CH_2–C_6H_4–CH_2^+ (which would have a closely similar spectrum in the ultraviolet and visible). The structural unit C_6H_5–CH_2 is present already in the alcohol, ester and ether, from which it can be abstracted by sulphuric acid alone, as the carbonium ion:

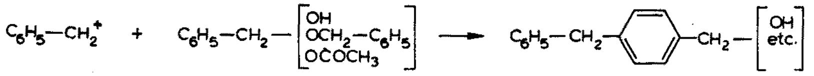
$$C_6H_5\text{—}CH_2\left[\begin{array}{l}\text{—}OH\\ \text{—}OCH_2\text{—}C_6H_5\\ \text{—}OCOCH_3\end{array}\right]\xrightarrow{H^+} C_6H_5\text{—}CH_2^+ + \left[\begin{array}{l}HO_2\\ C_6H_5\text{—}CH_2OH\\ CH_3COOH\end{array}\right]$$

Benzene cannot form this ion with sulphuric acid alone and thus yields no colour. It can be formed, however, with protonated formaldehyde in the sulphuric acid:

$$C_6H_6 + H_2\overset{+}{C}OH \longrightarrow C_6H_5\text{—}CH_2^+ + H_2O$$

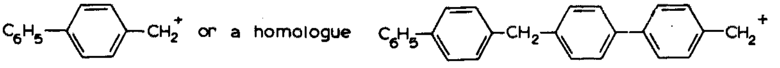
Diphenylmethane does contain the benzyl group but the C–C link is stable to sulphuric acid and no coloured product arises. The formaldehyde–sulphuric acid may, however, react:

A homologous ion of this sort could be formed also from the benzyl carbonium ion by further reaction with aromatic compound:



followed by the first reaction mentioned above. This formation of homologues can theoretically be extended indefinitely. Although this would not markedly influence the spectrum, it would soon lead to an insoluble polymeric product. Turbidity and even precipitation are sometimes encountered in the reactions between aromatic compounds and the formaldehyde–sulphuric reagent.

Brieskorn *et al.*[6,7] investigated the reaction between biphenyl and formaldehyde–sulphuric acid, which yields a blue solution with absorption maximum at 600 nm. They found that this absorption maximum was given also by the mixtures: *p*-phenylbenzyl alcohol with sulphuric acid; 4,4′-diphenylbenzhydrol with sulphuric acid; and bis(biphenylyl)methane with formaldehyde–sulphuric acid. By means of thin-layer chromatography, they were able to detect *p*-phenylbenzyl alcohol in the reaction mixture, biphenyl–formaldehyde–sulphuric acid, shortly after the start of reaction. The violet colour of these solutions migrated towards the cathode in electrophoresis, supporting the hypothesis of a carbonium ion as the coloured species; this would be



The production of colour from the two diaryl compounds hints that a diarylcarbonium ion, $(C_6H_5\text{–}C_6H_4\text{–})_2{}^+CH$ may also play a part.

BRIESKORN *et al.* were unable to detect the diarylcarbinol in the hydrolysate of the reaction mixture from biphenyl–formaldehyde–sulphuric acid (but identified it in the solid product obtained by adding water to the blue solution). The oxidising agent necessary for production of di-(and tri-)arylcarbonium ions remains unidentified. BRIESKORN *et al.* showed, for example, that the oxidation potential of sulphuric acid is inadequate for oxidising Ar–CH_2–Ar to Ar–CHOH–Ar. Moreover, they were able to show that the possible oxidising agent, performic acid (from autoxidation of the aldehyde) was not present and also that the biphenyl–formaldehyde–sulphuric acid mixtures gave colour even in absence of air; atmospheric oxidation evidently cannot play a part.

In the present work, a clue whether a mono-, di- or triarylcarbonium ion is responsible for the colour may be obtained by comparison with some absorption maxima of carbonium ions, cited by DENO *et al.*[8]. These are given in Table V, together with the absorption maxima observed in the present work for mixtures of formaldehyde and sulphuric acid with a number of aromatic compounds. This comparison indicates that a diarylcarbonium ion may be the (principal) coloured species from anisole (and phenol and diphenyl ether), although the absorption maximum at 340 nm could be ascribed to a monoarylcarbonium ion. Toluene, cumene and chlorobenzene possibly yield triarylcarbonium ions. The observed maximum for benzene (diphenylmethane, benzyl alcohol, benzyl acetate and dibenzyl ether) falls between those for the three types of ion. A closer study is clearly warranted.

TABLE V

COMPARISON OF ABSORPTION MAXIMA

Absorption maxima of carbonium ions[a]						*Absorption maxima observed with* $X\text{-}Ar/HCHO/H_2SO_4$	
$[X(p)\text{–}C_6H_4\text{–}]_3C^+$		$[X(p)\text{–}C_6H_4\text{–}]_2CH^+$		$X(p)\text{–}C_6H_4\text{–}C(CH_3)_2^+$ [b]			
X	*λ*	*X*	*λ*	*X*	*λ*	*X*	*λ*
H	404, 431	H	440–442	H	400	H	420–430
CH_3	452	CH_3	472			CH_3	452, 670
iC_3H_7	456					iC_3H_7	*ca.* 460
tC_4H_9	458	tC_4H_9	480				
Cl	465	Cl	485			Cl	465
OCH_3[c]	483	OCH_3	507			OCH_3	340, 512–522

[a] According to DEMO *et al.*[8].
[b] No value available for C_6H_5–CH_2^+.
[c] Methoxy group in only two of the nuclei.

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SUMMARY

A simple colorimetric determination of several aromatic compounds with the help of a formaldehyde–sulphuric acid reagent has been developed. Hydrocarbons, ethers and other unreactive molecules can be determined. The nature of the coloured reaction products is briefly discussed.

RÉSUMÉ

On décrit un dosage colorimétrique de plusieurs composé aromatiques. Il repose sur la réaction du formaldéhyde en milieu acide sulfurique. On discute brièvement le mécanisme de la réaction.

ZUSAMMENFASSUNG

Es wurde eine kolorimetrische Bestimmung einiger aromatischer Verbindungen beschrieben. Sie beruht auf der Reaktion mit einem Formaldehyd/Schwefelsäure-Reagens. Der Chemismus der Farbreaktion wurde kurz diskutiert.

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REDUKTIONS-TITRATIONEN ORGANISCHER VERBINDUNGEN MIT CHROM(II)-LÖSUNG

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Zweiwertiges Chrom ist eines der stärksten Reduktionsmittel in Lösung. Das Normalpotential Cr(III)/Cr(II) beträgt −410 mV und liegt etwa 500 mV negativer als beim dreiwertigen Titan. Trotz diesem stark negativen Normalpotential kann die Chrom(II)-Lösung durch Einhalten der weiter unten beschriebenen Vorsichtsmassnahmen über längere Zeit vor Zersetzung bewahrt werden.

Aufgrund der starken Reduktionswirkung lassen sich viele Reduktionen, welche bei Anwendung von Titan(III) unvollständig verlaufen, mit Chrom(II) rasch und quantitativ durchführen. Mit Chrom(II) lassen sich folgende Gruppen reduzieren[1–5]: Chinone, Nitroso-, Nitro- und Azoverbindungen. Chinone werden zu Hydrochinonen, die andern Verbindungen zu den entsprechenden Aminen quantitativ reduziert. Die Titrationen werden in Inertgas-Atmosphäre als direkte, häufiger aber als Überschuss-Titrationen durchgeführt. In den meisten Fällen erfolgt die Endpunktsanzeige potentiometrisch. Die Methode wird seit mehreren Jahren in unseren analytischen Laboratorien mit gutem Erfolg zur Qualitätskontrolle von Zwischen- und Endprodukten eingesetzt.

Die vorliegende Arbeit gibt für eine Reihe von Verbindungen die Titrationsbedingungen und die Standardabweichungen an. Für Substanzen, bei denen aus Löslichkeitsgründen die Reduktion in neutralem oder alkalischem Medium wünschbar ist, werden zwei einfache Bestimmungsmethoden angegeben. Es wird überdies eine Möglichkeit aufgezeigt, nach der Reduktion mit Chrom(II) durch die Wahl eines geeigneten Oxidationsmittels verschiedene funktionelle Gruppen differenziert zu erfassen.

EXPERIMENTELLES

Reagenzien

Chrom(II)-Lösung. Eine frisch zubereitete Lösung von 80 g Kaliumchromalaun [$KCr(SO_4)_2 \cdot 12\ H_2O$] in 1500 ml dest. Wasser und 30 ml Schwefelsäure 2.5 *M* wird in der von STONE[6] vorgeschlagenen Apparatur mit amalgamiertem Zink reduziert.

Die reduzierte Chrom(II)-Lösung wird direkt in einen mit Stickstoff unter Atmosphärendruck gefüllten Rundkolben gedrückt (Abb. 1), bis der Kolben zur Hälfte gefüllt ist. In diesem Kolben kann die Lösung praktisch ohne Titeränderung während Wochen aufbewahrt werden. Zum Gebrauch wird der Aufbewahrungskolben an eine Kolbenbürette angeschlossen, beim Öffnen des Hahnes fliesst die unter Druck stehende Reduktionslösung direkt in die Kolbenbürette. Die Chrom(II)-Lösung oxidiert sich rasch beim Kontakt mit der Luft. Deshalb ist es notwendig, die erste Füllung der

Kolbenbürette vollständig aus der Bürette wieder zu entfernen. Damit dies durchgeführt werden kann, befindet sich über dem Teflonkolben der Bürette soviel reines Quecksilber, dass es bei der höchsten Stellung des Kolbens das tote Volumen bis zum Hahnen gerade ausfüllt. Der Wirkungswert der Reduktionslösung wird mit eingestellter Eisen(III)-Lösung bestimmt.

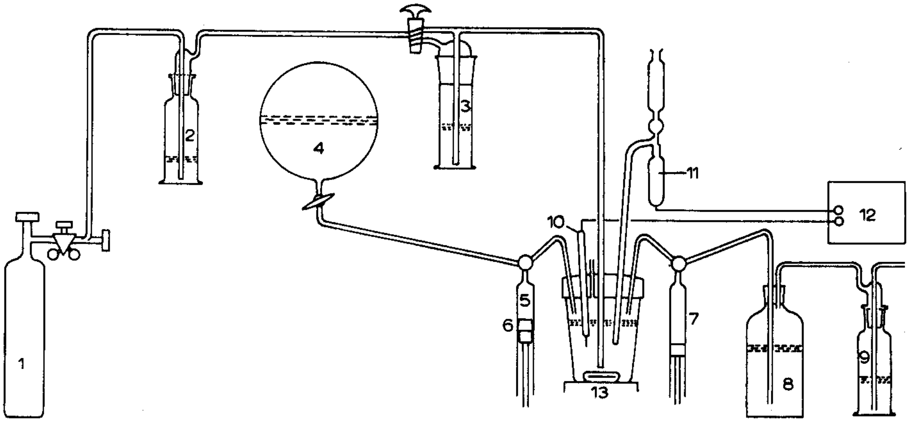


Abb. 1. Apparatur für Chrom(II)-Titrationen. (1) CO_2-Druckflasche (2) Gaswaschflasche mit $TiCl_3$-Lösung, (3) Gaswaschflasche mit sauerstoff-freier Schwefelsäure zum Ansäuern nach Reduktion in neutralem oder alkalischem Milieu, (4) Vorratskolben mit Chrom(II)-Lösung, (5) Kolbenbürette für Chrom(II)-Lösung, (6) Quecksilber zur Ausfüllung des Totraumes, (7) Kolbenbürette für die Oxidationslösung, (8) Vorratsflasche für die Oxidationslösung, (9) Gaswaschflasche mit Pyrogallol-Lösung zur Adsorption von Sauerstoff, (10) Messelektrode, (11) Bezugselektrode, (12) Potentiometer, (13) Rührmotor mit Teflon-Magnetrührer.

0.1 M Eisen(III)-Lösung. 48.5 g $NH_4Fe(SO_4)_2 \cdot 12H_2O$ werden mit dest. Wasser unter Zugabe von 20 ml konz. Schwefelsäure zu 1000 ml gelöst. Die Lösung wird jodometrisch eingestellt. Diese Lösung findet Verwendung bei der Einstellung der Reduktionslösung, bei der Titration von Chrom(II)-Überschüssen, sowie bei der Rückoxidation von leicht oxidierbaren Hydrochinonen.

0.1 N Chrom(VI)-Lösung. 4.9033 g $K_2Cr_2O_7$ z.A. werden mit dest. Wasser unter Zugabe von 20 ml konz. Schwefelsäure zu 1000 ml gelöst. Diese Lösung kann bei Bedarf jodometrisch eingestellt werden und findet Anwendung bei der Rückoxidation von schwer oxidierbaren Hydrochinonen.

0.05 N Anthrachinon-2-sulfosäure. 8.21 g Anthrachinon-2-sulfosäure (Natriumsalz mit 1 Kristallwasser) werden mit Schwefelsäure 1 *M* zu 1000 ml gelöst. Der Wirkungswert wird mit 0.1 *N* Chrom(II)-Lösung ermittelt.

Titrationsapparatur

Die Titrationsapparatur ist in Abb. 1 dargestellt.

Ausführung der Titrationen

Bei der Durchführung der Reduktion ist darauf zu achten, dass alle mit der Chrom(II)-Lösung in Berührung kommenden Glasteile keine rauhen Stellen aufweisen, wie sie etwa vom Rührstäbchen eines Magnetrührers herkommen können. Solche rauhe Stellen können nämlich bewirken, dass sich die Chrom(II)-Lösung während der Titration zersetzt und damit das Resultat verfälscht. Als Lösungsmittel sind geeignet: Wasser, Schwefelsäure, Äthanol, Dimethylformamid (nicht über 25°), Essigsäure und mit wenig Wasser verflüssigtes Phenol, das aber nicht dunkel gefärbt sein darf. Die Titration kann bei Bedarf auch bei höherer Temperatur durchgeführt werden, was am besten durch einen Wassermantel erreicht wird. Für alle Titrationsarten muss ein den gewählten Titrationsbedingungen entsprechender Blindversuch durchgeführt werden.

Die Endpunktsanzeige erfolgt bei allen Titrationen potentiometrisch; als Messelektrode dient ein Platindraht von 1 mm Dicke und 6 mm Länge und als Bezugselektrode eine *N*-Quecksilbersulfatelektrode.

Direkt-Titration. 1.5 bis 1.7 mVal werden im Reduktionsgefäss mit 60 ml Lösungsmittel und 10 ml 2.5 *M* Schwefelsäure gelöst, während 10 Min mit Kohlendioxid gespült und danach titriert. Bei der Titration ist die Geschwindigkeit der Reagenszugabe dem Reaktionsverlauf anzupassen, da die Reduktion nicht immer momentan erfolgt. Die Spannung der Platinelektrode wird an einem geeigneten mV-Meter gemessen, und der Umschlag in bekannter Weise ausgewertet.

Überschusstitration sauer. 1.5 bis 1.7 mVal werden im Reduktionsgefäss mit 60 ml Lösungsmittel und 10 ml 2.5 *M* Schwefelsäure gelöst und während 10 min mit Kohlendioxid gespült. Man gibt einen gemessenen Überschuss von *ca.* 3 ml an 0.1 *M* Chrom(II)-Lösung zu, lässt je nach Reaktionsgeschwindigkeit zwischen 2 und 20 Min unter Spülen mit Kohlendioxid stehen und titriert den Chrom(II)-Überschuss mit dem geeigneten Oxidationsmittel.

Überschusstitration alkalisch. 1.5 bis 1.7 mVal werden im Reduktionsgefäss mit 20 bis 40 ml dest. Wasser oder Äthanol plus 10 ml 1 *M* Natriumhydroxid gelöst. Nach Zusatz von 40 ml 0.1 *M* AeDTA[7] wird während 10 Min mit Stickstoff chem. rein gespült und danach ein gemessener Überschuss von *ca.* 3 ml an 0.1 *M* Chrom(II)-Lösung zugegeben, wobei Chrom(II) komplex gebunden in Lösung bleibt. Je nach Reaktionsgeschwindigkeit lässt man unter Spülen mit Stickstoff während 5 bis 20 Min stehen, drückt aus der Waschflasche (Abb. 1, Nr. 3) 10 ml 2.5 *M* Schwefelsäure, die zuvor mit Stickstoff gespült worden ist, in das Reduktionsgefäss und titriert den Chrom(II)-Überschuss mit dem geeigneten Oxidationsmittel.

Überschusstitration neutral. Bei einigen säureunlöslichen Substanzen, insbesonders bei gewissen Azofarbstoffen, welche Acetessiganilid als Kupplungskomponente enthalten, verläuft die Reduktion in alkalischem Milieu nicht vollständig. In solchen Fällen verfährt man wie bei der Überschusstitration alkalisch, mit der Ausnahme, dass anstelle von Stickstoff chem. rein Kohlendioxid chem. rein als Spülgas verwendet wird. In der dadurch entstehenden Bicarbonatlösung (gestättigt mit Kohlendioxid) verlief die Reduktion in den von uns untersuchten Fällen quantitativ.

RESULTATE UND DISKUSSION

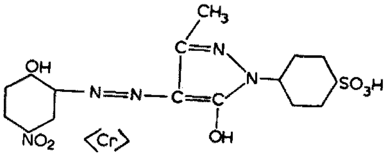
Tabelle I gibt eine Übersicht über die Arbeitsbedingungen und die Präzision für einige direkte und indirekte Titrationen mit Chrom(II). Die relative Standardabweichung liegt durchgehend im Bereich von 0.1–0.5%. Der potentiometrische Verlauf bei den verschiedenen Titrationsmethoden ist in der Abb. 2 dargestellt. Die Kurven der Abb. 2 geben 2 Beispiele für den Potentialverlauf bei direkten Reduktionen. Abbildung 2B zeigt die Potentialsprünge, die bei der Titration von Chrom(II)-

TABELLE I

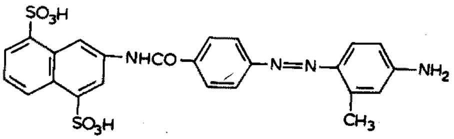
TITRATIONSBEISPIELE FÜR DIE DIREKT- UND ÜBERSCHUSSTITRATION

Verbindung	*Lösungsmittel*	*Art der Titration/ Rück-Titrant*	*Rel. Standardabweichung s_r (%)*	*Berechnet aus Anzahl Bestimmungen*
Anthrachinon	45 T. Phenol verflüssigt 90 T. Äthanol 12 T. 2.5 *M* Schwefelsäure	Direkt	0.3	10
Indigo	1.5 *M* Schwefelsäure	Direkt	0.3	10
2,3-Dichlor-1,4-naphthochinon	6 T. Dimethylformamid 1 T. 2.5 *M* Schwefelsäure	Direkt	0.1	7
Benzanthron	6 T. Dimethylformamid 1 T. 2.5 *M* Schwefelsäure	Überschuss sauer/ Eisen(III)	0.2	5
4-Chlor-2-nitrophenol	6 T. Dimethylformamid 1 T. 2.5 *M* Schwefelsäure	Überschuss sauer/ Eisen(III)	0.1	6
Nitroarginin	0.35 *M* Schwefelsäure	Überschuss sauer/ Eisen(III)	0.1	6
3,6-Dimethyl-4-benzoylaminonitrobenzol	6 T. Dimethylformamid 1 T. Schwefelsäure 2.5 *M*	Überschuss sauer/ Eisen(III)	0.1	5
p-Nitroacetanilid	6 T. Dimethylformamid 1 T. 2.5 *M* Schwefelsäure	Überschuss sauer/ Eisen(III)	0.1	5
4-Sulfobenzoesäure-2-azoacetessiganilid	6 T. Dimethylformamid 1 T. 2.5 *M* Schwefelsäure	Überschuss sauer/ Eisen(III)	0.3	6
Benzoesäure-2-azoacetessiganilid	6 T. Dimethylformamid 1 T. 2.5 *M* Schwefelsäure	Überschuss sauer/ Anthrachinon 2-sulfosäure	0.2	6
4-Nitrophenol-2-azo-4′-sulfophenylmethylpyrazolon, Chrom-Komplex[a]	7 T. 0.14 *M* Natriumhydroxid 4 T. 0.1 *M* ÄDTA	Überschuss neutral/ Eisen(III)	0.3	6
Benzoesäure-2-azoacetessig-N-methylanilid	10 T. 1 *M* Natriumhydroxid 45 T. Äthanol 40 T. 0.1 *M* ÄDTA	Überschuss neutral/ Anthrachinon-2-sulfosäure	0.2	5
Benzoesäure-(4′,8′-disulfo-2′-naphthyl amid)-4-azo (4′-amino-6′-methyl)-benzol[b]	55 T. 0.18 *M* Natriumhydroxid 40 T. 0.1 *M* ÄDTA	Überschuss alkalisch/ Eisen(III)	0.2	6

[a]



[b]



Überschüssen mit verschiedenen Oxidationsmitteln auftreten. Anthrachinonsulfosäure ist ein sehr schwaches Oxidationsmittel, welches mit Vorteil dan eingesetzt wird, wenn eine Rückoxidation oder eine bei Anwendung von Eisen(III)-Lösung mögliche Komplexbildung der Probe vermieden werden soll.

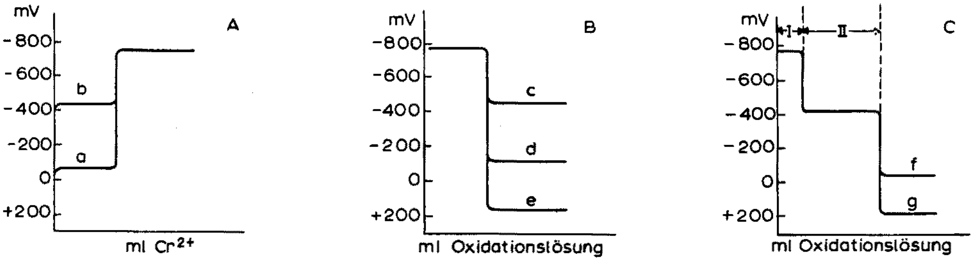


Abb. 2. Potentiometrischer Verlauf bei den verschiedenen Titrationsmethoden. (A) Direkt-Titration mit Chrom(II): (a) Titration von Eisen(III)-Lösung, (b) Titration von Anthrachinonsulfosäuren. (B) Titrationen von Chrom(II)-Überschüssen: (c) Anthrachinon-2-sulfosäure, (d) Eisen(III)-Lösung, (e) Chrom(VI)-Lösung. (C) Oxidimetrische Titrationen: (f) Eisen(III)-Lösung, (g) Chrom(VI)-Lösung, (I) Verbrauch für Chrom(II)-Überschuss, (II) Verbrauch für Oxidation der Hydrochinone.

Von besonderem Interesse sind die Kurven in Abb. 2C, welche die Reoxidation eines Hydrochinons wiedergeben. Der erste Sprung entspricht der Titration der unverbrauchten Chrom(II)-Lösung, und der Verbrauch vom ersten zum zweiten Sprung dient zur Berechnung des Hydrochinons. Beispiele für die Anwendung dieser Methode sind in Tabelle II angeführt.

TABELLE II

BEISPIELE FÜR DIE OXIDIMETRISCHE TITRATION NACH REDUKTION MIT CHROM(II)-LÖSUNG

Verbindung	*Lösungsmittel*	*Oxidationsmittel*	*Rel. Standardabweichung s_r (%)*	*Anzahl Bestimmungen*
Anthrachinon-1-sulfosäure	Essigsäure 30 %	Chrom(VI)	0.4	10
Anthrachinon-1, 8-disulfosäure	Essigsäure 30 %	Chrom(VI)	0.2	10
Anthrachinon-2, 6-disulfosäure	0.3 *M* Schwefelsäure	Eisen(III)	0.2	5

Die Kombination der Reduktionstitration mit Chrom(II) und der potentiometrisch verfolgten Reoxidation gibt generell die Möglichkeit, reversibel reduzierbare Stoffe und Gruppen neben nicht-reversibel reduzierbaren zu bestimmen. Der Verbrauch an Chrom(II) ergibt das Total von reversibel und nicht-reversibel reduzierbaren Gruppen, während die anschliessende Oxidationstitration selektiv die reoxidierbaren Gruppen erfasst. Als Beispiel sei die Bestimmung von 8-Nitroanthrachinonsulfosäure neben Anthrachinon-sulfosäure erwähnt. Der Verbrauch an Chrom(II) ergibt die Summe von Nitro- und Chinongruppen, während die Oxidation mit Chrom(VI) nur die Chinone erfasst.

Hierbei ergeben sich die folgenden Beziehungen:

$$\% \text{ 8-Nitroanthrachinon-sulfosäure} = \frac{(a-b) \cdot \text{Mol. Gew.}}{600 \cdot E}$$

$$\% \text{ Anthrachinon-sulfosäure} = \frac{(4b-\text{a}) \cdot \text{Mol. Gew.}}{600 \cdot E}$$

wobei: a = Verbrauch 0.1 N Cr^{2+} in ml
b = Verbrauch 0.1 N Cr^{6+} in ml
E = Einwaage in Gramm

Die in Tabelle III angeführten Resultate für Modellmischungen von 8-Nitroanthrachinon-sulfosäure und Anthrachinon-sulfosäure belegen die Brauchbarkeit der Methode.

TABELLE III

BESTIMMUNG VON 8-NITROANTHRACHINON-1-SULFOSÄURE, KALIUMSALZ NEBEN ANTHRACHINON-2-SULFOSÄURE, NATRIUMSALZ

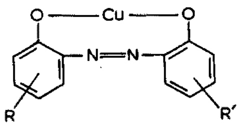
Eingesetzt % Nitroanthrachinon-sulfosäure	48.8	48.8	21.4	20.7	10.0	10.2
% Anthrachinon-sulfosäure	50.2	50.2	78.2	78.9	89.9	89.6
Gefunden % Nitroanthrachinon-sulfosäure	49.0	49.0	21.4	20.5	9.9	10.1
% Anthrachinon-sulfosäure	50.2	50.3	78.3	79.4	90.6	89.0

TABELLE IV

BESTIMMUNG VON KUPFER UND FREIEM FARBSTOFF IN EINEM KUPFERKOMPLEXFARBSTOFF

	Kupfer komplex	*Kupfer*	*freier Farbstoff*
Mittelwert (%)	58.0	5.12	52.7
Rel. Standardabweichung s_r (%) (7 Bestimmungen)	0.3	1.2	0.8

In ähnlicher Weise lassen sich der freie Farbstoff und der Kupfergehalt in einem Kupferkomplexfarbstoff in einem Arbeitsgang bestimmen. Mit Chrom(II) wird ausser der Azogruppe des Farbstoffes auch das komplex gebundene Kupfer quantitativ zum Metall reduziert, anschliessend wird mit Eisen(III)- oder Chrom(VI)-Lösung das Kupfer zum zweiwertigen Ion oxidiert. Für Kupferkomplexfarbstoffe der allgemeinen Formel



ergeben sich folgende Beziehungen:

$$\% \text{ Kupferkomplexfarbstoff} = \frac{a \cdot \text{Mol. Gew.}}{600 \cdot E}$$

$$\% \text{ freier Farbstoff} = \frac{(a-b) \cdot \text{Mol. Gew.}}{400 \cdot E}$$

$$\% \text{ Kupfer} = \frac{b \cdot 0.3177}{E}$$

wobei: a = Verbrauch 0.1 N Cr^{2+} in ml
b = Verbrauch 0.1 N Fe^{3+} oder Cr^{6+} in ml

In Tabelle IV ist ein Beispiel dieser Methodik angeführt.

ZUSAMMENFASSUNG

Für eine Anzahl von Substanzen aus der Farbstoff- und Pharmachemie werden die Titrationsbedingungen und die Standardabweichungen angegeben. Es werden zudem zwei Methoden beschrieben, welche bei Gegenwart von ÄDTA die Reduktion in neutralem oder alkalischem Medium erlauben.

Aus Gemischen mit reversibel und irreversibel reduzierbaren Gruppen können nach der Reduktion mit Chrom(II) durch Anwendung eines starken Oxidationsmittels die Komponenten einzeln bestimmt werden.

SUMMARY

Procedures and standard deviations are reported for the titration with chromium(II) of a number of compounds of interest in pharmaceutical and dyestuff chemistry. Two methods are described by which the reduction can be carried out in neutral or alkaline medium, in the presence of EDTA.

Depending on the nature of the functional groups, reduction can be reversible or irreversible. In mixtures, components of the two categories can be determined separately if the titration with chromium(II) solution is followed by titration with a strong oxidant.

RÉSUMÉ

Des méthodes sont proposées pour le titrage à l'aide de chrome(II) de composés organiques intéressant la chimie pharmaceutique et des colorants. La réduction peut s'effectuer en milieu neutre ou alcalin, en présence d'EDTA; elle peut être réversible ou irréversible suivant la nature de la fonction organique.

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THE COMPOSITION AND ION-EXCHANGE BEHAVIOR OF ZINC HEXACYANOFERRATE(II) ANALOGUES

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Considerable interest has been shown during the past few years in the ion-exchange properties of zinc hexacyanoferrate(II)[1-4], together with other hexacyanoferrates[5-14], since it was shown that this property may be exploited in the isolation of ^{137}Cs from other radionuclides. The authors have separated a mixture of sodium, potassium, rubidium and cesium by thin-layer chromatography on a plate consisting of cellulose powder containing potassium zinc hexacyanoferrate(II) or sodium zinc hexacyanoferrate(II) in only 16 min[15]. However, when mixtures of these ions were developed on a plate of cellulose powder containing zinc hexacyanoferrate(II) instead of sodium zinc hexacyanoferrate(II), the resulting spots tailed and could not be separated from each other.

Such different migration behaviors toward zinc hexacyanoferrate(II) analogues have led to a study of their relative compositions and the discrepancy of their adsorption behavior for alkali metal ions. Since these analogues have an exceptionally strong affinity for cesium ion, it was thought desirable to study in great detail an exchange involving this ion.

EXPERIMENTAL

Preparation of zinc hexacyanoferrate(II) analogues

All reagents used in this study were of analytical grade. The analogues were prepared by mixing 0.1 *M* sodium hexacyanoferrate(II) (200–300 ml) and 0.1 *M* zinc nitrate at ratios of 1:3, 1:2.5, 1:2, 1:1.5 and 1:1, respectively. The white slurries were obtained by adding these solutions dropwise and simultaneously into a beaker for 30 min while stirring. They were heated with stirring on a boiling water bath for 2 h, allowed to stand for 24 h, filtered or centrifuged, washed thoroughly and dried at 60° for 24 h. Slurries other than the 1:3 ratio were finely dispersed, and were centrifuged for 3 min at 8000 *g* rather than filtered. The precipitates labelled with ^{22}Na or ^{65}Zn were prepared by the same procedure as unlabelled ones.

Relative adsorption rate and batch distribution coefficient

Zinc hexacyanoferrate(II) analogues were compressed into pills under a pressure of about 300 kg/cm^2, allowed to break down in water for several days, air-dried, and sieved to 200–300 mesh[16]. The relative adsorption rates for cesium(I) were determined by mixing 20 mg of the analogues with 2 ml of aqueous solution containing cesium chloride tagged with ^{137}Cs, followed by centrifugation at 8000 *g* for 3 min. The radioactivity of the supernatant solution was measured by a well-type scintillation counter. Distribution coefficients for cesium (ml/g) were determined by equilibrating 0.1 g of the analogues with 5 ml of a solution containing $5 \cdot 10^{-2}$ mmoles of cesium nitrate tagged with ^{137}Cs in ammonium nitrate, followed by the same treatment as described in the determination of the relative adsorption rates.

Zn–Cs or Na–Cs exchange ratio

Exchanges of Zn–Cs (or Na–Cs) were studied by shaking 0.1 g of the ^{65}Zn (or ^{22}Na)-labelled zinc hexacyanoferrate(II) analogues with 5 ml of cesium chloride solution tagged with ^{137}Cs, respectively. After equilibrium had been attained, the mixtures were centrifuged and the radioactivity of the supernates was measured with a 400-channel pulse-height analyzer. The Zn–Cs or Na–Cs exchange ratio was calculated from the ratio of the amounts of adsorbed cesium to those of released ^{65}Zn (or ^{22}Na). The amounts of zinc or sodium released into the aqueous phase and the amount of cesium taken up by the analogues were obtained by the ^{137}Cs decrease and the ^{65}Zn (or ^{22}Na) increase in the aqueous phase, respectively.

Determination of zinc, hexacyanoferrate(II), chloride and sodium

Zinc, hexacyanoferrate(II) and chloride were determined titrimetrically, and sodium was determined by atomic absorption spectroscopy.

X-Ray measurement

X-Ray powder diffractions were measured on an apparatus from Rigaku Denki Co., Ltd. Tokyo, Japan with a copper target at a wavelength of 1.5418 Å.

RESULTS AND DISCUSSION

Relationship between mixing ratio and composition

Possible differences in the stoichiometric composition of the resulting hexacyanoferrate(II) analogues were checked by varying the mixing ratios of 0.1 *M* sodium hexacyanoferrate(II) to 0.1 *M* zinc nitrate. Table I shows that the compositions vary with the mixing ratio of the starting materials. The compositions of A (1:3) and D (1:1.5) are best represented as $Zn_2Fe(CN)_6$ and $Na_2Zn_3[Fe(CN)_6]_2$, respectively. D is a new adsorbent, the composition of which is identical with that of E (1:1). Although

TABLE I

RELATIONSHIP BETWEEN MIXING RATIO OF ZINC NITRATE TO SODIUM HEXACYANOFERRATE(II) AND THE COMPOSITION OF THE RESULTING ANALOGUES

Analogue	*Mixing mole ratio* $Na_4Fe(CN)_6$:$Zn(NO_3)_2$	*Analysis of the analogues*						*Formula*
		Per cent			*Ratio*			
		Zn	*Fe(CN)₆*	*Na*	*Zn*	*Fe(CN)₆*	*Na*	
A	1:3	33.2	54.6	0	1.98	1.0	0	$Zn_2Fe(CN)_6$
B	1:2.5	27.3	50.0	2.60	7.40	4.18	2	Mixture
C	1:2	24.5	47.9	3.43	5.02	3.02	2	Mixture
D	1:1.5	22.3	46.4	5.13	3.06	1.96	2	$Na_2Zn_3[Fe(CN)_6]_2$
E	1:1	22.6	46.3	4.92	3.22	2.02	2	$Na_2Zn_3[Fe(CN)_6]_2$

the mixing ratio varied from 1:1 (E) to 1:0.1, the composition and X-ray diffraction patterns remained unchanged with D or E.

Although A and D (or E) may be mixtures of two or more complexes with different structures, they give characteristic X-ray patterns as shown in Table II. Both chemical analysis (Table I) and X-ray data (Table II) showed that B (1:2.5) and C (1:2) were mixtures of A and D. The 0.1 M sodium hexacyanoferrate(II) used for the preparation of the analogues was itself basic (pH 8.5), so that there was some possibility of hydrolysis of zinc(II)[17]. Accordingly, the acidity of the 0.1 M sodium hexacyanoferrate(II) was lowered from 8.5 to 4.0 and used for the preparation of the complexes. The X-ray diffraction patterns and compositions of the analogues prepared in such a way remained unchanged from those prepared with 0.1 M sodium hexacyanoferrate(II) at pH 8.5. Therefore, it was the change in the mixing ratio of sodium hexacyanoferrate(II) to zinc nitrate that was responsible for the variations in their composition (Table I). In conclusion, the analogues prepared in this way are considered to be zinc hexacyanoferrate(II) (A) or sodium zinc hexacyanoferrate(II) (D) itself, or mixtures in varying proportion of A and D. Therefore, subsequent experiments were carried out principally with A and D.

TABLE II

X-RAY DIFFRACTION DATA FOR ZINC HEXACYANOFERRATE(II) ANALOGUES

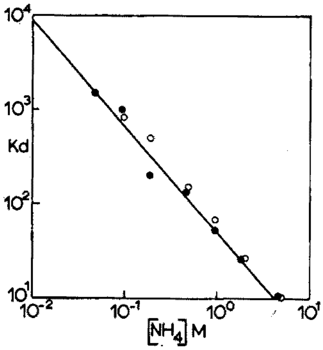
A		*B*		*C*		*D*	
d (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0
		6.19	0.14	6.24	0.16	6.28	0.22
		5.40	0.85	5.44	0.94	5.44	0.85
		4.51	0.42	4.53	0.42	4.53	0.59
4.33	0.85	4.33	1.00	4.33	0.05		
		4.13	0.98	4.13	1.00	4.13	1.00
		4.04	0.32	4.04	0.29	4.06	0.53
3.80	1.00	3.80	0.72	3.82	0.05		
		3.59	0.56	3.59	0.48	3.60	0.86
		3.48	0.20	3.48	0.15	3.48	0.40
3.29	0.19	3.29	0.16				
		3.19	0.36	3.19	0.32	3.16	0.57
		3.02	0.18	3.02	0.15	3.01	0.19
2.86	0.33	2.85	0.28	2.85	0.02		
		2.71	0.24	2.71	0.22	2.71	0.30
2.64	0.21	2.64	0.20			2.67	0.16
		2.58	0.20	2.58	0.12	2.57	0.28
		2.53	0.20	2.53	0.15	2.53	0.35
		2.43	0.20				
		2.38	0.20	2.38	0.17	2.38	0.33

Ion-exchange behavior

The ion-exchange behaviors of A and D for 0.01 M cesium ion were determined in ammonium nitrate solutions. As shown in Fig. 1, the observed points of log K_d of A and D *versus* log [NH$_4$] lie on a straight line of slope -1. These results suggest the reactions to be an ion exchange ruled by the mass action law. The ion-exchange behavior of A is in agreement with the results for zinc hexacyanoferrate(II) described by KOUŘÍM *et al.*[18]. The K_d values of A and D in nitric acid were almost constant until the concentration of nitric acid was increased above 1 *M*.

Relative adsorption rates of cesium

The relative adsorption rates of cesium(I) on A and D were determined by varying the shaking time in batch experiments. Figure 2 shows that the adsorption rate on A was extremely slow; however, cesium(I) was rapidly adsorbed on D within at most 15 min. It is of interest that these great differences in the adsorption rates were observed between these analogues.



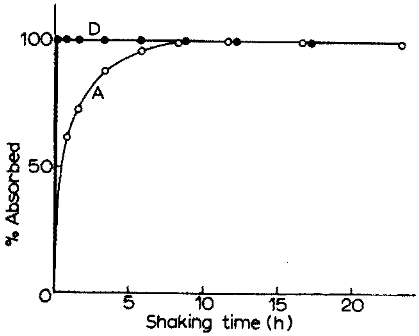


Fig. 1. Relationship between distribution coefficient K_d (ml/g) and ammonium ion concentration. (●) Zinc hexacyanoferrate(II) A, (○) sodium zinc hexacyanoferrate(II) D.

Fig. 2. Relative adsorption rate for cesium(I) on zinc hexacyanoferrate(II) and sodium zinc hexacyanoferrate(II). (A) Zinc hexacyanoferrate(II), (D) sodium zinc hexacyanoferrate(II).

Zn–Cs or Na–Cs exchange ratio

The exchange of elements in the analogues for cesium(I) in the external solution was determined by batch experiment (Table III). With 0.01 *M* cesium chloride and analogue A, the atomic ratio of released zinc to adsorbed cesium was *ca.* 0.5, *i.e.* one zinc atom in A is replaced by two cesium atoms from the external solution. This result agrees with that of BARTON *et al.*[1]. With 0.01 or 0.1 *M* cesium chloride and D (or E), the ratio of released sodium to adsorbed cesium is *ca.* 1, which means that 1:1 exchange takes place between sodium in D (or E) and cesium(I). Sodium ion in ^{22}Na-labelled D was completely replaced by cesium(I). However, with 0.1 *M* cesium chloride and analogue A, the ratio of zinc released to cesium adsorbed was only 0.33; the cause for such

TABLE III

Zn–Cs OR Na–Cs EXCHANGE RATIO ON ZINC HEXACYANOFERRATE(II) ANALOGUES

Analogue	*Exchange ratio*			
	10^{-2}M CsCl		*10^{-1}M CsCl*	
	Zn/Cs	*Na/Cs*	*Zn/Cs*	*Na/Cs*
A	0.49	0	0.33	0
C	0.06	0.90	0.17	0.52
D	0	1.02	0	0.96
E	0	0.96	0	1.08

a disproportion in the zinc–cesium exchange ratio was examined in detail. The amounts of cesium adsorbed, zinc released from the analogue, and chloride adsorbed were determined after shaking analogue A with 0.1 *M* cesium chloride solution. Immediately after the shaking, it was found that the total amount of chloride adsorbed plus twice the amount of zinc released was almost equal to the amount of cesium adsorbed. However, when the solid phase A was washed thoroughly with water until no chloride was detected in the wash solution, the amount of cesium remaining in A was shown to be equal to half the zinc released. Thus in 0.1 *M* cesium chloride, retention of cesium(I) and ion exchange on analogue A occur simultaneously. It was found that the exchange of elements in the analogues varied markedly with their composition.

Change in X-ray data caused by ion exchange

As shown in Table IV, the X-ray diffraction patterns of analogue A were entirely different before and after batch experiments with 0.1 *M* cesium chloride. The final pattern was identical with that of synthesized $Cs_2ZnFe(CN)_6$[1]. This indicates that the ion exchange causes profound variation in the crystal structure, and provides further confirmation that a 2:1 exchange takes place between cesium(I) and zinc in A as shown in Table III. In contrast, the X-ray data for D remained unchanged before and after batch experiments, although a 1:1 exchange between cesium(I) and sodium in D was demonstrated. The finding that the ion-exchange adsorption rate of D is markedly faster than that of A might be due to the constancy of the crystal structure of D before and after the ion exchange. Analogue D was unfavorable for column work, since it was relatively fine powder and was broken down slightly in aqueous suspension. However, it could advantageously be applied to a rapid separation of sodium, potassium, rubidium and cesium by thin-layer chromatography[15], because of its rapid adsorption rate.

TABLE IV

X-RAY DIFFRACTION DATA OF ZINC HEXACYANOFERRATE(II) ANALOGUES BEFORE AND AFTER BATCH EXPERIMENTS WITH 0.1 *M* CESIUM CHLORIDE

$Zn_2Fe(CN)_6$,A				Synthesized $Cs_2ZnFe(CN)_6$		$Na_2Zn_3[Fe(CN)_6]_2$,D			
Before		After				Before		After	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
4.33	0.85					5.40	0.89	5.47	0.32
3.80	1.00					4.51	0.41	4.53	0.46
		3.69	1.00	3.66	1.00	4.11	1.00	4.13	1.00
3.29	0.19					3.59	0.54	3.62	0.60
3.16	0.08	3.01	0.14	3.01	0.18	3.47	0.22	3.49	0.28
2.86	0.33					3.16	0.40	3.15	0.42
2.64	0.21	2.59	0.35	2.59	0.38	3.02	0.13	3.02	0.26
2.29	0.41					2.71	0.23	2.71	0.22
		2.13	0.17	2.10	0.28				

The authors wish to express their gratitude to Dr. M. IZAWA for his interest and encouragement.

SUMMARY

The dependence of the composition of zinc hexacyanoferrate(II) complexes on the mixing ratio of sodium hexacyanoferrate(II) and zinc nitrate solutions is demonstrated, and the ion-exchange behavior of the different complexes is described. Depending on the mixing ratios of the two components, $Zn_2Fe(CN)_6$ or $Na_2Zn_3[Fe(CN)_6]_2$, or mixtures of these compounds, may be formed. The adsorption rate for cesium(I) on zinc hexacyanoferrate(II) is extremely slow, whereas it is very rapid on disodium trizinc hexacyanoferrate(II). The Zn–Cs and Na–Cs exchange rates for the different complexes are discussed.

RÉSUMÉ

On examine la relation dans la composition d'un complexe hexacyanoferrate(II) de zinc et d'un mélange hexacyanoferrate(II) de sodium et nitrate de zinc. On décrit le comportement de ces différents complexes avec échangeurs d'ions. Il peut se former suivant les proportions des deux composants, $Zn_2Fe(CN)_6$ ou $Na_2Zn_3[Fe(CN)_6]_2$, ou des mélanges de ces composés. La vitesse d'adsorption du césium est très lente sur l'hexacyanoferrate de zinc; tandis qu'elle est très rapide avec le disodium trizinc hexacyanoferrate(II). On examine les vitesses d'échange de Zn–Cs et Na–Cs pour les différents complexes.

ZUSAMMENFASSUNG

Die Abhängigkeit der Zusammensetzung des Zinkhexacyanoferrat(II)-Komplexes vom Mischungsverhältnis der Natriumhexacyanoferrat(II)- und Zinknitratlösung wird beschrieben, ebenso das Ionenaustauscherverhalten der verschiedenen Komplexe. In Abhängigkeit von den Mischungsverhältnissen können $Zn_2Fe(CN)_6$ oder $Na_2Zn_3[Fe(CN)_6]_2$ oder Mischungen dieser Verbindungen gebildet werden. Die Absorptionsgeschwindigkeit des Cäsiums an Zinkhexacyanoferrat(II) ist extrem langsam, dagegen sehr schnell an Dinatriumtrizinkhexacyanoferrat(II). Die Zn–Cs- und Na–Cs-Austauschgeschwindigkeiten der verschiedenen Komplexe werden diskutiert.

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DECOMPOSITION OF OXIDE AND SULPHIDE MINERALS AND ORES BY FUSION WITH AMMONIUM SALTS

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Fusion methods are frequently used to bring mineral samples into solution for analytical purposes[1,2]. In contrast to fusion agents such as the hydroxides, carbonates, bisulphates and pyrosulphates of sodium and potassium, sodium peroxide and tetraborate, and potassium hydrogen fluoride, little has been reported on the use of ammonium salts as fusion agents in quantitative analysis. ISAKOV[3] used ammonium chloride, ammonium nitrate, and mixtures of ammonium salts (nitrate/chloride, bromide/nitrate and fluoride/nitrate) for decomposing some oxide, sulphide, carbonate and silicate minerals for qualitative and quantitative analysis. Mixtures of ammonium chloride and ammonium nitrate were employed by LYAKH *et al.*[4] for decomposing complex zinc ores for polarographic analysis. CHEAD AND SMITH[5] used fusion with ammonium fluoride for the determination of silica in glass sand, while JOSEPH AND MONY[6] used the flux to attack monazite. DOLEŽAL *et al.*[2], and STANTON[7], have commented on the use of ammonium fluoride and ammonium iodide for decomposing mineral samples.

Ammonium salts possess properties which make them useful as fluxes. They have low melting and boiling points which can be easily reached with a Bunsen burner flame, and, with the exception of the fluoride, may be easily handled in borosilicate glass apparatus when molten. In particular, their acidic properties, which result from the capacity of the ammonium ion to donate a proton, would seem to indicate the possibility of their use for the decomposition of basic material.

These considerations have led to the investigation of several ammonium salts for the decomposition of some sulphide and oxide minerals and ores (iron pyrites, zincblende, copper concentrates, copper ore, lead concentrates, Nimba iron ore, burnt pyrites and manganese ore) for the quantitative analysis of their major metallic components. Since mineral sulphides and oxides are considered to be basic substances (sulphide and oxide groups are donors of electron pairs) one would choose an acidic flux such as a hydrogen sulphate, sulphate or persulphate (containing electron deficient groups capable of accepting electron pairs) in order to decompose them. This work deals mainly with the use of ammonium hydrogen sulphate and ammonium hydrogen sulphate containing ammonium nitrate and ammonium chloride additives. Because the use of these salts introduces sulphates into the sample, they cannot be used when sulphur in sulphide minerals is to be determined.

EXPERIMENTAL

Apparatus

Pyrex test-tubes, 15 cm long and 2.5 cm internal diameter. Pyrex long-neck boiling flasks, 50-ml capacity.

Reagents

Ammonium sulphate and ammonium chloride were dried at 105° for 1 h. Ammonium hydrogen sulphate and ammonium nitrate were dried at 50° overnight. All chemicals used were of "analytical reagent grade" or "chemically pure".

Mineral samples

The source and relevant analytical data for the mineral and ore samples used are shown below. Analytical results marked with an asterisk are figures obtained from analysis by conventional methods, of the sample, as received, after grinding by hand to a fine powder and drying for 1 h at 105°. Figures marked with a double asterisk are the certificate values given by the supplier.

Sulphides: Iron pyrites (Bureau of Analysed Samples Ltd., Middlesbrough, England) 39.9% Fe*. The sample also contained about 48% S and 0.3% Cu.

Iron pyrites (African Explosives and Chemical Industries Ltd., P.O. Northrand, Transvaal, South Africa) 40.1% Fe*. The sample also contained about 42% S.

Zincblende (Hoepfner Gebr., Hamburg, Germany) as received was hand-ground to a fine powder. 48.5% Zn**.

Copper concentrates (Bureau of Analysed Samples Ltd.) 27.8% Fe* and 25.6% Cu*. The sample also contained about 32% S.

Copper ore (Hoepfner Gebr.) 33.7% Fe*. The sample also contained about 36% S, 8.4% Cu and 1% Zn.

Lead concentrates (Bureau of Analysed Samples Ltd.) 67.6% Pb* and 4.9% Zn**. The sample also contained about 16% S.

Oxides: Nimba iron ore (Bureau of Analysed Samples Ltd.) 66.1% Fe**. The sample also contained about 2.6% SiO_2, 1.1% Al_2O_3, 0.1% TiO_2, 0.1% MnO, 0.05% P and 0.01% S.

Burnt pyrites (Bureau of Analysed Samples Ltd.) 57.6% Fe*. The sample also contained about 2% S and 1% Cu.

Manganese ore (Bureau of Analysed Samples Ltd.) 49% Mn**. The sample also contained about 5% Fe, 6% SiO_2, 4% Al_2O_3, 0.1% P and 0.03% S.

The following oxide and sulphide samples were also used for some of the preliminary investigations.

Pyrolusite—B.D.H. "laboratory grade" manganese dioxide. Galena—from Leeuwenkloof, Transvaal, South Africa. Bornite and chalcocite—from Messina, Transvaal, South Africa.

Qualitative aspects of the fusions with ammonium salts

The feasibility of using ammonium sulphate, ammonium hydrogen sulphate and ammonium persulphate as fluxes for the dissolution of some sulphide and oxide minerals and ores was tested qualitatively by observing the extent of any reaction which occurred during fusion and, in this way, the ammonium salt which was likely to prove most useful in quantitative analysis was identified. Because the selected salts all have comparatively low decomposition temperatures (ammonium sulphate begins to decompose above 250°, ammonium hydrogen sulphate above 350° and ammonium sulphate above 180°) a large flux-to-sample ratio (15:1) was used.

Fusions with ammonium sulphate were carried out by mixing the flux (*ca.* 4.5 g) and mineral sample (*ca.* 0.3 g) in a fusion tube and then heating the latter carefully about 5 cm above the top of a Meker flame. The tube, held at an angle of 45°, was gradually lowered to increase the temperature and melt the flux. The melting process took about 15 min and the contents of the tube were then kept molten for a further 10 min at a temperature of about 310°. Throughout the entire fusion process, the tube was gently shaken.

Fusions with ammonium hydrogen sulphate or ammonium persulphate were performed by carefully heating about 4.5 g of flux in the tube until just molten, and then dropping the powdered mineral (*ca.* 0.3 g) into the melt, little by little, and keeping the charge molten for about 20 min. Care was taken in heating the ammonium persulphate because of its vigorous decomposition into ammonium pyrosulphate and oxygen at 180°.

These tests showed that while decomposition of iron pyrites, galena, zincblende and bornite was complete after about 15, 5, 5 and 15 min, respectively, of fusion with the ammonium salts, chalcocite, burnt pyrites and pyrolusite were incompletely decomposed after 15 min of fusion since visual examination of their melts at this stage indicated the presence of unattacked mineral. It was also observed that ammonium hydrogen sulphate caused smoother decomposition of all these samples than did either ammonium sulphate or ammonium persulphate. Both the latter salts produce ammonium hydrogen sulphate by thermal decomposition[8] at the temperatures used in these fusions; but ammonium sulphate spattered and crept considerably before it eventually formed a quiet melt, and ammonium persulphate needed great care of handling because of its vigorous decomposition. Because of these factors it was decided to use ammonium hydrogen sulphate for subsequent investigations.

FUSION CONDITIONS FOR THE QUANTITATIVE ANALYSIS OF SULPHIDE AND OXIDE MINERALS AND ORES WITH AMMONIUM HYDROGEN SULPHATE

Since the qualitative investigations had indicated that ammonium hydrogen sulphate might be suitable as a flux for the dissolution of sulphide and oxide minerals and ores, information on the efficiency of such fusions was then obtained. This was done by fusing known quantities of analysed samples with ammonium hydrogen sulphate, dissolving the cooled melts in a suitable mineral acid and analysing the resulting solutions for the major metallic components. During the course of these experiments, the effect of ammonium chloride and nitrate additives on the dissolution of samples incompletely decomposed by pure ammonium hydrogen sulphate was also investigated.

Iron pyrites—Determination of iron

An accurately weighed sample (0.3–0.4 g) of pyrites, dried at 105° for 1 h, was placed in a dry test-tube. About 0.5 g of a 6.0-g sample of ammonium hydrogen sulphate was added and mixed with the pyrites by rotation of the tube. The remainder of the flux was stored in a desiccator. The tube and its contents were carefully heated, with swirling, over a Meker flame until a quiet melt was obtained. As soon as the charge showed signs of solidifying, a further small portion of the flux was added. This procedure was continued until the entire 6-g sample of ammonium hydrogen sulphate had been added. In between additions of flux, the walls of the tube were heated to allow deposited material to run back into the melt and to burn away deposited sulphur.

When all the flux had been added, the tube was strongly heated in the flame for about 8 min, or until the charge began to solidify, if this occurred sooner. Any sulphur on the walls of the tube was burnt away and the tube and its contents allowed to cool. The total time needed for the fusion was about 15 min.

About 5 ml of 6 *M* hydrochloric acid was added to the cooled contents of the tube and the tube was carefully warmed. When the contents had dissolved, the solution was transferred to a 500-ml conical flask, up to 25 ml of 6 *M* hydrochloric acid being used as a wash liquid. Iron was determined titrimetrically[9] with potassium dichromate, after tin(II) chloride reduction, in presence of sodium diphenylamine sulphonate as indicator.

Decomposition of the pyrites was observed to commence as soon as the flux melted, the melt appearing yellow in colour and sulphur being deposited on the upper walls of the tube. The melt was quiet and did not spatter. Frothing tended to occur if the heating was too rapid, or if portions of flux larger than about 0.7 g were added. The frothing was accompanied by creeping of the melt. Among the gases evolved were hydrogen sulphide and ammonia.

The results obtained for the determination of iron in two pyrites samples are shown in Table I together with the results obtained on these samples by conventional dissolution methods (nitric acid attack[1] and sodium peroxide fusion[9]).

TABLE I

DETERMINATION OF IRON IN IRON PYRITES (% Fe)

Sample	*NH_4HSO_4 fusion*	*HNO_3 attack*	*Na_2O_2 fusion*
1	40.2, 39.8, 39.7, 40.1	40.0, 39.9, 39.8	
	40.1	40.0, 39.9	
	Mean 40.0 ±0.10[a]	Mean 39.9 ±0.04	
2	39.8, 40.3	40.0, 40.1, 40.3	40.0, 40.3

[a] All limits quoted are standard deviations of the mean result.

Comparison of the results obtained by the different dissolution procedures confirms the completeness of the decomposition in the fusion with ammonium hydrogen sulphate. The precision of the results, while perhaps acceptable, is not as good as that obtained from the dissolution with nitric acid. The ammonium salt fusion procedure would not be much quicker than the acid attack if a number of samples have to be analysed, but would eliminate the need for the evaporations called for by the nitric acid procedure. The main advantage of the ammonium salt fusion over a peroxide fusion is that the former may be carried out in glass instead of nickel or iron containers. Both fusion procedures, however, require considerable attention by the analyst.

Zincblende—Determination of zinc

An accurately weighed sample (*ca.* 0.5 g) of zincblende, dried at 105° for 1 h, was placed in a dry test-tube. Ammonium hydrogen sulphate (5 g) was added to the tube and mixed with the zincblende by gentle agitation of the tube. The tube was gently warmed, with a swirling motion, in a Bunsen flame, at a temperature such that the froth which formed did not reach the neck of the tube. When the froth had died down, the tube was more strongly heated until a clear, translucent yellow melt was formed. The whole operation took about 8 min.

The neck of the tube was then carefully warmed to dislodge any deposited material and to oxidise the sublimed sulphur. The melt was again heated for 3 min and any fresh sublimed sulphur was then burnt away. The tube was allowed to cool and its contents were dissolved in 10 ml of 1 *M* sulphuric acid. The solution was transferred to a 200-ml beaker, up to 25 ml of 1 *M* sulphuric acid being used as a wash liquid. Zinc was determined titrimetrically with potassium hexacyanoferrate(II) solution[10].

During the first fusion stage the charge, on being warmed, rapidly turned from black to brown and then to a light yellow colour. At the same time a heavy deposit of sulphur formed on the upper cooler parts of the tube. The melt smelt strongly of sulphur dioxide. The final melt, when cool, was white and contained no visible specks of undecomposed sample.

TABLE II

SULPHIDE ORES

Sample	*Results*	*Mean*[a]
Zincblende (48.5% Zn)	%Zn 48.4, 48.3, 48.4, 48.5, 48.4, 48.5	48.4 ±0.03
Copper ore (33.7% Fe)	%Fe 33.6, 33.8, 33.4, 33.4	33.6 ±0.1
Copper concentrates (27.8% Fe, 25.6% Cu)	Fusion method %Fe 27.7, 27.7, 27.7, 27.9 %Cu 25.3, 25.5, 25.0, 25.2 HNO_3 method %Fe 27.8, 27.8, 27.8 %Cu 25.5, 26.0	27.8 ±0.06 25.3 ±0.13
Lead concentrates (67.6% Pb, 4.9% Zn)	%Pb 67.7, 67.7, 67.2, 67.6 %Zn 4.9, 4.9, 5.0, 4.7	67.6 ±0.12 4.9 ±0.04

[a] All limits quoted are standard deviations of the mean result.

The results for the determination of zinc are shown in Table II. The accuracy and precision of these results indicate that ammonium hydrogen sulphate is an acceptable substitute for the conventional methods of decomposition of zincblende. The procedure described is rapid and eliminates the time-consuming evaporations with mineral acid which are part of the conventional procedures in the analysis of zinc in zincblende.

Copper ore—Determination of iron

Fusion with ammonium hydrogen sulphate (method as for the decomposition of iron pyrites) proved unsatisfactory and it was evident that not all the sample had been decomposed. Results for the determination of iron ranged from 31.6% to 33.7%. Three possible reasons for the incomplete attack were considered. First, removal of the sample from the body of the melt by the creeping flux; secondly, too large a sample weight; last, a portion of the sample could be inert to the chemical action of the flux. This would be in line with the results from the qualitative tests on bornite and chalcocite.

The first two possibilities were overcome by the use of a long-neck boiling flask, to deal with the effects of creeping and any mild spattering of the melt, and by taking a smaller sample weight. In view of the fact that sulphide ores of copper are normally dissolved in aqua regia or nitric acid[1,9], it was considered that the third possibility could be overcome by the use of oxidising additives in the flux.

About 0.2 g (accurately weighed) of the ore was placed in a long-necked pyrex boiling flask of 50-ml capacity. A mixture of 2 g of ammonium hydrogen sulphate, 1.5 g of ammonium nitrate and 1.5 g of ammonium chloride was added to the flask and mixed with the ore sample by agitation of the flask. The flask was then gently warmed for 10 min, about 6 cm above the tip of a Bunsen flame, before being heated, with occasional swirling, in the body of the flame for 5 min. In order to wash down any sample material deposited in the neck of the flask by spattering, the flask was then tilted and 2 g of ammonium hydrogen sulphate was placed in the neck and heated. The molten flux was allowed to run into the bulb and the contents were again fused for 5 min. The ammonium hydrogen sulphate addition and the fusion was repeated once more.

The cooled melt was dissolved in 10 ml of 2 *M* hydrochloric acid. If any solid residue of undecomposed material was observed at this stage, the supernatant liquid was poured off into a suitable container and the flask was carefully warmed over a small flame until almost dry. One third of a mixture of 0.5 g of ammonium nitrate, 0.5 g of ammonium chloride and 2.0 g of ammonium hydrogen sulphate was then added to the flask and the fusion repeated, with continuous swirling, until the charge set to a semi-solid mass. The neck of the flask was strongly heated to decompose any nitrate in the flux deposited there. The cooled melt was lixiviated with 10 ml of 2 *M* hydrochloric acid and the liquid drained off into the main sample solution. The drying of the flask and subsequent fusion procedure were then repeated twice more using the remaining portion of the flux mixture. Iron was separated by hydroxide precipitation and then determined titrimetrically as before.

During the initial 5 min of heating, the colour of the charge was lime-green. The charge tended to froth slightly and fumes of nitrogen dioxide were freely evolved. During the next 5 min of heating the colour of the melt turned to an orange-yellow. The charge continued to foam during this period. During the final 5-min period of fusion, the foaming stopped and the melt acquired a pale green colour.

The second fusion was also accompanied by the above colour changes; but they followed each other in quick succession. During the final fusion the charge did not show the green coloration observed before, and this was taken as an indication of the complete reaction of the copper ore.

The results obtained are shown in Table II; they are more precise and more accurate than those obtained by means of an ammonium hydrogen sulphate fusion, and indicate the success of the fusion procedure.

Copper concentrates—Determination of iron and copper

The suitability of the ammonium hydrogen sulphate–ammonium chloride–ammonium nitrate method for dissolution of copper sulphide ores was confirmed on a sample of copper concentrates. The experimental details were the same as those given for the copper ore. In addition to the iron determination, copper was determined titrimetrically by the short iodide method[10]. The filtrate and wash liquid, obtained from the iron(III) hydroxide separation, was used for this determination.

The same colour changes which were previously described were observed, and it was found necessary to repeat the fusion four times to obtain complete solution of the sample of concentrates. The results for the determination are shown in Table II, together with the results obtained using conventional nitric acid dissolution[1,9]. These results confirm the efficiency of the fusion procedure, which could be substituted for the conventional method of nitric acid attack in the decomposition of copper–iron sulphide ores. The fusion procedure is not, however, rapid by comparison with the conventional method, particularly if replicate analyses are required.

Lead concentrates—Determination of lead and zinc

Fusion of a sample of lead concentrates with ammonium hydrogen sulphate did not appear to attack the sample completely and this was confirmed by the results of the analysis for lead which gave low values, varying from 66.0 to 67.0, and one anomalous result of 69.2% Pb. Fusion with ammonium hydrogen sulphate containing ammonium nitrate as an additive was more satisfactory, but again the sample did not appear to be completely attacked and the results, although, in general, higher than previously, again indicated that this was so. As a further development of the fusion procedure, it was decided to attempt repetitive fusions with the oxidising flux mixture.

A mixture of 5 g of ammonium hydrogen sulphate and 2 g of ammonium nitrate was added to an accurately weighed sample (*ca.* 0.4 g) of lead concentrates in a fusion flask. The flask was clamped in a vertical position and gently heated with a Bunsen flame until the evolution of brown fumes of nitrogen dioxide had ceased (*ca.* 8 min); it was then heated more strongly for 8 min. The melt was then cooled and 4 g of a 3:1 mixture of ammonium hydrogen sulphate and ammonium nitrate was placed in the neck of the flask and gently warmed so that the molten flux ran into the bulb of the flask and cleared the neck of deposited material. The bulb was then strongly heated for 10 min. The cooled melt was lixiviated with 10 ml of 0.5 *M* sulphuric acid and transferred to a 400-ml beaker. The flask was washed several times with water and the wash liquid added to the beaker. The solution in the beaker was left overnight to allow for complete precipitation of the lead. The lead sulphate was filtered off and the filtrate and washings made up to 100 ml in a volumetric flask to provide a solution for the determination of zinc by atomic absorption spectrophotometry. The lead sulphate was dissolved in hot ammonium acetate and the lead determined gravimetrically as lead chromate[9].

During the initial fusion stage the colour of the melt turned from black through grey-white to yellow. The cooled melt was white. In contrast to the fusions with pure ammonium hydrogen sulphate no black film was seen in the flask. A few minute black specks could, however, be seen at the bottom of the flask.

The results for the determination of lead and zinc are shown in Table II. The results indicate that while the method of fusion enables a satisfactory result to be obtained, the sample may not always be completely decomposed in two fusions. The result of 67.2% Pb may be due to incomplete attack of the sample, although the result for the zinc determination on this sample was not correspondingly low. Once again, if a number of samples must be analysed, the fusion technique would not result in much saving of time over that needed for decomposition by acids.

Nimba iron ore and burnt pyrites—Determination of iron

Preliminary experiments showed that fusion involving addition of 10 g of ammonium hydrogen sulphate to about 0.1 g of Nimba ore and fusion for 15 min, followed by addition of two further 5-g portions of flux and fusion for 30 min in each case, led to the extraction of only about 25% of the iron in the sample. Fusion of an 11:1 mixture of flux:sample for 1 h gave about 34% extraction. Because of the conventional use of hydrochloric acid[8] for solution of iron oxide ores, it was decided to use an ammonium chloride additive in the flux.

About 0.14 g (accurately weighed) of the iron ore was mixed with 3 g of a mixture of 5 g each of ammonium hydrogen sulphate and ammonium chloride in a fusion flask. The remainder of the flux was stored in a desiccator until required. The flask and its contents were carefully heated over a Bunsen flame with continuous swirling to prevent the froth which formed from entering the neck of the flask. The neck of the flask was warmed from time to time to dislodge deposits.

Heating was continued until ammonium chloride was no longer evolved, as was evidenced by a sudden change in colour of the melt from deep orange-yellow to pale yellow-green. When the cold cake, which was white in colour, was treated with warm 1 *M* hydrochloric acid, the solution showed signs of the presence of undecomposed sample. The supernatant liquid was carefully poured into a 600-ml beaker and the flask was warmed over a small Bunsen flame until almost dry. A further 1-g portion of the flux was then added to the flask, and the fusion and hydrochloric acid extraction of the cold cake was repeated. These processes were repeated three more times before no visible signs of unattacked sample were seen. The whole procedure took about 35 min. Iron was determined titrimetrically, as before, in the combined 2 *M* hydrochloric acid solutions. The results (Table III) indicate complete attack of the sample.

TABLE III

OXIDE ORES

Sample	*Results*	*Mean*[a]
Nimba iron ore (66.1% Fe)	%Fe 66.1, 66.0, 66.2	66.1 ±0.06
Burnt pyrites (57.6% Fe)	%Fe by fusion 57.9, 57.8, 57.4	57.7 ±0.15
	%Fe by HCl attack 57.7, 57.4, 57.8	57.6 ±0.12
Manganese ores (49.0% Mn)	%Mn 48.9, 48.9, 48.9, 48.8, 48.8, 48.8	48.9 ±0.03

[a] All limits quoted are standard deviations of the mean result.

The same procedure was used to prepare a sample of burnt pyrites for analysis. The results are also shown in Table III.

The ammonium hydrogen sulphate–ammonium chloride fusion procedure was not found to be especially rapid when compared with conventional hydrochloric acid attack. Use of the procedure, however, eliminates the evaporations of mineral acid which are necessary to dissolve iron oxide ores for iron analysis.

Manganese ore—Determination of manganese

Initial experiments showed that ammonium hydrogen sulphate fusion resulted in only about 73% extraction. A single fusion with ammonium nitrate additive present gave only a slightly improved efficiency (78% extraction). In addition it was observed that larger flux: sample ratios than previously used would be necessary in order to prevent early solidification of the melt.

A flux consisting of 7.5 g of ammonium hydrogen sulphate and 2.5 g of ammonium nitrate was mixed with an accurately weighed sample of about 0.25 g of the manganese ore in a fusion flask. After about 10 min of gentle heating in a Bunsen flame, care being taken to avoid the froth which first formed creeping into the neck of the flask, the flask was more strongly heated for a further 20 min. During this time the neck of the flask was occasionally heated to dislodge material deposited there by spattering. The colour of the melt during the 10-min heating period was dark mauve-brown, but this changed to a pale yellow during the 20-min fusion period.

The cooled melt showed specks of undecomposed ore and the above fusion procedure was repeated twice more. The final cake was taken up in 50 ml of warm nitric acid (s.g. 1.135) and manganese was determined titrimetrically by the bismuthate method[9]. The results obtained are shown in Table III.

The accuracy and precision of the results indicate that the manganese ore can be satisfactorily dissolved in ammonium hydrogen sulphate containing ammonium nitrate additive. Repeated fusions, involving the use of a large amount of flux, were required to decompose the sample completely. The process, therefore, requires constant attention by the analyst over a long period of time, and for this reason, the conventional mineral acid attack is preferable.

CONCLUSIONS

Fusion with ammonium hydrogen sulphate has proved to be a successful method for dissolving iron pyrites and zincblende for the determination of iron and zinc respectively. Fusion with ammonium hydrogen sulphate containing ammonium nitrate and ammonium chloride has been found to be suitable for the dissolution of copper–iron sulphide ores for the determination of iron and copper. Fusion with ammonium hydrogen sulphate containing ammonium nitrate has proved suitable for the dissolution of lead concentrates and manganese ore for the analysis of lead and manganese respectively. Fusion with ammonium hydrogen sulphate containing ammonium chloride has been found suitable for the dissolution of iron ore and burnt pyrites for the determination of iron. These fusions have been carried out in pyrex glass apparatus.

Two or more fusions on residues remaining from an acid extraction of the cooled melts were required in the majority of cases and, while the fusion procedure is not, in itself, lengthy, the repetitive nature of the procedure requires considerable analyst-time when a number of samples must be analysed. In addition the fusion mixture must be carefully handled to avoid loss of sample by spattering or creeping. Thus while time may be gained over conventional methods involving evaporations of acids when few samples must be analysed, when a number of samples are to be analysed the fusion technique would require more operator time and overall time, yet give no increase in accuracy or precision of results.

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SUMMARY

The use of fusion with ammonium salts for the decomposition of some oxide and sulphide ores and minerals has been investigated. Iron pyrites, zincblende, copper ore, copper concentrates, lead concentrates, Nimba iron ore, burnt pyrites, and manganese ore can be completely decomposed by ammonium hydrogen sulphate or ammonium hydrogen sulphate containing ammonium nitrate or ammonium chloride additives. In some cases repetitive fusions are necessary. The cooled melt can be leached with a mineral acid to produce a solution shown to be suitable for the quantitative analysis of the major metallic component(s) of the sample.

RÉSUMÉ

On a examiné la décomposition de quelques minerais (oxydés et sulfurés) par fusion avec des sels d'ammonium. Les pyrites ferreuses, la blende, les minerais de cuivre, de fer, de manganèse, les concentrés de cuivre, de plomb, les pyrites grillées peuvent être totalement décomposés par l'hydrogénosulfate d'ammonium ou l'hydrogénosulfate d'ammonium contenant nitrate d'ammonium ou chlorure d'ammonium comme additifs. Dans certains cas, des fusions répétées sont nécessaires. Le résidu de fusion refroidi est traité avec un acide minéral pour obtenir une solution destinée à l'analyse quantitative des principaux composants métalliques de l'échantillon.

ZUSAMMENFASSUNG

Es wurde die Zersetzung einiger oxidischer und sulfidischer Erze und Mineralien durch Schmelzen mit Ammoniumsalzen untersucht. Pyrite, Zinkblende, Kupfererze, Kupferkonzentrate, Bleikonzentrate, Eisenerze, Pyritabbrände und Manganerze können durch Ammoniumhydrogensulfat oder Ammoniumhydrogensulfat, das Ammoniumnitrat oder Ammoniumchloridzusätze enthält, völlig zersetzt werden. In einigen Fällen ist wiederholtes Schmelzen erforderlich. Die abgekühlte Schmelze kann mit Mineralsäure ausgelaugt werden, um eine Lösung zu bekommen, die für die quantitative Analyse der metallischen Hauptbestandteile geeignet ist.

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RAPID COMPLEXIMETRIC DETERMINATION OF ALUMINIUM AND TITANIUM IN COMMON ORES AND SILICATES

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Although aluminium and titanium are common components of rocks, minerals, silicates and ceramic products, rapid methods for their analysis, particularly for aluminium, have presented difficulties. The standard gravimetric methods are lengthy and their accuracy is often questionable. For instance, if the separation of silica is not complete, the result for aluminium will be in error.

The colorimetric methods available for determining aluminium tend to be restricted to small amounts of this element whereas those available for titanium do not suffer from this drawback. Many compleximetric methods have been proposed but if aluminium and titanium are to be determined without separation, erroneous results are obtained owing to partial hydrolysis of titanium(IV). PŘIBIL[1] reviewed the methods available and critically discussed the stability of aluminium– and titanium–EDTA complexes and the problems of interfering elements. Later work by JUREZYK[2] and CULP[3] does not appear to have overcome the problems discussed by PŘIBIL[1].

The purpose of this paper is to present a method in which those problems are overcome; hydrolysis is prevented by using a very weak base to adjust the pH of the solution, no separations are required and aluminium and titanium can be separately determined.

EXPERIMENTAL

Reagents

Buffer solution, ca. pH 5. Mix 78 ml of glacial acetic acid with 200 ml of 50% (w/v) ammonium acetate solution and add 200 ml of aqueous 20% (w/v) hexamethylenetetramine solution.

Standard copper solutions. Prepare a 0.05 M solution by dissolving 12.485 g of copper(II) sulphate pentahydrate in water, adding 30 ml of buffer solution and diluting to 1 l. Prepare 0.01 M and 0.02 M solutions from this stock solution.

Standard combined 0.01 M copper and 0.01 M zinc solution (standard 0.02 M copper + zinc). Prepare from 0.05 M copper solution and zinc sulphate heptahydrate, adding 10 ml of buffer solution per litre before diluting to volume.

Xylenol orange solution. Aqueous 0.2% solution; prepare fresh weekly.

1-(2-Pyridylazo)-naphthol solution (PAN). Methanolic 0.1% solution.

Standard 0.02 M aluminium solution. Dissolve 0.539 g of pure aluminium in hydrochloric acid and dilute to 1 l.

TABLE I

RESULTS OF TITRATIONS OF ALUMINIUM AND TITANIUM IN SOLUTIONS SIMULATING SAMPLE SOLUTIONS

Simultaneous titration of Al + Ti
(Applicable for all contents of Al and Ti)

Simulating conditions of analysis of:	*Added solutions*			*Cu consumed for Al + Ti*		*Diff.*[e]
	Ti 0.01 M (ml)	*Al 0.02 M (ml)*	*Si, Fe Ca (ml)*	*0.01 M (ml)*	*0.02 M (ml)*	
Bauxites	1.00	—	—	1.00	—	0.00
	5.00	—	—	5.00	—	0.00
	1.80	—	12.5	1.79	—	+0.01
	1.80	5.0	12.5	—	5.91	−0.01
	1.80	10.0	12.5	—	10.93	−0.03
	1.80	15.0	12.5	—	15.88	+0.02
	1.80	20.0	12.5	—	20.94	−0.04
	1.80	25.0	12.5	—	25.92	−0.02
	1.80	25.0	12.5[a]	—	25.93	−0.03
	1.80	25.0	12.5[b]	—	25.87	+0.03
	1.80	25.0	12.5[d]	—	26.92	−0.02[f]
Residues from autoclaving bauxites	3.60	—	25.0	3.60	—	0.00
	3.60	2.0	25.0	7.58	—	+0.02
	3.60	5.0	25.0	13.63	—	−0.03
	3.60	7.0	25.0	17.64	—	−0.04
	3.60	10.0	25.0	23.58	—	+0.02
	3.60	15.0	25.0	—	16.78	−0.02
Conc. iron sands and ilmenites	5.00	—	25.0	5.0	—	0.00
	25.00	1.00	25.0	27.02	—	−0.02
	25.00	2.00	25.0	28.95	—	+0.05
	30.00	2.00	25.0	33.97	—	+0.03
	30.00	2.00	25.0[b]	33.95	—	+0.05
	30.00	2.00	25.0[c]	33.92	—	+0.08
	30.00	2.00	25.0[d]	35.97	—	+0.03[f]

Stepwise titration of Al and Ti
(Applicable for low Al, high Ti contents)

Simulating conditions of analysis of:	*Added solutions*			*0.01 M Cu consumed for:*				*Total 0.01 M Cu consumed for: Al + Ti*
	Ti 0.01 M (ml)[a]	*Al 0.02 M (ml)*[b]	*Si, Fe Ca (ml)*	*Ti*		*Al*		
				ml	*Diff.*	*ml*	*Diff.*	
Conc. iron sands	3.60	—	—	3.60	0.00	—	—	3.60
	3.60	2.0	25.0	3.58	+0.02	4.02	+0.02	7.60
	3.60	5.0	25.0	3.57	+0.03	9.97	−0.03	13.54
	3.60	7.0	25.0	3.62	−0.02	13.94	−0.06	17.56
	3.60	10.0	25.0	3.61	−0.01	20.02	+0.02	23.63
Ilmenites	5.00	—	25.0	5.00	0.00	—	—	5.00
	25.00	1.00	25.0	25.02	−0.02	1.98	+0.02	27.00
	25.00	2.00	25.0	24.98	+0.02	3.97	+0.03	28.95
	30.00	2.00	25.0	29.97	+0.03	3.98	+0.02	33.95
	30.00	2.00	25.0	30.02	−0.02	3.95	+0.05	33.97
	30.00	2.00	25.0[c]	30.10	−0.10	3.40	+0.60	33.50
	30.00	2.00	25.0[d]	30.15	−0.15[f]	5.87	+0.13[f]	36.02

The following were added to the compensating solutions:

[a] 0.5 mg Ni ($NiCl_2$), to simulate contamination from Ni crucible.

[b] 0.5 mg Ni + 0.3 mg Mn ($MnCl_2$).

[c] 5.0 mg Mn.

[d] 2.0 ml 0.01 *M* $ZrOCl_2 \cdot 8H_2O$ dissolved in H_2SO_4.

[e] Added Al + Ti solutions minus equiv. amount of Cu solution consumed.

[f] Added Al + Ti + Zr solutions minus equiv. amount of Cu solution consumed.

Standard 0.01 M titanium solution. Fuse 0.2005 g of titanium dioxide (National Bureau of Standards sample 154a) with 10 g of potassium pyrosulphate, dissolve in 5%(w/v) sulphuric acid and dilute to 250 ml with the same acid.

Iron, silicon and calcium compensating solution. Fuse together 0.3 g of iron(III) oxide, 0.025 g of silicon oxide and 0.035 g of calcium carbonate with sodium hydroxide, and dissolve, as described in the method.

Decomposition of samples

By treatment with any convenient acid (*e.g.* hydrochloric acid, applicable to cements).

By fusion with sodium hydroxide (applicable to most bauxites and residues from the autoclaving of bauxites). Transfer 0.5 g of sample (200 mesh) to a nickel crucible with 10 g of sodium hydroxide previously melted and cooled. Heat the crucible progressively to obtain complete fusion. Pour the melt onto a large nickel crucible lid. Wash the crucible, lid and tong tips with 30 ml of 1:1 hydrochloric acid and hot distilled water into a 600-ml glass beaker which already contains a further 30 ml of 1:1 hydrochloric acid. Transfer the cold melt into the beaker. Boil to dissolve the melt and to expel any chlorine. Transfer this solution to a 250-ml volumetric flask, cool and make up to the mark. Retain as sample stock solution.

Other types of fusion. Sodium peroxide (at 500°) or a fusion mixture of sodium and potassium carbonates, potassium nitrate and borax, may be used and the fusion carried out in a platinum crucible.

Titration procedures

Simultaneous titration of aluminium and titanium (recommended for samples with less than about 6% titanium content). Transfer a 25-ml aliquot of the stock sample solution to a 600-ml tall beaker and add 20 ml of 0.05 *M* EDTA; add aqueous 20% (w/v) hexamethylenetetramine solution dropwise until the pH is about 5 (pH test paper), add 20 ml of buffer solution, boil for 1–2 min, cool and dilute to *ca.* 250 ml. Add 5 drops of xylenol orange solution and, continuously stirring, titrate the excess of EDTA with 0.02 *M* copper + zinc solution until the colour becomes brownish-green. Add 2–3 drops of PAN and xylenol orange indicators, and titrate dropwise until the colour changes to a clear violet.

Add 25 ml of aqueous saturated, filtered sodium fluoride solution, boil, add 3 drops of xylenol orange solution and titrate again with 0.02 *M* copper solution. Another aliquot of the sample solution is taken and titanium is determined by standard colorimetric methods. The amount of aluminium is found by difference.

Stepwise titration of aluminium and titanium (recommended for samples with more than about 6% titanium content). For the determination of titanium, take a 25-ml aliquot of stock sample solution and follow the method described for the simultaneous titration to the end of the titration of excess of EDTA. Add 10 ml of 20% sodium dihydrogen phosphate solution, boil for 2 min and cool. Add 2–3 drops of xylenol orange solution and titrate with 0.01 *M* copper solution, stirring continuously, until a brownish colour is obtained. Add a further 1–2 drops of xylenol orange and titrate dropwise until the colour changes sharply to violet. This titration corresponds to the titanium content in the aliquot.

For the determination of aluminium, add (to the same solution) 25 ml of the saturated solution of sodium fluoride and boil. Add 1–2 drops of xylenol orange solution and titrate the hot solution with 0.01 *M* copper solution. The volume of titrant consumed corresponds to the aluminium.

RESULTS AND DISCUSSION

The precision and accuracy of the method for the simultaneous and stepwise titrations were confirmed by titrating aliquots of standard aluminium and titanium solutions as described above. The results of these analyses are shown in Table I. The variations (standard deviations less than 0.03%) were similar in both the simultaneous and stepwise titrations, and the total volume of standard copper solution used in the

TABLE II

RESULTS OF DETERMINATIONS OF ALUMINIUM AND TITANIUM IN ORES BY CLASSICAL AND PROPOSED COMPLEXIMETRIC METHODS

(Results are expressed as % Al_2O_3 or TiO_2)

A. Simultaneous titration[a]

Sample	*Methods*		*Diff.*
	Classical	*Complex.*	
Bauxite No. 138	51.79	51.67	−0.12
Bauxite No. 235	50.45	50.36	−0.09
Bauxite No. 358	51.91	51.80	−0.11
Bauxite No. 882	50.17	50.09	−0.08
Bauxite No. 993	51.90	51.82	−0.08
Bauxite No. 225	49.59	49.51	−0.08
Bauxite No. 265	49.54	49.48	−0.06
Bauxite No. 325	50.09	50.19	+0.10
Bauxite NBS 69	55.0	54.89	−0.11
Burnt refr. NBS 76	37.67	37.53	−0.14
Burnt refr. NBS 78	69.87	69.97	+0.10
Cement NBS 177	5.27	5.16	−0.11
1011	5.38	5.30	−0.08
1013	3.30	3.30	0.00
1014	6.38	6.36	−0.02
1015	5.04	4.97	−0.07
1016	4.97	4.92	−0.05

B. Stepwise titration

Sample	*TiO_2*			*Al_2O_3*		
	Classical	*Complex.*	*Diff.*	*Classical*	*Complex.*	*Diff.*
Iron sand conc. Waikato N.Z.	8.0	7.9	−0.1	4.0	3.8	−0.2
Conc. ilmenite North Island N.Z.	41.30	41.15	−0.15	0.7	0.6	−0.1
Conc. ilmenite South Island N.Z.	46.5	46.4	−0.10	2.8	2.7	−0.1

[a] Alumina found by difference.

stepwise titration of given amounts of titanium and aluminium were similar to those obtained for the simultaneous titration. When the content of manganese (expressed as Mn_2O_3) in the aliquot taken was greater than 5 mg, interference occurred and a lower figure was obtained for aluminium in the stepwise titration. Moreover, zirconium will be determined as aluminium in the proposed method; if zirconium is detected it can be easily determined separately[1].

The results of the determination of aluminium and titanium in a series of samples are shown in Table II. These results (averages of 5 or more determinations) were in good agreement with the values for the N.B.S. samples. Thorium, lanthanum, cerium, tin, comparatively large amounts of manganese (>5 mg in aliquot), phosphate and fluoride ions interfered, but these elements are rarely found in the materials under consideration.

The success of the present method depends on the fact that titanium and zirconium are not hydrolysed when the pH is adjusted. The results obtained titrimetrically (Table I) show that these elements can be kept in solution at pH 5; these results were confirmed by polarographic measurements. However, hydrolysis always occurs unless the pH is adjusted by slowly adding (dropwise) a weak base such as hexamethylenetetramine or ammonia. The use of a strong base, no matter how carefully added to the solution, causes precipitation of titanium, even below pH 2. Even hexamethylenetetramine, when added as a solid, was found to cause slight precipitation. From the above evidence, it can only be postulated that hydrolysis and the resulting precipitation caused by the use of strong bases are due to transient local hydroxyl ion concentration; once hydrolysis occurs, irreversible precipitation follows immediately. The results show that the careful addition of a weak base which is only slightly dissociated effectively avoids the occurrence of this type of reaction. In practice, it was found that hexamethylenetetramine was preferable to ammonia as it is a weaker base and also gives a sharper end-point with xylenol orange.

The use of fluoride ion for masking titanium does not appear to have been used previously in the titration of titanium presumably because of the problem of titanium

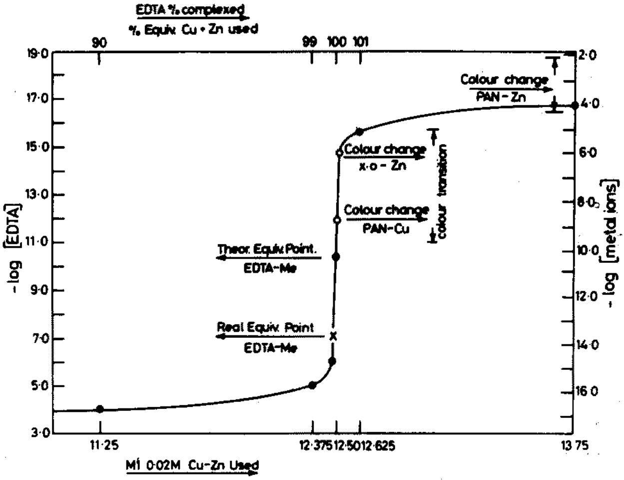

Fig. 1. Back-titration curve of EDTA with 0.02 *M* copper + zinc solution at pH 5 in the presence of xylenol orange and PAN as indicators.

hydrolysis. In the stepwise titration, sodium dihydrogen phosphate is used to release EDTA and determine selectively large amounts of titanium in the presence of aluminium. The advantage of using this reagent is that it does not precipitate elements other than thorium, cerium, and lanthanum, which will also form complexes with EDTA, nor does it change the pH of the solution. Also, the white precipitate of titanium phosphate formed does not hide the colour transition at the end-point. However, when the titanium content is below about 6%, and precipitation is slow, it is recommended that the separate determination of titanium be used.

Titration of the excess of EDTA with copper and zinc ions at pH 5 was investigated and it was found that at the visual end-point, more than 99.95% of both the copper and zinc ions were complexed. The results are shown graphically in Fig. 1. However, because the determination of aluminium and titanium, combined or alone, is based on two titrations, the first being unrecorded, the over-titration which occurs in the first titration is almost cancelled out in the second, so that overall the titration is close to the theoretical value.

SUMMARY

A rapid compleximetric method is presented for the determination of aluminium and titanium in ores and silicates such as bauxite, clay, ilmenite, cements and ceramic products. Excess of EDTA is added to an aliquot of the acid sample solution, the pH is adjusted with hexamine and the excess of EDTA is titrated with a combined solution of copper and zinc in the presence of xylenol orange and PAN as indicators. For the simultaneous titration, fluoride is added to release the EDTA combined with both aluminium and titanium. For the stepwise titration, phosphate is added to release the EDTA combined with titanium, and then fluoride is added to release the EDTA combined with aluminium. The method avoids the problem of titanium hydrolysis encountered by previous workers.

RÉSUMÉ

On propose une méthode complexométrique rapide pour le dosage de l'aluminium et du titane dans les minerais et silicates, tels que bauxite, ilménite, ciments et céramiques. L'excès d'EDTA ajouté à la solution à analyser est titré avec une solution cuivre–zinc, en présence de xylénol orange et de PAN comme indicateurs. Le dosage simultané aluminium–titane est possible par addition de phosphate pour libérer EDTA combiné au titane, puis par addition de fluorure pour libérer l'EDTA combiné à l'aluminium. Ce procédé permet d'éviter le problème de l'hydrolyse du titane.

ZUSAMMENFASSUNG

Eine schnelle komplexometrische Methode zur Bestimmung von Aluminium und Titan in gewöhnlichen Erzen und Silikaten wird vorgeschlagen. Zu einem aliquoten Teil der sauren Probelösung wird ein Überschuss von ÄDTE zugegeben, der pH-Wert wird mit Hexamin eingestellt und der Überschuss an ÄDTE mit einer kombinierten Lösung aus Kupfer und Zink in Gegenwart von Xylenolorange und PAN als

Indikatoren titriert. Bei der gleichzeitigen Titration wird Fluorid zugegeben, um das ÄDTE frei zu machen, welches sowohl mit dem Aluminium als auch mit dem Titan gebunden ist. Zur schrittweisen Titration wird Phosphat gegeben, um das ÄDTE in Freiheit zu setzen, das mit Titan verbunden ist. Dann wird Fluorid zur Freimachung des an das Aluminium gebundenen ÄDTE zugegeben. Die Methode vermeidet eine mögliche Titanhydrolyse.

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SHORT COMMUNICATIONS

The determination of paracetamol and aspirin in mixtures by non-aqueous potentiometric titrimetry or by ultraviolet spectrophotometry

Paracetamol (*p*-acetamidophenol) has been separated from aspirin by paper chromatography[1], ion exchange[2] and column chromatography[3]. The purpose of the present work was to develop a simple routine method for the determination of paracetamol and aspirin in the same tablet. A non-aqueous titrimetric method and two ultraviolet spectrophotometric methods are suggested. Which of these methods is the most satisfactory depends on the relative amounts of paracetamol and aspirin, and on the excipients present in the tablet.

Non-aqueous titrimetric method

The method of ALLEN AND GEDDES[4] for the non-aqueous titration of phenolic compounds was applied.

Method. Potentiometric measurements were made with a Pye 290 pH meter. A shielded glass electrode, previously soaked in formdimethylamide, was used as indicator electrode. Slightly better end-points were obtained with a saturated ethanolic calomel reference electrode than with the corresponding methanolic electrode; a calomel-type electrode filled with formdimethylamide saturated with tetraethylammonium bromide gave similar potential jumps to the methanolic calomel electrode but responded more rapidly to changes in potential and was therefore preferred.

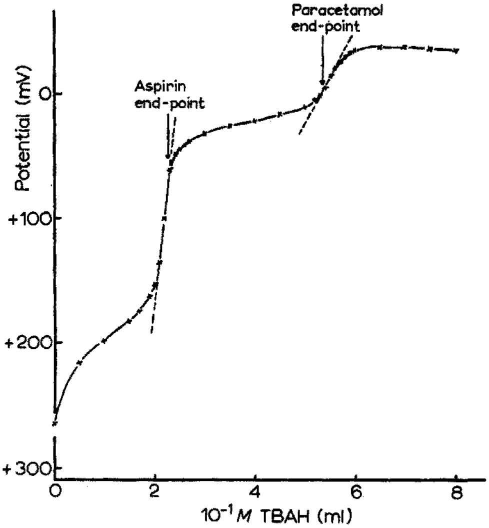

Fig. 1. Non-aqueous titration curve for a mixture of paracetamol and aspirin.

Tetra-*n*-butylammonium hydroxide solution (10^{-1} *M*) was protected from atmospheric carbon dioxide by soda-lime guard tubes, and was standardised by titrating weighed amounts of benzoic acid dissolved in 50 ml of formdimethylamide. Nitrogen gas was bubbled through the solutions during titrations, and blank titrations were done.

Results. An example of a titration curve for a mixture of paracetamol and aspirin is given in Fig. 1. The aspirin end-point is well defined, but the change of potential at the paracetamol end-point is small (usually 20–30 mV). In the absence of aspirin, the potential jump at the paracetamol end-point increased slightly. Apparently, the acetylsalicylate ion present during the titration of the paracetamol in the mixture caused the decrease in the potential change; the addition of tetraethylammonium bromide also caused a decrease. Simultaneous titration of known amounts of paracetamol and aspirin indicated that the aspirin end-point should be taken near the top of the potential jump, whereas the paracetamol end-point should be taken near the bottom of the corresponding jump, as indicated in Fig. 1. When either paracetamol or aspirin was present alone, the end-point was best taken in the conventional way.

Results obtained with pure samples of paracetamol and aspirin, and with a sample of tabletting material, are given in Tables I and II.

TABLE I

NON-AQUEOUS TITRATION OF WEIGHED AMOUNTS OF PURE PARACETAMOL AND ASPIRIN IN THE SAME SOLUTION

Weight taken (mg)		*Weight found (mg)*	
Paracetamol	*Aspirin*	*Paracetamol*	*Aspirin*
72.4	74.7	74.5	74.1
51.4	56.6	53.6	54.1
53.2	40.4	53.3	39.7
49.0	39.3	49.2	39.3
49.9	43.1	51.4	41.4

TABLE II

ANALYSIS OF TABLET MIX CONTAINING 43.1% (w/w) PARACETAMOL AND 34.5% (w/w) ASPIRIN, BY DIFFERENT METHODS

Method	*No. of detns.*	*Paracetamol found (mean %)*	*Standard deviation*	*Aspirin found (mean %)*	*Standard deviation*
Titration	13	45.9	0.9	34.2	1.1
Direct U.V.	5	43.4	1.4	35.6	1.1
Extraction	6	44.3	0.2	33.9	0.3

Direct spectrophotometric method

Paracetamol and aspirin both dissolve in 10^{-1} *M* sodium hydroxide solution. Paracetamol ionises to give the *p*-acetamidophenolate ion, but aspirin is hydrolysed quantitatively to the salicylate ion. The $E_{1\,\mathrm{cm}}^{1\%}$ values for paracetamol and aspirin at the peak absorbances of the ions formed are given below.

	Paracetamol	*Aspirin*
$E_{1\,\mathrm{cm}}^{1\%}$ (258 nm)	721	44.6
$E_{1\,\mathrm{cm}}^{1\%}$ (297 nm)	244	196

Unfortunately, the *p*-acetamidophenolate ion absorbs more strongly than the salicylate ion even at the wavelength of maximum absorbance by the latter; the absorbance peaks are therefore not resolved when the two ions are present in about equal amounts. Nevertheless, application of the simultaneous equations:

$$E_{258} = 44.6\,C_a + 721\,C_p$$
$$E_{297} = 196\,C_a + 244\,C_p,$$

where C_a and C_p are the concentrations (% w/v) of aspirin and paracetamol respectively, has given good results (Table II).

Spectrophotometric method involving extraction with n-*butanol*

Under certain circumstances, *e.g.*, when a third constituent of the tablet absorbs in the ultraviolet region, a preliminary separation of the paracetamol and aspirin may be needed. Aspirin dissolves in sodium hydrogen carbonate solution to give acetylsalicylate but the phenolic proton of paracetamol does not ionise under these conditions. However, the unionised paracetamol cannot be quantitatively extracted into chloroform, because it is only slightly more soluble in chloroform (1 part in 50) than in water (1 part in 70)[5]. Paracetamol is reported to be insoluble in ether[5], but appreciable quantities of paracetamol were extracted when attempts were made to extract aspirin from a mixture of aspirin and paracetamol in a Soxhlet extractor.

On the other hand, both paracetamol and aspirin are appreciably soluble in ethanol (1 part in 10, and 1 part in 7, respectively)[5], and in several higher alcohols, including *n*-butanol. The $E_{1\,\mathrm{cm}}^{1\%}$ values obtained for paracetamol and aspirin in *n*-butanol at the peak absorbances of both compounds are given below.

	Paracetamol	*Aspirin*
$E_{1\,\mathrm{cm}}^{1\%}$ (250 nm)	910	33
$E_{1\,\mathrm{cm}}^{1\%}$ (277 nm)	200	63

The following spectrophotometric method, in which the paracetamol and aspirin are separated by extraction with *n*-butanol, was developed for the analysis of tablet samples. Absorbance measurements were made in 1-mm cells because *n*-butanol usually contains traces of ketones which absorb at 280 nm, and because less dilution of the extract was then required.

Procedure. Weigh accurately *ca.* 0.18 g of the finely ground sample into a 150-ml separating funnel. Add analytical reagent-grade *n*-butanol (25 ml) and 5% sodium bicarbonate solution (25 ml), and shake the mixture until the paracetamol has dissolved in the *n*-butanol and the aspirin has dissolved in the sodium bicarbonate solution. Separate the layers and wash the *n*-butanol layer with two 25-ml portions of water, adding the washings to the original aqueous layer. Back-wash the combined aqueous layers with three 15-ml portions of *n*-butanol, adding these washings to the original *n*-butanol layer.

For the determination of *paracetamol*, dilute the combined *n*-butanol layers to 100 ml with *n*-butanol in a volumetric flask, and mix the solution thoroughly. Add 10 ml of this solution from a safety pipette into a second 100-ml volumetric flask and dilute the solution to the mark with *n*-butanol. Mix the solution thoroughly and measure its absorbance at 250 nm in 1-mm silica cells against *n*-butanol.

For the determination of *aspirin*, acidify the combined aqueous layers with dilute sulphuric acid (2.5 *M*) and extract the aspirin with four 15-ml portions of *n*-butanol. Dilute these combined *n*-butanol layers to 100 ml with *n*-butanol in a volumetric flask. Mix the solution thoroughly and measure its absorbance at 277 nm in 1-mm silica cells against *n*-butanol.

Calculate the amount of paracetamol and aspirin present from standard curves obtained from measurements on standard solutions of paracetamol and aspirin in *n*-butanol in the 1-mm silica cells which were used for the determination. Note that *n*-butanol solutions of aspirin show signs of hydrolysis after about 24 h.

Results obtained using the tablet sample are given in Table II.

Discussion

The non-aqueous titration method is equally sensitive to both aspirin and paracetamol, as both compounds are monobasic acids. Titrimetric methods are intrinsically more precise than spectrophotometric methods, and, although the aspirin can be determined with much greater precision than paracetamol, the titrimetric method may be considered to be suitable for routine purposes.

The spectrophotometric method is much more sensitive to paracetamol than to aspirin, and this allows the paracetamol to be determined with only a relatively minor correction for the aspirin present. The direct spectrophotometric method, in which the sample is dissolved in 0.1 *M* sodium hydroxide, is more convenient than the method involving *n*-butanol separation, which is rather lengthy. The direct method is recommended for routine use; the *n*-butanol separation may be essential in the presence of a third constituent absorbing in the ultraviolet region.

For greatest precision the combined use of the non-aqueous titrimetric method and the direct spectrophotometric method is suggested. The paracetamol content is determined spectrophotometrically, the absorbance at 250 nm being corrected for the amount of aspirin found to be present. The aspirin content is determined titrimetrically.

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The liquid-state electrode
(A preliminary communication)

Ion-sensitive electrodes enjoy renewed interest and their number is growing rapidly. They vary in shape, material and performance, but for the sake of convenience they are often classified as solid-state electrodes, Pungor-type electrodes and liquid–liquid membrane electrodes[1]. The aim of this communication is not, however, to introduce a new term in the already complicated nomenclature, but to describe a new type of a general electrode, a liquid-state electrode[2], which is likely to replace the liquid–liquid membrane electrode.

Many very useful electrodes are of the solid-state type; however, we believe that the best way to obtain reproducible potentials is to measure them at the liquid–liquid interface rather than on solid surfaces, which are difficult to make uniform and which suffer from leaching and asymmetrical swelling of the boundary layer. This idea is, of course, not new in electrochemistry, for the success of polarography is largely due to the renewing surface of Heyrovský's dropping mercury electrode. In potentiometry the liquid–liquid membrane electrodes are widely used. The potential formed at the interface between the measured aqueous solution and the liquid ion-exchanger[9]

$$E = E_0 + \frac{RT}{nF} \ln\left(a_{M^{n+}} + K_1 \left[a_{M^{z+}}\right]^{n/z}\right) \qquad (1)$$

is said to be a membrane potential formed analogously to that of the glass electrode[1,3]. Moreover, the selectivity of liquid membrane electrodes has been evaluated[1,3] in the same way as that of the glass electrode, as suggested by EISENMAN[4].

Recent work in this laboratory has resulted in some observations which briefly may be summarized as follows. An electrode can be constructed without any membrane at all, and this electrode has no physical resemblance either to the glass, or to the liquid–liquid membrane electrode (Fig. 1), but it exhibits the same potential dependence as that described by eqn. (1). The electrode consists only of a thin layer of organic liquid immiscible with water and can therefore be referred to as the liquid-state electrode[2].

The organic phase is either a liquid ion-exchanger saturated with the ionic species to be detected or an organic solvent containing an extractable ion-associate (as described by COETZEE AND FREISER[5]) or a metal chelate extracted in a water-immiscible solvent. Metal chelates have proved to be extremely useful for the present pur-

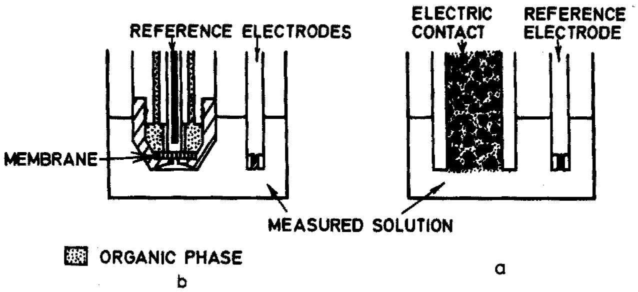

Fig. 1. The liquid-state electrode (a) and the liquid–liquid membrane electrode (b).

TABLE I

EXAMPLES OF LIQUID-STATE ELECTRODES

Ion	*Organic reagent*	*pH-range*[a]	*mV/pM*[b]
K^+	K-dipicrylaminate	5–12	50
Cs^+	Cs-tetraphenylborate	9.5–12	59
Zn^{2+}	Zn-dithizonate	7.5–12	~23
Cu^{2+}	Cu-diethyldithiocarbamate	3–12	29
Cu^{2+}	Cu-dithizonate primary	3– 4.5	29
Cu^{2+}	Cu-dithizonate secondary	4.5–12	59
Ag^+	Ag-dithizonate	2–12	~59
Pb^{2+}	Pb-dithizonate	7–12	~29
Cd^{2+}	Cd-dithizonate	6.5–12	~29
H^+	Quinhydrone	(1)– 5.5	59
H^+	Quinhydrone	5.5– 8.5	29

[a] Approximate value depending on organic solvent. Measured at $pM = 3$.
[b] For pM-change from 3–4.

TABLE II

THE EXTRACTION CONSTANTS OF DI-2-ETHYLHEXYLPHOSPHATES OF SOME MONO- AND DIVALENT METALS[a]

Metal ion	*log K*	*Metal ion*	*log K*
Be^{2+}	1.28	Cd^{2+}	−3.7
Zn^{2+}	−1.3[b]	Na^+	−3.8[b]
Ag^+	−1.8[b]	K^+	−3.9[b]
Pb^{2+}	−2.5[b]	Rb^+	−4.0[b]
Tl^+	−2.6[b]	Mg^{2+}	−4.4[b]
Mn^{2+}	−3.3[b]	Cs^+	−4.4[b]
Ca^{2+}	−3.5	Ba^{2+}	−4.5
Cu^{2+}	−3.5[b]	Co^{2+}	−4.0[b]

[a] Data obtained from the Russian enlarged edition (1966) of ref. 6.
[b] $K = \frac{[M(HA)_n]_{org}[H^{n+}]}{[M^{n+}][H_2A_2]^n_{org}}$.

pose as it was found easy to choose the metal chelate according to the required electrode function (Table I).

The selectivity of the liquid-state electrode can be closely related to the extraction data. In contradistinction to the glass electrode and the solid-state electrodes, there is a rapid change in the composition of the electrode liquid surface, if it comes in contact with a solution containing an ion with a higher extraction constant or a much more favourable distribution ratio. Thus, for example, from Table II[6] it can be seen that the surface of the electrode originally consisting of calcium di-2-ethylhexylphosphate would immediately change to beryllium di-2-ethylhexylphosphate when the electrode is dipped into a solution containing beryllium(II). As a result of this, the electrode will be permanently "poisoned" by beryllium, becoming sensitive to beryllium rather than to calcium. This is indeed the case with the Orion calcium-sensitive liquid–liquid membrane electrode. Clearly this electrode is beryllium-*selective*, but calcium-*sensitive*. In connection with this, it should be pointed out that the otherwise correct procedure of evaluating the selectivity of glass electrodes, is not very suitable for evaluating the liquid electrodes.

The present measurements indicate that in the case of the liquid-state electrode, containing an extractable metal chelate, the symbols of eqn. (1) have the following meaning:

E_0 involves the extraction constant of the metal chelate, its concentration and the properties of conducting material which serves as a support for the organic phase.

K_i is the ratio of the extraction constant of the foreign metal ion M^{z+} to the extraction constant of measured ion M^{n+}.

R, T, F, n and z are defined in the usual manner[4,9].

The above observations have enabled us to make a number of electrodes, the properties of which are stated in Table I. All of these exhibited a faster response than the glass electrode, and a very small drift of E_0; their resistance was 10^4–10^5 ohms with conducting organic solvents and about 10^7 ohms with carbon tetrachloride. If any decrease in the slope of the electrode function occurred during prolonged use, the function could be restored or improved by dipping the electrode briefly into the solution of organic solvent. The absence of an inner conventional reference electrode and of the plastic membrane makes the construction simple, and the electrode robust and easy to use. Only a straightforward electrical contact with the carbon support of the organic phase is required (Fig. 1).

However, the main advantage of the electrode lies in the fact that the liquid-phase electrode can be used for measurement of activity of any ionic species in solution, provided that a suitable extraction system exists and that the distribution data are favourable. The best source is the book of STARÝ[6] and reviews of MORRISON AND FREISER[7]. In the first approximation the theory of substoichiometric solvent extraction[8] can be used as a guide for the choice of the electrode filling.

The practical use of liquid-state electrodes in analytical and complex chemistry can be envisaged to be the same as that of the other ion-sensitive electrodes. Further, the electrode should become useful for distribution studies, for the electrode can be filled with the extractant whose properties are being investigated.

The theory and use of liquid-state electrodes in direct potentiometry and titrimetric analysis are being investigated at this laboratory and will be reported in the near future.

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The amperometric and indirect polarographic determination of palladium(II) with selenophene-2-aldoxime

Various workers have reported methods for the amperometric determination of palladium(II) with either a dropping mercury electrode[1,2] or solid electrodes[3-7]. Many organic reagents, mainly oximes, have been used to give palladium-reagent complexes. Thiophene-2-aldoxime[8] and selenophene-2-aldoxime[9] have been reported as gravimetric reagents for palladium(II), and the latter oxime has been reported to be much more selective for palladium(II) than are most other oximes. The conditions for achieving this selectivity have been discussed elsewhere[9].

This paper reports the use of this reagent for the direct amperometric and indirect polarographic determination of palladium(II).

Apparatus

The polarograph used was a Davis Differential Cathode Ray Polarograph, with a single dropping mercury electrode and a mercury pool as the anode. The cell (supplied with the instrument) was thermostatted at 25±0.5° for all measurements.

Solutions

Oxime. Aqueous 10^{-3} M solutions of selenophene-2-aldoxime, synthesised as described previously[9], were prepared by direct weighing of the purified reagent. Further solutions were made by suitable dilution.

Buffer solutions. A buffer in the pH range 1.5-3.5 was prepared from u.c. grade sodium acetate and acetic acid. (Whilst the values quoted were obtained with a buffer of pH 2.3, identical results were subsequently obtained over the pH range quoted.)

Palladium(II) solutions. A *ca.* 10^{-2} M solution of palladium(II) chloride was assayed gravimetrically after precipitation with dimethylglyoxime and 4-methylcyclohexane-1,2-dionedioxime. Other solutions were prepared by suitable dilution.

Other solutions. An aqueous 0.01 M solution of purified potassium chloride was used as the supporting electrolyte. No maximum suppressor was used.

Cell solution. The solutions used contained 5 ml of 10^{-3} M selenophene-2-aldoxime solution, 10 ml of 10^{-2} M potassium chloride solution, and 5 ml of buffer; this mixture was diluted to 25 ml with water.

All solutions were de-oxygenated by bubbling a fine stream of oxygen-free nitrogen through them for 2-3 min before use. During the titration, nitrogen was passed through the cell solution for 0.5-1 min between additions of titrant.

The voltage sweep used in all experiments was from −0.90 V to −1.40 V, measured against the mercury pool.

Direct titration (for palladium concentrations greater than $5 \cdot 10^{-4}$ M)

An aliquot (5 ml) of the above cell solution, containing an accurately known amount of oxime, was titrated with the unknown palladium(II) solution from a suitable micro-burette, in 0.05-ml amounts until near the end-point (as indicated by the i_p values approaching constancy), and then in 0.02-ml portions. The i_p values (corrected for volume change) were plotted against the volume of titrant added.

Typical results for the titration of 5 ml of cell solution containing $2 \cdot 10^{-3}$ *M* or $2 \cdot 10^{-4}$ *M* oxime, with palladium(II) solution are given in Table I.

Indirect method (for palladium concentrations greater than 1 p.p.m. or ca. 10^{-5} M)

A calibration curve of i_p *versus* concentration of selenophene-2-aldoxime was constructed by polarographing solutions containing a suitably diluted oxime component of the above cell solution. The calibration graph was linear over the range $4 \cdot 10^{-6}$ *M*–$1 \cdot 10^{-2}$ *M*; the slope of the line depended entirely on instrumental parameters.

TABLE I

DETERMINATION OF PALLADIUM BY AMPEROMETRIC TITRATION AGAINST SELENOPHENE-2-ALDOXIME

Oxime used (M)	*Pd(II) required (ml)*	*Pd(II) found (mg)*	*Error*[a] *(%)*
$2 \cdot 10^{-3}$	0.51, 0.52, 0.52	0.538	−0.37
$2 \cdot 10^{-4}$	0.50, 0.50, 0.49	0.0524	−2.8

[a] % Error calculated from gravimetric standardisation of the palladium(II) solution.

TABLE II

INDIRECT POLAROGRAPHIC DETERMINATION OF PALLADIUM(II)

Wt. of Pd(II) used (µg)	*Wt. of Pd(II) found (µg)*[a]	*Error (%)*
19.12	18.20	−4.8
10.64	10.14	−5.0
5.32	4.84	−9.2
1.986	1.820	−8.3

[a] The arithmetic mean of not less than 3 results.

For a determination, a known volume of palladium(II) solution was added to an aliquot of selenophene-2-aldoxime in a cell solution. After de-oxygenation for 2–3 min, the i_p was measured and from the concentration of selenophene-2-aldoxime remaining uncomplexed, the amount of palladium present, and fully complexed, was thus determined. Various concentrations of palladium(II) from 10^{-3} *M* to 10^{-6} *M* were used.

The results are shown in Table II. Below 1 *µg* of palladium(II) per ml (*i.e.* below 1 p.p.m.), the scatter of results was above 10% and thus the method was not below 2 p.p.m.

Interferences

Only the ions reported by BARK AND GRIFFIN[9] showed any interference; removal of these ions by the methods suggested by these workers is necessary.

Discussion

The methods proposed have the following advantages. Over the pH range chosen, 1.5–3.5, the reagent is highly selective, reacting with fewer metals than furan-2-aldoxime[6] or thiophene-2-aldoxime[8]. Moreover, the water solubility and stability to hydrolysis of selenophene-2-aldoxime makes it an ideal reagent for routine use.

For concentrations of palladium lower than 500 p.p.m., the indirect method is suggested, its main advantage being in its selectivity and the overall time taken for a determination. The usual methods for the determination of palladium(II) in this range require a longer time; colorimetric methods usually involve chelate formation and subsequent solvent extraction before the final measurement, and the precision of all these methods is of the same order.

For concentrations greater than $5 \cdot 10^{-4}$ *M*, the direct amperometric determination is recommended since the inherent error is relatively low. A comparison of the results obtained with furan-2-aldoxime[6] and selenophene-2-aldoxime indicates that the precision and accuracy with the latter reagent are superior.

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The colour reaction of 2,3-dihydroxypyridine with iron(III) in 1 *N* mineral acids

Katyal *et al.*[1] have reported that 2,3-dihydroxypyridine (DHP) forms a series of coloured solutions when added to iron(III) at various pH levels, and recommend the determination of iron by forming a purple colour at pH 4.5 to 7.5

Independent work in this laboratory suggested that DHP can be used for colorimetric determination of iron(III) in 1 *M* hydrochloric acid medium. This is of practical interest, as the hydrolysis of iron(III) makes it convenient to separate and maintain iron(III) in strongly acid solutions[2]. Pyrocatechol[3], "tiron"[4], protocatechuic acid[5] and other reagents having vicinal dihydroxy groups which form colours with iron(III) have been used for analysis, but tend to require higher pH values at which hydrolysis or precipitation of uncomplexed iron will occur, and at which oxidation of the functional groups, or other degradation of the reagent may contribute to instability of the measured absorbance.

Studies on the colour formation between iron(III) and DHP in solutions 1 *M* in hydrogen ion prepared from hydrochloric, perchloric, and sulfuric acids are reported in this communication. In 1 *M* nitric acid, DHP rapidly gives a gold-coloured solution which does not react with iron(III). Preliminary experiments with 0.33 *M* phosphoric acid showed formation of a purple colour unlike the blue formed in the other acids.

Reagents

The 2,3-dihydroxypyridine available (Aldrich Chemical Co.) was found to be of insufficient purity; solutions prepared from this light-brown powder darkened in a few hours, and dissolving the solid in a minimum of hot water left a black insoluble material of appreciable volume.

The reagent as received was placed in an M-porosity fritted glass thimble and extracted with boiling water in a vapour-jacketed Soxhlet extractor, leaving a black residue. As the extract cooled, brown-tinted needles crystallized out. These were filtered off on a glass frit, briefly oven-dried, and stored in a vacuum desiccator over silica gel. Vacuum sublimation at 180–220° then gave white crystals, leaving traces of a bulky but very lightweight black residue.

The sublimate showed a DTA curve which was featureless up to the melting endotherm (start 240°, peaks at 255°). Microanalytical results: found, 53.6%C, 4.8% H, 28.8% O, 12.7% N; required for $C_5H_5O_2N$, 54.05% C, 4.54% H, 28.80% O, 12.6% N.

The sublimate was scraped into brown bottles with a glass rod, for storage. Stock solutions were prepared by dissolving an appropriate weight of crystals in nitrogen-deaerated acid solution in a volumetric flask. About 100 mg could be dissolved conveniently in 25 ml of 1 *M* acid; to hasten dissolution, the flask was immersed for 2–5 min in the tank of an ultrasonic cleaner before dilution to the mark. No spectral changes occurred in solutions prepared from sublimate for at least 72 h, but no solution was used for quantitative studies after 24 h.

Iron solutions (0.1 *M*) were prepared by dissolving an accurate weight of iron powder (Alfa Inorganics 99.99% purity) in 1:3 nitric acid, taking to dryness, and evaporating with one or more portions of the appropriate acid to drive off the nitrate. The resulting salt was made up to a known volume in 1 *N* acid and standardized conventionally by reduction with tin(II) chloride and titration with a known solution of primary standard dichromate.

Other chemicals were reagent grade, and were tested as necessary for the absence of interfering impurities.

All water was deionized, distilled in an all-glass still and deaerated with nitrogen in an all-glass apparatus from which it was dispensed under nitrogen pressure.

Apparatus

Spectra were recorded on a Cary 14 spectrophotometer. Certain absorbances were checked, and Beer's law was tested on a Beckman DU instrument. Time-studies of colour stability were run on a modified Beckman DB[6] and controlled by a Beckman programmer. Fused quartz cells were used. Measurements were made at 25°. All volumetric ware was Class A, and all pipets were calibrated. Computations were performed on an IBM 360/75 computer.

Experimental

Determination of solution constituents. Series of solutions of varying DHP concentrations without iron(III), and varying iron(III) without DHP, were prepared in each acid, and their spectra were recorded from 700 to 300 nm. Series of solutions were then prepared in each acid containing both iron(III) and DHP so that the total molarity of the two species was constant (*ca.* $4 \cdot 10^{-3}$), but the metal-to-ligand ratio varied. All spectra were recorded beginning 2 min after mixing the active reagents.

Absorbances at 5-nm intervals were read from the spectra and analyzed by the procedure of VARGA AND VEATCH[7] as modified for the computer available[8]. This method produces both contour maps of absorbance on a wavelength *vs.* concentration plane (Figs. 1–3) and estimates of the number of absorbing species present. In each acid, one complex species was found to be contributing to the absorbance, and the metal-to-ligand ratio in that species appeared to be 1:1.

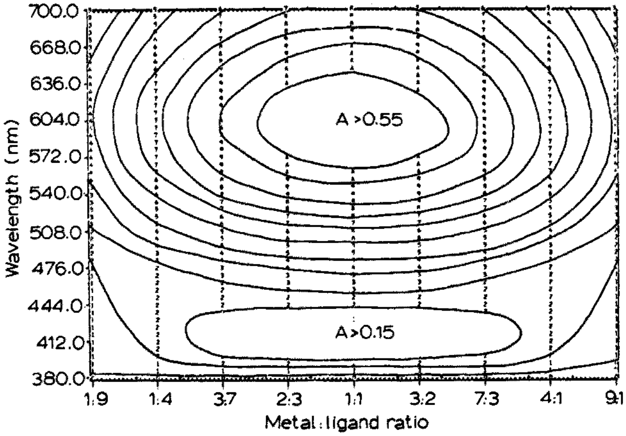

Fig. 1. Absorbance map for complex in chloride medium. Contour interval *ca.* 0.05 absorbance units.

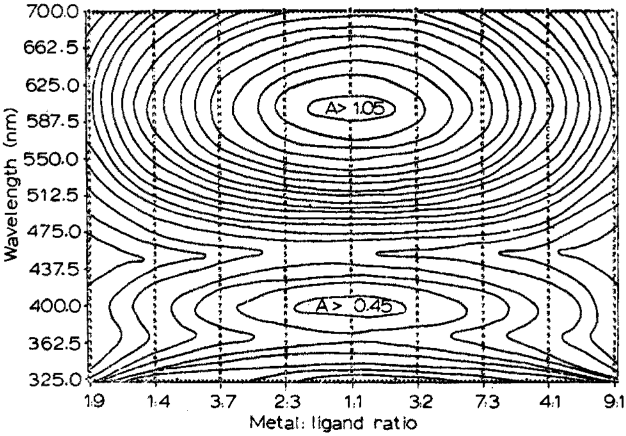

Fig. 2. Absorbance map for complex in perchlorate medium. Contour interval *ca.* 0.05 absorbance units.

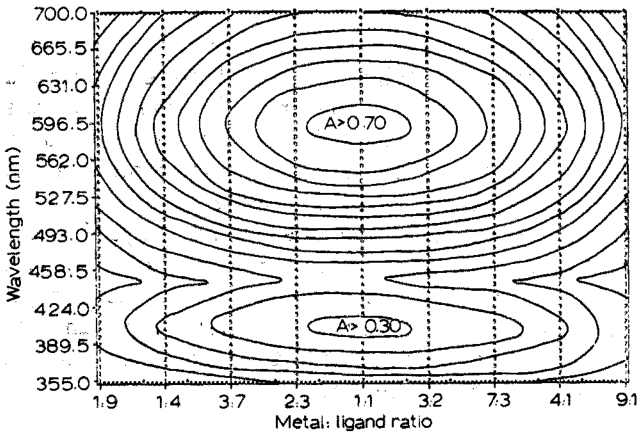

Fig. 3. Absorbance map for complex in sulfate medium. Contour interval *ca.* 0.05 absorbance units.

Conformity to Beer's law. Various amounts of iron(III) solutions in each acid, together with DHP sufficient to give a 25-fold molar excess of ligand with the largest amount of iron chosen, were made up in 25-ml volumetric flasks. Two minutes after mixing, absorbances were read in the Beckman DU at the wavelength of the principal peak. Results are shown in Table I.

Stability of colour with time. A sample the same as that which gave maximum peak absorbance in the first series of experiments was prepared and placed in the Beckman DB spectrophotometer. Spectra were automatically recorded at suitable time intervals. Results are shown in Fig. 4.

Discussion

In each acid, a bright blue 1:1 complex showing a broad absorbance maximum near 600 nm is observed. The perchlorate medium gives the greatest molar absorptivity, $1.543 \cdot 10^3$, corresponding to 0.036 μg of iron(III) per ml for an absorbance of 0.001 in a 1-cm path. The molar extinction is 8% lower in sulfate, but fading is much less. If unpurified DHP is used, the time-dependent changes of absorbance are generally greater.

TABLE I

MOLAR ABSORPTIVITY AND RANGE IN DIFFERENT MEDIA

Anion and its molarity	*Peak wavelength (nm)*	*Molar absorptivity* ($\cdot 10^3$)	*Std. dev. on concentrations measured (as % of conc. read)*	*Iron(III) concentration at which Beer's law deviations appear (mole/l)*
Cl^- (1 *M*)	600	1.271	0.72	$8 \cdot 10^{-4}$
ClO_4^- (1 *M*)	600	1.543	0.36	$>8 \cdot 10^{-4}$
SO_4^{2-} (0.5 *M*)	590	1.420	0.48	$8 \cdot 10^{-4}$

In 0.33 *M* phosphoric acid, a different, purple, complex is formed. Increasing the

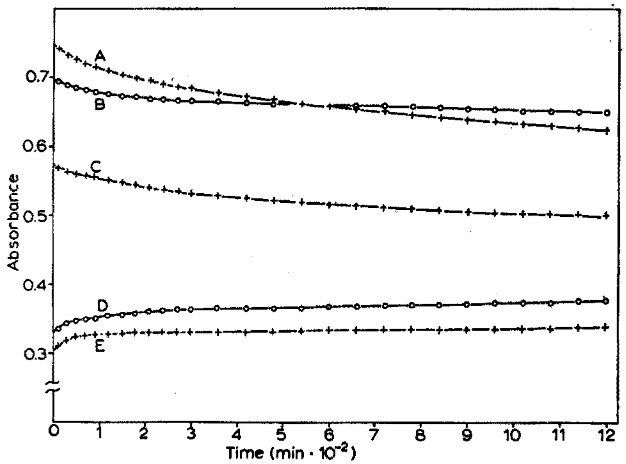

Fig. 4. Changes of absorbance with time (some early points omitted for clarity).

Curve	*Anion*	*Wavelength (nm)*	*% Change in 1 h*	*% Change in 20 h*
A	ClO_4^-	600	−3.2	−16.2
B	SO_4^{2-}	590	−1.6	− 6.3
C	Cl^-	600	−1.9	−12.4
D	SO_4^{2-}	400	+5.8	+ 8.8
E	ClO_4^-	400	+7.3	+12.6

phosphoric acid concentration (by adding drops of 85% acid) causes the purple colour to fade, but does not change it to blue. Studies on the phosphate medium will be reported later, but a possible interpretation is that iron(III) phosphate complexes have a stability intermediate between those of the blue and violet complexes of iron(III) with DHP.

The present work indicates that a satisfactory colour reaction for the determination of iron(III) with DHP can be carried out in any one of the three mineral acids used.

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Microdetermination of lead as chromate by the ring-oven technique*

Owing to its widespread occurrence and application, as well as its high toxicity, lead is one of the most important elements in the human environment. Small amounts of lead are usually determined by the very sensitive spectrophotometric dithizone method. However, the preparation of samples and the steps required to eliminate interferences can make this method rather time-consuming, expensive and tedious. For a large-scale survey, a faster and simpler method which would be as sensitive and reliable as the dithizone method would be very useful. For this purpose, a suitable colorimetric reaction, which could be performed by the ring-oven technique[1], was sought.

The tetrahydroxyquinone method[2,3] was considered, but though it may give reliable results in industrial hygiene studies, where lead is the predominant metal, in the general environment where the ratio of lead to other metals is less favourable, more serious interferences can be expected.

An attempt was made to adapt the dithizone method for ring-oven analysis, but the interferences could not be removed satisfactorily on the filter paper.

Finally the chromate method was tested and found to give reliable results. The relative insolubility of lead sulphate in diluted sulphuric acid was used to separate lead from the soluble compounds, and the selective solubility of lead sulphate in ammonium acetate, to separate it from the cations precipitated as insoluble sulphates.

Apparatus and accessories

Weisz ring-oven apparatus (ROFA) with accessories and capillary pipettes.

Munktell's filter paper No. 00, 5.5 mm diameter.

Recommended procedure

To the center of a filter paper, placed on the Weisz ring-oven maintained at about 90°, add a 5-µl portion of 0.05 *M* sulphuric acid, followed by one or more 5–10-µl portions of the sample solution. The filter paper must be nearly dry before each portion is added, so that the wet spot never approaches the ring zone. Finally, add another 5-µl portion of 0.05 *M* sulphuric acid, place the filter paper on the washing ring and wash the soluble salts out to the periphery of the filter paper with six 10-µl portions of 0.005 *M* sulphuric acid. When dry, center the filter paper again on the ring-oven and wash the lead sulphate out to the ring zone with about six 10-µl portions of saturated ammonium acetate solution. Care should be taken to prevent flooding of the ring. As soon as the ring begins to separate from the wet spot, remove the filter paper from the ring-oven and dry it immediately, first with a warm and then with a cool stream of air from a hair drier. Then dip the filter paper into an aqueous 1% (w/v) potassium chromate solution, wash thoroughly under the tap, and dry first between two filter papers, and then in the air. When dry, match the rings obtained from an unknown solution with a set of standards.

Prepare standard rings containing 1, 2, 3, 4, 6 and 10 µg of lead, from a standard lead solution (100 µg/ml) in the same way as the unknowns. The precision of the

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estimation is increased if three rings are prepared from different aliquots of the unknown solution and matched against standard ring, the weighted average being used as the final result[4].

If the method is to be applied to the analysis of air-borne particulates collected on the filter paper[5], it is best to perform the analysis directly on the sample. In this case the sample spot, which should not exceed 14 mm in diameter, is moistened with 0.05 *M* sulphuric acid, dried in the air, put on the washing ring and further treated as described above.

The limit of detection for lead by the recommended procedure is 0.5 μg and the analytical range is 1–10 μg.

Interferences

The interfering effect of foreign ions was investigated by the procedure of WEST[6]. Two rings were prepared for each ion at two concentration levels (10 and 40 μg), one containing the respective ion and the other both lead and the foreign ion in the ratio 1:10. If the first ring was identical with the blank and the second with the corresponding lead standard, the ion was considered as non-interfering.

The following ions were investigated for possible interference in the recommended procedure:

Group I	Na^+, K^+, Cu^{2+}, Ag^+
Group II	Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}
Group III	$B_4O_7^{2-}$, Al^{3+}, Ce^{3+}, Tl^+
Group IV	CO_3^{2-}, $Oxal^{2-}$, Ac^-, $Tart^{2-}$, Zr^{4+}, Sn^{2+}
Group V	NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, HPO_4^{2-}, SbO_3^{3-}
Group VI	S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, Cr^{3+}, CrO_4^{2-}, $Cr_2O_7^{2-}$, WO_4^{2-}
Group VII	F^-, Cl^-, Mn^{2+}, MnO_4^-, Br^-, I^-, CN^-, SCN^-
Group VIII	Fe^{3+}, Co^{2+}, Ni^{2+}

Only barium and bismuth interfered when present in concentrations ten times higher than lead. In the presence of barium, the washing-out was incomplete, most probably because of the formation of mixed crystals of barium and lead sulphate. The interference decreased with decreasing concentration of barium and at the 1:1 concentration ratio, no interference was observed at either the 1-μg or the 4-μg level.

The interference of bismuth was positive, and was most probably caused by the partial solubility of bismuth sulphates, so that some of bismuth was washed into the ring and increased the colour of the ring by forming the yellow dichromate. At the 1:1 concentration ratio the interference disappeared, for both the 1- and 4-μg levels.

Sample solutions in strong acids cannot be used for the analysis, because lead sulphate will be partly dissolved and washed out to the periphery of the filter paper, and because strong acids will cause the rupture of the filter paper.

Discussion

The recommended procedure for the determination of lead as chromate by the ring-oven technique is highly selective. The observed interferences should not give any trouble in the analysis of normal environmental samples, since lead is normally present in concentrations several times higher than barium or bismuth. None of the other investigated ions caused any interference under the described experimental conditions.

The sensitivity of the method, though not very high, is adequate. If the strictest hygienic standard for lead in the outdoor atmosphere, *i.e.* the Soviet Union standard of 0.7 μg of lead per m^3 of air in an average 24-h sample, is taken as a basis for calculation, a standard smoke sample of about 2 m^3 of air should contain enough lead for analysis even if the maximum permissible concentration has not been exceeded.

Whatman No. 1 and 41, and Munktell's No. 00 and 00R filter papers were examined for their suitability in the ring-oven lead analysis. The Munktell's papers proved more suitable, and the filter paper No. 00 showed a better collection efficiency for air-borne particulates.

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A bomb for the hydrofluoric decomposition of inorganic materials

During the past ten years the use of hydrofluoric acid as a decomposing agent for inorganic materials has increased considerably, the main reasons for this being that (*a*) decompositions can be made in vessels of inexpensive plastic materials, (*b*) silicon can be determined in samples attacked by hydrofluoric acid, and (*c*) hydrofluoric acid is now produced in a purer state than before. This renewed interest in the hydrofluoric acid decomposition technique has initiated the construction of various types of polytetrafluoroethylene (Teflon)- or platinum-lined bombs[1-9].

The present note describes a bomb which can be heated more rapidly than the bombs used previously in this laboratory, has an improved temperature regulation, and has a volume of about 120 ml, which permits dilutions to 100 ml in the bomb.

The construction of the bomb is shown in Fig. 1*. The body and the screw cap were made from a seawater-resistant aluminium alloy (1.0% Si, 0.9% Mg) to avoid the tendency of technically pure aluminium to smear. The inner vessel and lid were made from a 2″ diameter rod of dense Teflon (Habia, Sweden).

The body was heated with 1.7 m of Thermocoax heating element (Philips 1-Nc-I-10). The temperature was adjusted by means of an iron–constantan thermocouple and a Philips Plastomatic temperature regulator (450°). A circuit diagram is shown in Fig. 2.

During decompositions the bomb was placed on a magnetic stirrer; the magnet must be covered with Teflon.

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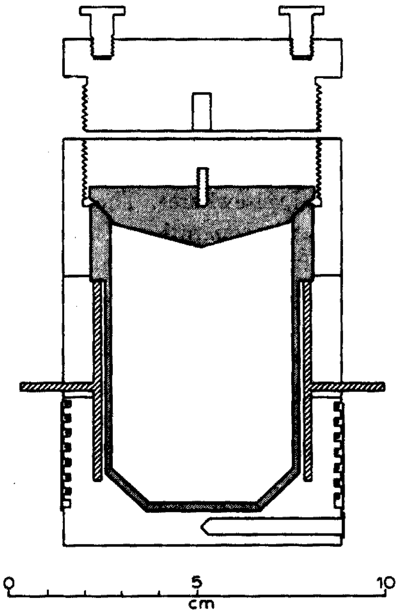
* Detailed specifications of the bomb are obtainable from the authors.



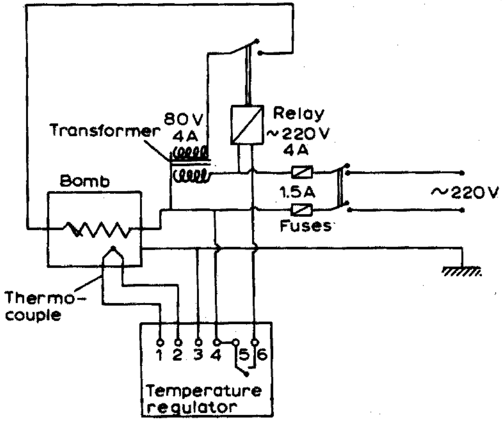


Fig. 1. Section through polytetrafluoroethylene-lined aluminium bomb for hydrofluoric acid decomposition of inorganic materials.

Fig. 2. Circuit diagram for heating and temperature control.

The bomb has been used for the decomposition of silicate minerals and rocks, slags, ores, etc., at temperatures up to 200°. The heating times required to reach the temperatures 110°, 150° and 200° were 10, 15 and 20 min, respectively. The regulator maintained the temperature within ±0.5°.

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Separation of metal–EDTA complexes by anion-exchange chromatography

In this paper is described an investigation of the separation of some transition metal complexes with EDTA, by means of column displacement chromatography. This technique provides more quantitative results than those which can be achieved by thin-layer chromatography, which has been discussed, elsewhere[1]. The present study is intended as a supplement to the previous qualitative separation. The major reason why the work was undertaken lies in the necessity for simple quantitative methods for plant physiological studies of the uptake, transport and metabolism of metal chelates by plants, as mentioned by WALLACE[2].

EDTA has been widely used in the separation of cations, particularly the rare earths[3–6]. An ion-exchange method involving EDTA has been proposed by FRITZ AND UMBREIT[7] for the separation of several binary mixtures of metal ions; the pH is adjusted so that the EDTA complex of one metal is quantitatively formed while the complex of the other one is largely dissociated. The adsorbabilities of a number of divalent metals have been studied by NELSON *et al.*[8] as functions of EDTA concentration, electrolyte concentration and pH.

Reagents and solutions

All the experiments were carried out on Dowex 2-X8, 200–400 mesh (74–36 μ). The resin was thoroughly washed successively with 1 *M* hydrochloric acid and 1 *M* ammonia solution, followed by distilled water, until the effluent was neutral. The resin was then converted to the chloride form with 1 *M* sodium chloride, rinsed with water and dried at 65° to constant weight. The finest were discarded by sedimentation in water. The exchange capacity of the resin amounted to 2.84 meq/g of dry resin.

For each metal a synthetic metal–EDTA solution was prepared by dissolving a known weight of the pure solid product obtained by the method described by SAWYER AND MCKINNIE[9]. The concentration of the metals in solution was up to 0.2 mg/ml. To their respective solutions, the tracers ^{65}Zn, ^{54}Mn, ^{60}Co and ^{59}Fe were added, followed by 1 ml of 10^{-3} *M* EDTA solution. Each solution was then heated for 6 h on a waterbath.

Procedure

The columns were filled with the ion exchanger, and the eluant to be used was passed until the concentration of the effluent equalled that of the eluant. The mixture for separation was obtained by taking a few ml of the metal–chelate solutions and evaporating almost to dryness. After addition of 1 ml of the eluant, the solution was warmed and transferred carefully to the top of the column. The optimal flow rate was found to be 0.2–0.5 ml min^{-1} cm^{-2}. The effluent was collected in aliquots of 5 ml with an automatic fraction collector. The contents of Mn, Fe, Co and Zn were determined radiochemically and those of Cr, Cu and Ni colorimetrically[10], after destruction of the organic sequestering agent.

Results

The elution curves obtained with 0.1 *M* potassium chloride, 0.5 *M* sodium acetate, 0.5 *M* ammonium acetate, and hydrochloric acid as eluants are shown in

Figs. 1–4. The concentrations of the metals in the fractions, expressed in arbitrary units, are plotted against the volume of the effluent.

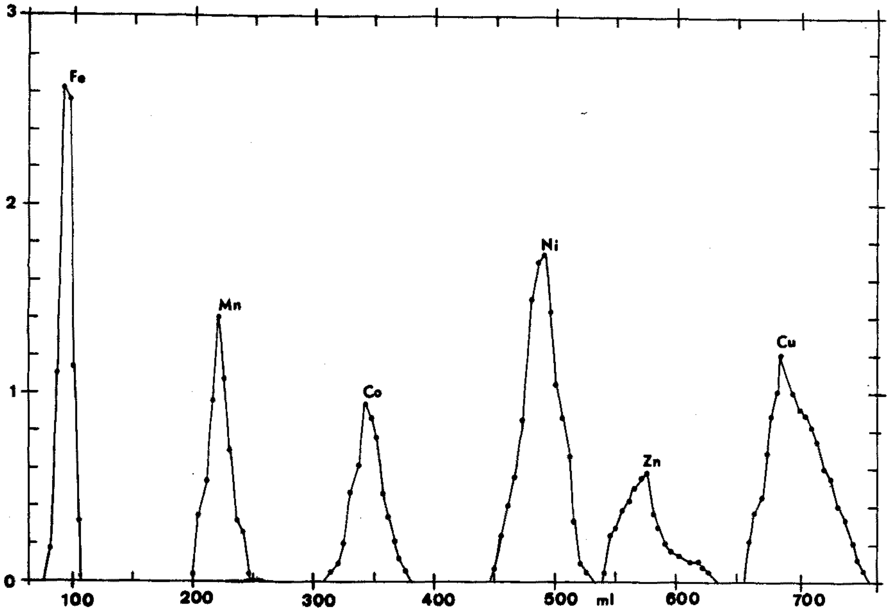

Fig. 1. Separation of Fe(III)–, Mn(II)–, Co(III)–, Ni(II)–, Zn(II)– and Cu(II)– EDTA, with 0.1 *M* potassium chloride as eluant. Column: 24.5 cm × 0.95 cm². Flow rate: 0.25 ml min^{-1} cm^{-2}.

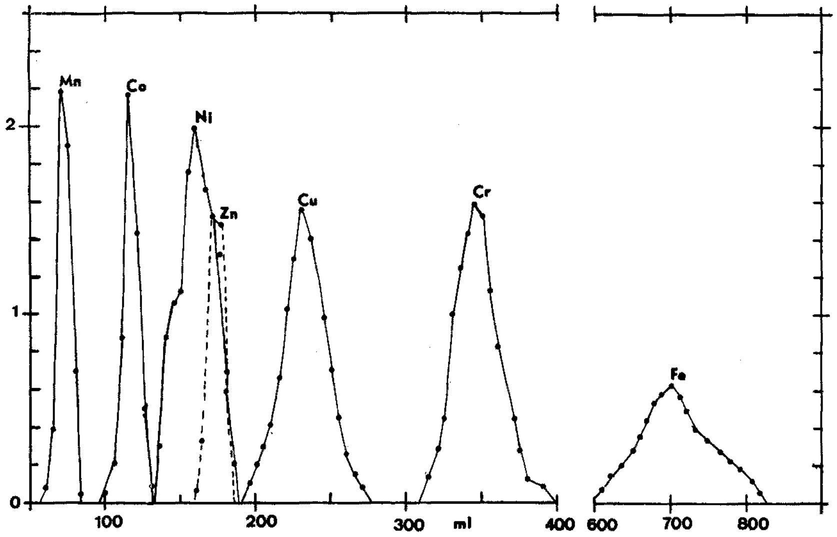

Fig. 2. Separation of Mn(II)–, Co(III)–, Ni(II)–, Zn(II)–, Cu(II)–, Cr(III)– and Fe(III)-EDTA with 0.5 *M* sodium acetate as eluant. Column: 27.2 cm × 0.95 cm². Flow rate: 0.21 ml min^{-1} cm^{-2}.

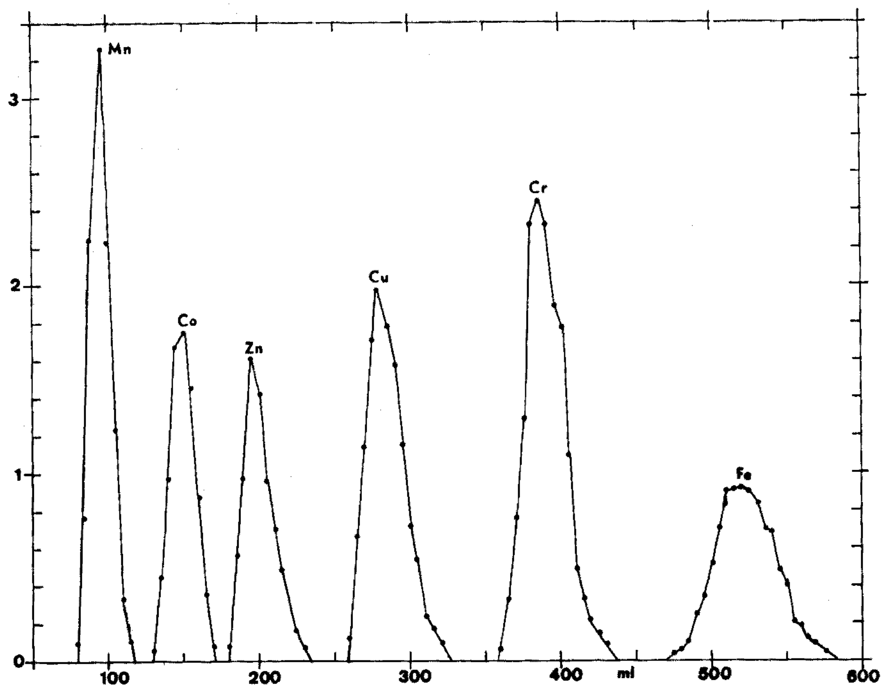

Fig. 3. Separation of Mn(II)–, Co(III)–, Zn(II)–, Cu(II)–, Cr(III)– and Fe(III)-EDTA with 0.5 *M* ammonium acetate as eluant. Column: 17.3 cm × 0.95 cm². Flow rate: 0.47 ml min⁻¹ cm⁻².

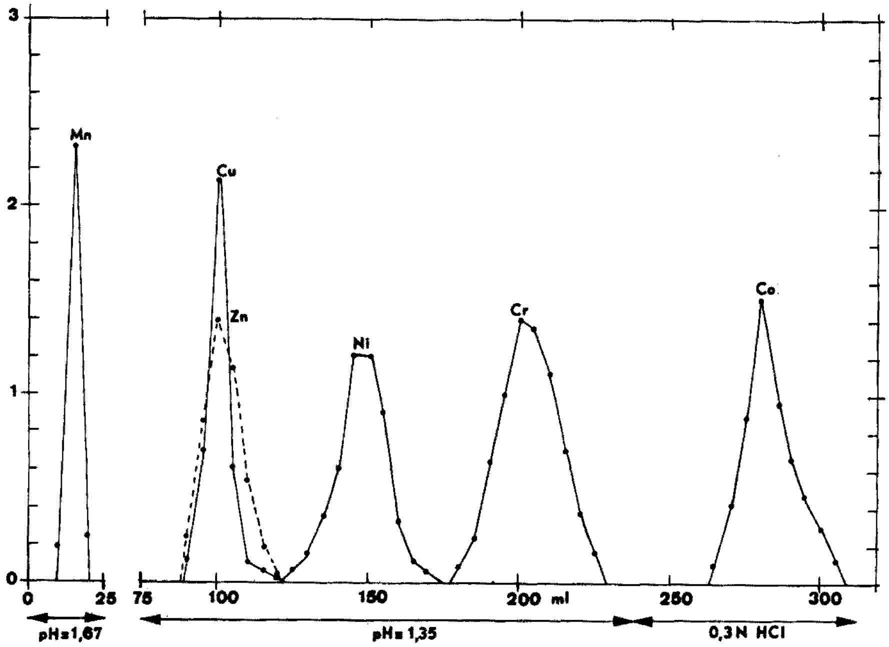

Fig. 4. Separation of Mn(II)–, Cu(II)–, Zn(II)–, Ni(II)–, Cr(III)– and Co(III)-EDTA with hydrochloric acid as eluant. Column: 21.7 cm × 0.95 cm². Flow rate: 0.31 ml min⁻¹ cm⁻².

Discussion

The separation factor of metal ions with different valences is usually high enough to allow separation of such metals on the same cation exchanger. The difference in valence state between divalent and trivalent ions persists even in slightly acidic medium after complexation with EDTA, as the complexes MY^{2-} and MY^{-} are formed.

The behaviour of these compounds on an anion exchanger with a neutral eluant, potassium chloride, is shown in Fig. 1. The pH of the effluent allows the formation of MY^{n-4} so that univalent complexes are eluted before the divalent ones; MnY^{2-} is eluted between FeY^{-} and CoY^{-}, possibly because manganese(II) can be oxidized to manganese(III) so that the univalent complex MnY^{-} is formed. The existence of this complex has been proved by YOSHINO *et al.*[11]. A similar behaviour for manganese is also indicated for elution with sodium acetate (Fig. 2) and ammonium acetate (Fig. 3). In a strongly acidic medium (Fig. 4), the parallelism between manganese and the other trivalent metal ions does not seem to exist. According to the above-mentioned authors, at pH values below 3, the protonated complex HMnY could be formed; it is not surprising that this complex, if it exists at pH 1.67, could still interact with the anion exchanger. However, it must be pointed out that the elution position of manganese in Fig. 4 can also be explained on the basis of manganese(II); it can be calculated that EDTA has no complexing properties for manganese(II) at pH 1.67. Further, it may be concluded from Fig. 4 that the elution sequence of the metal–EDTA complexes is inversely proportional to their formation constants. However, a comparison of the elution volumes, according to the maximal peak heights of copper(II)–EDTA and nickel(II)–EDTA, would lead to the erroneous conclusion that $K_{NiY^{2-}}$ must be greater than $K_{CuY^{2-}}$; the copper chelate is eluted before the nickel one. But the stability constants, obtained by different methods for these chelates, are of the same order of magnitude, and can thus not cause such a different behaviour in an acid medium. The present author would try to explain this phenomenon by means of the different kinetics of the reactions leading to protonated metal–EDTA complexes.

The different behaviour of the trivalent metal ions iron(III), cobalt(III) and chromium(III) with EDTA is shown by the corresponding position of their elution peaks with sodium acetate (Fig. 2) and ammonium acetate (Fig. 3). According to its negative charge, CoY^{-} is always eluted before ZnY^{2-}, CuY^{2-} and NiY^{2-} in a not too acidic medium. For the complexes FeY^{-} and CrY^{-} a metal–carboxylic bond will be broken[12] and replaced by a metal–hydroxyl one. These compounds thus obtain a second negative charge because of the formation of $M(OH)Y^{2-}$ complexes. A second carboxylic group could also be replaced in the coordination sphere of the metal by a hydroxyl group, so that a complex of the type $Fe(OH)_2Y^{3-}$ could be formed. According to the value[13] of its dissociation constant, $10^{-12.2}$, the dihydroxo chromium(III)–EDTA complex will only be formed in a strong alkaline medium.

From the foregoing discussion, it may be concluded that EDTA is an efficient agent for separation of transition metal ions by ion exchange. The complexes can be eluted with aqueous solutions, and by choosing a suitable pH for the eluting agent, a variation of the charge can be induced in the complexes. A further advantage is that the movement of some of these complexes can be followed without auxiliary means, owing to their specific and intense color.

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Organic multi-element analysis with a small mass spectrometer as detector. A preliminary note

In the field of organic elemental analysis there is a great interest in methods allowing simultaneous determination of several elements. Well-known in this respect are the commercially available "CHN analysers" based on the combustion of a small sample and detection of the products formed (CO_2, H_2O, N_2) by measurement of the thermal conductivity after chemical or gas chromatographic separation. Extension of these techniques to include other elements (*e.g.* sulfur or halogens) has been reported, *e.g.* by BEUERMAN AND MELOAN[1] and by DUGAN AND ALUISE[2], but this involves more complicated procedures. A potential problem is presented by the greater reactivity of combustion gases containing compounds like sulfur dioxide, hydrogen chloride and bromine. This may cause trouble from adsorption or mutual reactions during the relatively lengthy separation period.

We thought it worth while to investigate a different approach with mass-spectrometric detection of the combustion products. Here the almost instantaneous expansion of the gas mixture into the mass spectrometer and the extremely rapid separation of its components would greatly reduce the chance of interaction. The experimental arrangement is shown in Fig. 1. Milligram amounts of organic material, weighed into aluminium capsules, were dropped into the vertical "flash" combustion tube and rapidly burnt in a stream of oxygen. A small part of the resulting gas mixture was directly fed into an AEI MS-10 mass spectrometer which was adjusted to the

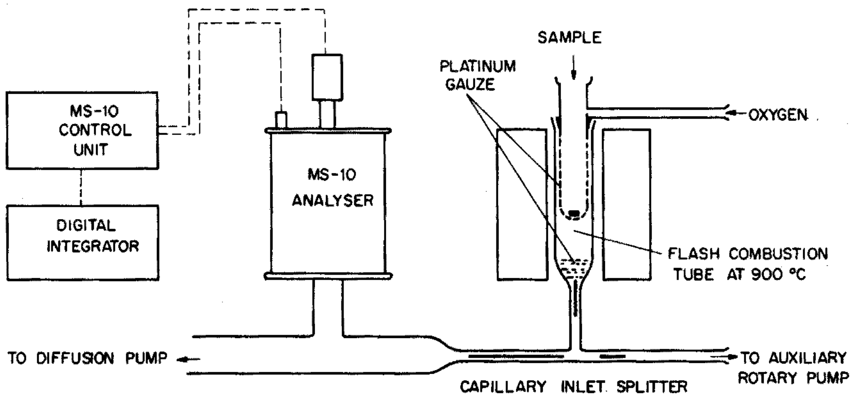

Fig. 1. Diagram of the apparatus.

m/e value of the combustion product containing the element to be detected. The resulting signal was electronically integrated.

So far, the elements carbon, hydrogen, nitrogen, sulfur, chlorine and fluorine have been considered. Special attention has been paid to adsorption effects, fragmentation patterns, sensitivity and reproducibility. In general the measurements were based on the parent ions (see Table I), but for fluorine SiF_3^+ was used. This ion was the main fragmentation product of SiF_4, which was formed, apparently, when organically bound fluorine was burnt in the quartz combustion tube.

TABLE I

ELEMENTS TESTED

Element	*Test sample*	*Ion detected*	*m/e*	*Range (μg)*
C	mannitol	CO_2^+	44	1–1000
H	mannitol	H_2O^+	18	0.2–100
S	elemental sulfur	SO_2^+	64	1–500
N	acetanilide	NO^+	30	1–500
Cl	*p*-chlorobenzoic acid	HCl^+	36	1–500
F	*p*-fluorobenzoic acid	SiF_3^+	85	1–300

The results of these preliminary experiments were very encouraging. Presumably because of the presence of a continuous stream of oxygen through the system, hardly any adsorption was experienced; in all cases signal integration was complete within 1–2 min. In the microgram-to-milligram range linear relations were obtained when integrator counts were plotted against the respective amounts of the element burnt. Moreover, the combustion products did not interfere at the selected mass values.

With the MS-10 mass spectrometer only one element could be determined per combustion. A multi-channel instrument, however, would allow simultaneous determination of a number of elements, so that the elemental composition of an organic sample would be obtainable within a few minutes. This will be the subject of future work.

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Detection of traces of zinc by activation of apoalkaline phosphatase

Few tests are available that will detect appreciably less than 1 μg of zinc[1], and even fewer are applicable as spot tests carried out on filter paper. Reagents that can be recommended for use on filter paper are dithizone (limit of identification: 0.05 μg)[1], and uranyl hexacyanoferrate(II)[1] (identification limit: 0.1 μg), although both tests are subject to appreciable interference by other metals. It was recently shown that the apoenzyme obtained by removal of zinc from alkaline phosphatase could be re-activated by traces of zinc, and that few other metals caused re-activation[2]. The present paper describes a simple preparation of the apoenzyme, and its use for the sensitive and selective detection of zinc.

Experimental

Preparation of apoalkaline phosphatase. Calf-intestinal alkaline phosphatase (Seravac Labs., Maidenhead, U.K.) (10 mg) and disodium-EDTA (20 mg) were dissolved in water (25 ml) at room temperature. The solution was allowed to stand for 4 h at 3° before use. It was also stored at 3°.

Buffered substrate solution. A mixture of $5 \cdot 10^{-3}$ *M* *p*-nitrophenyl phosphate solution (5 ml) and pH 9.8 Tris buffer (5 ml)[3] was prepared daily.

Detection of zinc (20 ng–2 μg). Filter the apoenzyme solution (1 ml) through a 2-cm diameter Millipore filter (100-nm pore diameter). Wash 2–3 times with water (1 ml) to remove EDTA; excessive washing removes apoenzyme. Divide the filter into halves. Place a drop (0.025 ml) of water on one half as a blank and a drop of test solution on the other. Spread both drops with a fine glass rod. After 2–3 min, suck through any excess liquid. Place on each half two drops of the buffered substrate solution. A yellow colour indicates the presence of zinc.

Results and discussion

Apoalkaline phosphatase has no catalytic effect on the hydrolysis of *p*-nitrophenyl phosphate, unlike the zinc-containing parent enzyme. However, the apoenzyme binds with zinc and is re-activated[2], so that the appearance of the yellow hydrolysis product, *p*-nitrophenol, in the presence of the apoenzyme indicates that zinc is also present. With the above procedure, this simple test has an identification limit of 10 ng of zinc, and a dilution limit of $1:2.5\cdot10^6$. In the presence of 2 μg of zinc, the yellow colour develops immediately, but it is appreciably slower when only 20 ng of zinc are present.

There are two ways in which ions can interfere with the test—by re-activating the apoenzyme, with the result that positive responses are given by cations other than zinc, and by inhibition of the zinc re-activated enzyme, so that negative responses for zinc are obtained even when zinc is present. Apart from zinc, only cobalt(II), magnesium and the alkaline earth metals re-activated the apoenzyme in solution, and much larger concentrations than that of zinc were required. In the spot test, however, only calcium (>1 μg) gave a positive response, and even in this instance the colour developed slowly. If zinc (80 ng) and calcium or cobalt (1 μg) were present together, the appearance of the yellow colour was speeded up, and thus improved the test. Beryllium, lead and $>10^{-5}$ M amounts of zinc, most strongly inhibited the activity of calf-intestinal alkaline phosphatase when *p*-nitrophenyl phosphate was used as substrate[3]. Most other metal ions and all anions had little or no inhibitory action when present in μg amounts, and would not be expected to interfere with the present test. In the present study, lead (5 μg) and cadmium (3 μg) merely delayed the appearence of the yellow colour, and beryllium, the most potent inhibitor, could be tolerated in amounts <0.1 μg. The original enzyme, when inhibited by beryllium, never loses more than 50% of its activity, but the re-constituted enzyme is completely inhibited.

The blank should be colourless. The slow formation of a yellow colour in the blank indicates incomplete deactivation of the parent enzyme, and decreases the sensitivity of the test. More EDTA may be required in the apoenzyme preparation to eliminate this effect.

Methods for the determination of zinc and calcium based on the re-activation of apoalkaline phosphatase will be published later[4].

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Determination of platinum in basic rocks by solvent extraction and atomic absorption spectroscopy

Determination of platinum in geological samples presents certain difficulties because of the low concentrations involved. At the same time workable occurrences only need concentrations of around a few parts per million. A research project carried out at this Institute in cooperation with Greenland Geological Survey involves the examination of a series of basic rocks in Greenland. Apart from the usual sulphides of iron, copper, and nickel, the rocks are known to contain small amounts of platinum metals. Parallel with the conventional mineralogical and geological examinations, it was decided to carry out a geochemical study of the platinum content in these rocks. This proved to be possible by means of atomic absorption spectroscopy.

STRASHEIM AND WESSELS[1] have investigated the determination of platinum by atomic absorption spectroscopy. Inter-element interferences were found to be caused even for small amounts of other platinum metals. A detection limit of 5 p.p.m. was reported for platinum in aqueous solution. The concentration of platinum in geological samples usually is so small that it is difficult to obtain an aqueous solution with a platinum concentration of this magnitude, hence the platinum content of the dissolved sample must be concentrated. This can be accomplished, for instance, by organic solvent extraction. Different extraction systems have been described, especially for the purposes of atomic absorption spectroscopy. SWIDER[2] has proposed the use of methyl isobutyl ketone to extract a hexaiodoplatinate(IV) complex; however, interfering metals such as palladium are coextracted. Moreover, in a solution of a geological sample in which platinum has to be present in the tetravalent state, it is difficult to avoid the presence of oxidising substances which can give rise to formation of free iodine instead of the desired iodo-complex.

In connection with other analytical methods than atomic absorption spectroscopy, a procedure by which platinum is extracted selectively from an aqueous solution with dithizone (diphenylthiocarbazone) in tetrachloromethane has been described[3,4]; at the optimal acidity, very few metals, including platinum, can be extracted with dithizone, and platinum is only extracted in the divalent state. After removal of interfering metals by a preliminary dithizone extraction, while platinum is present in the tetravalent state, platinum can be extracted selectively after reduction to the divalent state. This selective extraction procedure was described in connection with the titrimetric determination of platinum. The solution of the platinum–dithizone complex in tetra- or tri-chloromethane is not suitable for atomic absorption analysis because of the poor sensitivity obtained with these solvents.

In the present work, this selective extraction procedure was modified by extracting with methyl isobutyl ketone (MIBK) rather than the chlorinated solvents, the former solvent being much better suited to atomic absorption. The solubility of dithizone in ketones has been generally reported as poor[5], but the results obtained with MIBK in this application to rocks proved to be entirely satisfactory.

Apparatus

A Perkin-Elmer 303 atomic absorption spectrophotometer equipped with a

Hitachi Perkin-Elmer 159 recorder was used with a platinum "intensitron" lamp. A three-slot Boling burner, length 10.7 cm, was used with a lean air–acetylene flame. The operating conditions were as follows:

Grating: ultraviolet	Lamp current: 30 mA
Wavelength: 2659 Å	Scale expansion: 10 ×
Slit: 4 (7 Å)	Noise suppression: 3

Reagents

All the reagents used were of analytical-reagent grade.

Aqua regia. Mix 3 parts of concentrated hydrochloric acid, 1 part of concentrated nitric acid and 1 part of demineralized water.

Dithizone solution. Dissolve 22.5 mg of dithizone under vigorous stirring in 100 ml of methyl isobutyl ketone. Dilute 10 ml of this solution to 100 ml with methyl isobutyl ketone. Prepare the solution daily.

Stannous chloride solution. Dissolve 35 g of stannous chloride in 100 ml demineralized water.

Platinum standards. Prepare daily from a 1000 p.p.m. platinum stock solution, to contain from 0.02 to 1.0 p.p.m. of platinum in 3 *M* hydrochloric acid. Prepare the stock solution from chloroplatinic acid (5% w/v); this is stable for at least a month.

Procedure

Weigh 5-g aliquots of the pulverized samples into 100-ml teflon beakers. Add 1 ml of concentrated nitric acid and 25 ml of 40% hydrofluoric acid and evaporate to dryness. Then add 25 ml of aqua regia. Cover the beakers and heat at 95–100° for 2 h. Remove the covers and evaporate to dryness. Add 25 ml of concentrated hydrochloric acid, cover the beakers and heat for a further 10 min. Then dilute the sample solutions with demineralized water to about 70 ml, filter into 100-ml volumetric flasks and dilute to volume with demineralized water. These solutions have pH values of −0.5–0. Prepare one or more reagent blanks by the same procedure.

Transfer 50-ml aliquots of standards, samples and blanks to 100-ml separatory funnels and extract each with dithizone solution (added in 5-ml portions) until no colour change occurs. Separate the aqueous phases and to each add 2 ml of aqueous 35% (w/v) tin(II) chloride solution. After 5 min, shake the aqueous phases with 6 ml of dithizone solution. Separate the organic phases, and determine the platinum content by atomic absorption spectroscopy.

Results and discussion

Fixed amounts of platinum were added to basic rock samples known not to contain platinum, as well as to rock samples containing platinum. Data on the recovery of platinum and the reproducibility of the platinum determination by the described procedure are presented in Table I.

The detection limit was 0.005 μg Pt/ml in the aqueous solution obtained after dilution of the hydrochloric acid solution to 100 ml, corresponding to 0.1 p.p.m. platinum in the basic rock. A lower detection limit could probably be obtained if a smaller amount of a more concentrated dithizone solution were applied for the last extraction. The solution obtained after treatment of the sample with aqua regia contains platinum in the tetravalent state. Interfering metals are removed from the solution at *ca.*

TABLE I

DETERMINATION OF PLATINUM IN BASIC ROCK

Basic rock no.	*Pt in basic rock found (p.p.m.)*	*Pt added (p.p.m.)*	*Pt found (p.p.m.)*
1	0.0	1.0	1.0
	0.0	2.0	1.9
	0.0	3.0	2.9
	0.0	4.0	4.2
2	4.0	1.0	4.9
	3.9	2.0	6.1
	3.9	3.0	6.8
	4.0	4.0	7.9

pH 0 by extraction with a solution of dithizone in methyl isobutyl ketone. After reduction of platinum to the divalent state, it can then be extracted with a solution of dithizone in methyl isobutyl ketone. This relatively concentrated organic solution is entirely suitable for the determination of platinum by atomic absorption spectroscopy.

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2 R. T. SWIDER, *Atomic Absorption Newsletter*, 7 (1968) 111.
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Anal. Chim. Acta, 49 (1970) 368–370

Determination of oxalate ions in irradiated alkali metal oxalates

In the radiation chemistry of solid oxalic acid and oxalate salts, an important analytical problem is the determination of the remaining oxalate which is not destroyed by radiolysis. The presence of radiolytic products prevents the direct use of some simple and otherwise reliable methods such as titration with permanganate or certain spectrophotometric determinations. In the case of oxalic acid, the spectrophotometric copper–benzidine method[1] is mostly used for the determination of the remaining oxalate ions in irradiated samples. Radiolytic products such as hydrogen peroxide up to a concentration of $1 \cdot 10^{-2}$ *M* and traces of organic acids do not interfere. However, an attempt to apply this method to irradiated crystalline alkali metal oxalates failed because the main radiolytic product is the metal carbonate (in analogy to carbon dioxide which is formed in irradiated oxalic acid). Carbonate salts seriously interfere with the copper–benzidine method and therefore must be removed.

The present note describes a modified copper(II)–benzidine method for the determination of oxalate ions in irradiated alkali metal oxalates. In addition, the copper–benzidine complexes of various inorganic anions, including some radiolytic products of oxalate salts, in the presence of alkali metal ions, are discussed; the results obtained give useful information on possible interferences in the determination of oxalate ions in irradiated samples.

Analytical procedure

Dissolve the irradiated sample in water and make the solution up to volume. Take an aliquot containing 0.03 g of alkali metal oxalate and evaporate it carefully to dryness. Add 2 ml of 0.1 *M* hydrochloric acid and evaporate again to dryness. Repeat this step, which destroys the metal carbonate and removes carbon dioxide, twice. Dissolve the residue in distilled water, transfer it to a 100-ml volumetric flask, and dilute to volume with water. Take a 1-ml aliquot and apply the copper–benzidine method[1]. To the aliquot in a 25-ml volumetric flask, add 5 ml of the reagent solution, dilute to volume, and measure the absorbance at 253 nm against the reagent solution (5 ml reagent in 25 ml water). For the reagent, mix equal volumes of $3.75 \cdot 10^{-3}$ *M* copper acetate and $1.25 \cdot 10^{-3}$ *M* benzidine hydrochloride solutions; prepare the latter by dissolving the benzidine salt in 30% acetic acid and diluting so that the solution contains 1 ml of acetic acid per 100 ml.

Results and discussion

In the above analytical procedure, the alkali metal oxalate is converted to the

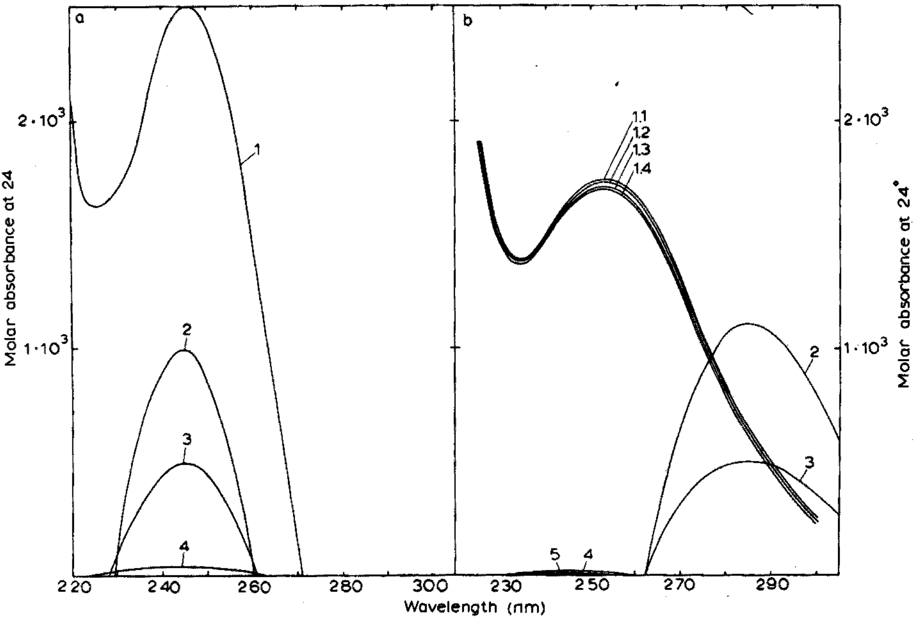

Fig. 1. Absorbance spectra for acids and their salts in equimolar amounts. (a) Acids: (1) oxalic; (2) sulfuric; (3) hydrochloric; (4) acetic.
(b) Salts: (1) oxalates—(1.1) ammonium, (1.2) sodium, (1.3) lithium, (1.4) potassium; (2) carbonates; (3) acetates; (4) sulfates; (5) chlorides.

chloride and oxalic acid, the latter being determined as a copper(II)–benzidine complex[1]; alkali metal carbonate, the main radiolytic product, is converted to the chloride and the interfering carbonate ion is removed.

Interference of other anions. The interference of carbonate, sulfate, chloride and acetate was studied spectrophotometrically by recording the spectra of the copper–benzidine solution in presence of the anion. The solutions were prepared as described in the original procedure[1], and measured on a Unicam SP 500 instrument at 24°. As shown in Fig. 1a, the shape of the spectra and the position of the peaks are nearly identical for all anions, but there are large differences in the intensities of the peaks. It can be seen that carbonate will interfere seriously with the determination of oxalate, while chloride in equimolar amounts will have a negligible effect. Figure 1b shows that the cations can cause an increase in the pH of the solution, which shifts the absorbance peak towards longer wavelengths. The presence of alkali metal ions also causes a decrease in the intensity of the absorption peak of oxalate and other anions. In the case of oxalic acid, the molar absorptivity is 30% lower, while for hydrochloric and sulfuric acids the decrease is much greater (up to 90%). In the presence of most alkali metal cations, Beer's law is valid only over a very small concentration range, although in the case of lithium oxalate, the curve relating absorbance and concentration deviates only slightly from a straight line. Accordingly, calibration curves must be prepared for the analytical procedure. Moreover, freshly prepared solutions should be measured, as a slight decrease of the absorbance after standing was observed on standing; for lithium oxalate, this fading was 1% in 24 h.

TABLE I

DETERMINATION OF LITHIUM OXALATE

Sample		*Pretreatment*	*Li oxalate (M)*	
			Spectr. method	*$KMnO_4$ method*
Li oxalate		None	$9.31 \cdot 10^{-2}$	$9.53 \cdot 10^{-2}$
Mixture of 1:1 ratio of Li oxalate and Li carbonate		Evaporated to dryness	$8.33 \cdot 10^{-2}$	$9.56 \cdot 10^{-2}$
		Evaporated and treated once with 0.1 *M* HCl	$9.50 \cdot 10^{-2}$	$9.66 \cdot 10^{-2}$
		Evaporated and treated twice with 0.1 *M* HCl	$9.45 \cdot 10^{-2}$	$9.65 \cdot 10^{-2}$
		Evaporated and treated three times with 0.1 *M* HCl	$9.50 \cdot 10^{-2}$	$9.57 \cdot 10^{-2}$
Aqueous solutions of irradiated Li oxalate[a]	Solution No. 1	Evaporated and treated three times with 0.1 *M* HCl	$1.84 \cdot 10^{-1}$	$1.87 \cdot 10^{-1}$
	Solution No. 2		$1.46 \cdot 10^{-1}$	$1.43 \cdot 10^{-1}$
	Solution No. 3		$1.50 \cdot 10^{-1}$	$1.54 \cdot 10^{-1}$

[a] The amount of carbonate in solution before treatment was 10–15% of the amount of oxalate.

Although the absorbance peak of carbonate is shifted towards longer wavelengths, carbonates interfere seriously with the determination of oxalate (Fig. 1b), and so must be destroyed. Chlorides do not interfere seriously and therefore hydrochloric acid is used to destroy the alkali metal carbonate, but free acid interferes (even an excess of acetic acid can hardly be tolerated), hence the evaporation of excess of acid is essential.

Table I shows results obtained for artificial samples (an equimolar mixture of lithium carbonate and lithium oxalate) and for neutron-irradiated samples of lithium oxalate, by the above method, and by titration with permanganate after several evaporations to dryness with 0.1 *M* hydrochloric acid. The two methods are in good agreement, thus the evaporation procedure must remove other radiolytic products which would interfere in the permanganate titration, as well as carbonates.

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1 Z. DRAGANIĆ, *Anal. Chim. Acta*, 28 (1963) 394.

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ANNOUNCEMENT

SHORT COURSE IN X-RAY SPECTROMETRY

State University of New York at Albany
June 8–19, 1970

A two-week short course in modern X-ray spectrometry will be offered at the State University of New York at Albany from June 8 to 19, 1970. The course will be instructional and will develop the basic theory and techniques starting from elementary principles. No previous knowledge or experience is required. The first week will cover basic principles and techniques and the second week will continue with further fundamentals and practical applications. The latter part of the second week will emphasize non-dispersive analysis, advanced techniques, mathematical methods and computer automation of modern X-ray spectrometers. Registration may be made for one week, either week, at a registration fee of $250.00 or for the entire two-week session at a registration fee of $450.00. For further information and to register, communicate with Professor HENRY CHESSIN, State University of New York at Albany, Department of Physics, 1400 Washington Avenue, Albany, N.Y. 12203.

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BOOK REVIEWS

JOHN ROBOZ, *Introduction to Mass Spectrometry. Instrumentation and Techniques*, Interscience–J. Wiley and Sons, Inc., New York, 1968, xvii+539 pp., price 187 s.

The author set out to provide a comprehensive introduction to instrumentation and techniques in mass spectrometry and has accomplished this objective most successfully. After an introductory chapter, in which the fundamental concepts and scope of applications are discussed, the following eight chapters, which comprise Part I, are devoted to instrumental considerations. The principles, design, and operation of mass analysers, ion sources, and ion detectors are thoroughly reviewed, as well as vacuum techniques and sample introduction systems. Part I is concluded with a very useful chapter on the merits and limitations of the various commercial systems available in 1967.

Part II deals with applications and commences with a chapter on ionization processes and types of ions in mass spectra. Rearrangement and fragmentation patterns are discussed in this chapter although the emphasis throughout is not on the structure-determining applications of mass spectrometry. Qualitative and quantitative analysis in organic and inorganic chemistry are dealt with in chapters 10 and 11. Techniques for the analysis of solids, liquids, and gases, and the use of field ionization in order to simplify the spectra of mixtures are discussed. The link-up of a GLC column to the spectrometer, and, the utilization of computers and presentation of spectra, using the element-mapping technique developed by BIEMANN, are also covered in this section. Two further chapters; one dealing with ionization and appearance potentials, high temperature work, and reaction mechanism studies, and the other with miscellaneous applications in such diverse fields as nuclear physics and biochemistry, complete the technical content of the book. The concluding chapter is devoted to information and data; it has a fairly complete bibliography of books and reviews, both historical and recent, as well as a list of current information sources. Tables of nuclidic masses and relative abundances for naturally occurring isotopes and a compilation of atomic and some molecular ionization potentials are given in the appendices.

The presentation and illustrations are excellent throughout and the balance between instrumental considerations and applications is just about right. No serious errors were detected. It should prove to be a valuable text and source of reference for those who are not deterred by the rather high price.

V. GUTMANN, *Coordination Chemistry in Non-aqueous Solutions*, Springer-Verlag, Vienna, 1968, viii+174 pp., price Cloth, 302 s; DM 48.—; U.S. $12.00.

Analytical chemists have made surprisingly little use of reactions in non-aqueous solvents, except for the determination of acids and bases. The present text, however, emphasizes the wealth and novelty of co-ordination reactions that occur in various non-aqueous media, so that it will serve the analytical chemist as an excellent source book on such reactions, and perhaps induce the development of some novel analytical procedures.

The book, which is well produced, opens with a brief introduction to various concepts of non-aqueous chemistry, followed by a general account of the co-ordinating properties of solvents and of co-ordination equilibria. The bulk of the book gives detailed information on a host of co-ordination reactions in a large variety of solvents, including such unusual solvents as liquid iodine, hydrogen sulphide and arsenic(III) fluoride. Finally, the behaviour of halides and pseudohalides as competitive ligands for transition metals is reviewed.

SIGNEY SIGGIA, *Survey of Analytical Chemistry*, McGraw-Hill Book Company, New York, 1968, xiii+304 pp., price 93 s.

The penchant amongst publishers at the present time to provide bigger and better compendiums and treatises on analytical chemistry is admirable, but few individuals can afford either the money to own them or the time to read them. Instead many of these books, so full of chemical detail and minutia must remain on dusty library shelves to be used for purposes of reference only. Such a fate should not befall the present text which, as its title suggests, looks in a general way at the whole field of analytical chemistry as a rapidly growing part of chemical technology. Here, instead, is a book which presents an up-to-date broad picture of modern analytical chemistry, and views it as an applied science using a great number and variety of physical and chemical processes for its elaboration and intent.

Obviously, in 300 pages, the treatment must be somewhat circumscript, but Professor SIGGIA has deliberately avoided involvement with detail. Instead he has aimed to provide the reader with an easily assimilable account of the various types of problem which the analyst is called on to tackle and the many different methods he can use to solve them. The text is organised as follows. A brief introductory chapter leads directly into accounts of inorganic and organic elemental analysis, functional group analysis, identification and structure determination; then molecular weight methods, methods relying on particular physical properties and the gross and surface examination of materials are discussed. The techniques of trace analysis, assays in the high purity range, tracers, and analytical separations are described and the book concludes with a post-script on automatic analysis. Each chapter has a list of suitable references and suggested texts for further reading.

This is an excellent and incomparable text. The author's long experience as an industrial analyst has enabled him to pinpoint the major problems and outline the most useful approaches to their solution. It should provide valuable reading not only for the student of analytical chemistry but for the many practising analysts who must feel a little divorced from many of the advances which their subject is constantly generating.

Anal. Chim. Acta, 49 (1970) 376–377

GUSTAV KORTÜM, *Reflexionsspektroskopie. Grundlagen, Methodik, Anwendungen*, Springer Verlag, Berlin–Heidelberg–New York, 1969, viii + 378 pp., price DM 86—.

Professor KORTÜM's fundamental contributions in reflection spectroscopy are well known to those interested in this rather new field in analytical chemistry. In the present detailed monograph he provides us with a systematic and comprehensive treatment of the topic. After a short introduction chapter 2 deals with regular and diffuse reflection in general. Single and multiple scattering is dealt with in a separate chapter (3), followed by phenomenological theories of absorption and scattering on close packed particles (4). Here both the exponential and hyperbolic derivation of what is known as the KUBELKA–MUNK equation is presented, though the simplified treatment of SCHUSTER, which opens the chapter, might satisfy those who would like to use as little mathematics as possible. Further parts of this very important chapter try to elucidate the same problem from different angles. Chapter 5 deals with the experimental verification of the KUBELKA–MUNK theory, which in the course of the last fifteen years has been largely done by the author himself and his coworkers. The experimental methods themselves are summarised in the chapter that follows (6), while applications of the method are critically reviewed separately (7). The obtaining of reflection spectra by damped total reflection measurements is described in the last chapter (8), while some useful tables are collected into the Appendix—among them a detailed table of the KUBELKA–MUNK function and its logarithm. An index concludes the book.

The clear presentation of the subject, the thoroughness and comprehensiveness of the theoretical treatment and—last but not least—the authority of the writer commend this book, despite its price, to all who are interested in the theoretical and practical backgrounds of reflectance spectroscopy and in spectroscopy in general.

Anal. Chim. Acta, 49 (1970) 377

Chemical Applications of Spectroscopy, Edited by W. West, *Technique of Organic Chemistry*, Vol. IX, Part I, 2nd Edn., Interscience Publishers–J. Wiley and Sons, Inc., New York, 1968, x+486 pp., price 160 s.

It is twelve years since the first edition of Volume IX was first published. As with many of the other volumes of this excellent series, the rapid progress of chemistry has necessitated a complete revision. Inevitably, the proliferation of spectroscopic techniques, especially NMR, ESR and fluorimetry, has caused the second edition to be issued in two parts. This first part includes an introduction to molecular spectra (103 pp.), the theory (94 pp.) and interpretation (138 pp.) of electronic spectra, and phosphorimetry and fluorimetry (122 pp.). The discussions are comprehensive, but can readily be understood by non-specialists. The presentation is of the high standard usually associated with this series, and the text should be invaluable for organic and analytical chemists alike.

Computer Programs for Chemistry, Edited by Delos F. Deftar, Vol. I, W. A. Benjamin, Inc., New York, 1968, xix+208 pp., price $ 14.75.

This volume is the first of a proposed series collecting, in catalogue form, a range of fortran programmes for use in analysing physical chemistry problems. A chapter is devoted to each type of problem and describes the basic numerical principles used in the programme, together with adequate descriptions of the data input plus a listing of the programmes with suitable test data and outputs. The present volume is concerned with describing programmes for analysing NMR and kinetic data, the latter through a least square formulation to give first order reaction constants. From the presentation of the programme it should be possible for any chemist who is familiar with computing techniques, to use the programmes directly, although it would be tedious to try to reproduce them from the compact listings. The editor is aware of this problem and the publishers are willing to issue a master tape containing all the programmes. The difficulty with a catalogue presentation of computer programmes is that inevitably the analysis is divorced from both the experimental and theoretical principles used in obtaining the data. In the present text this is overcome to a considerable extent by the explicit list of references given with the programme. In general this and the subsequent volumes should fill a space in chemical reference literature as well as serve as a useful standard for future programmers when publishing their programmes.

A. DADIEU, R. DAMM AND E. W. SCHMIDT, *Raketentreibstoffe*, Springer-Verlag, Berlin, xviii + 805 pp., Clothbound, D.M. 340,—; $ 85.00.

This book, written in German, provides an excellent treatment of the subject of rocket propellants. It will be useful to engineers, chemists, and technicians working or associated with rocket motors and engines. The analytical chemical techniques suggested are satisfactory for the analysis of the principal oxidizers and fuels presently being used, but the discussion of these methods is limited. The authors give adequate treatment of several mixtures of hydrazines and of the impurities found in such oxidizers as fluorine, chlorine trifluoride, and oxygen. While many more analytical techniques could have been discussed, the methods presented are those most often used, including gas chromatographic and infrared methods. The authors have done an excellent job of presenting the data on propellant properties, discussing the problems associated with the use of rocket propellants, and providing a thorough reference list to the work of most of the principal contributors to this subject.

Y. MARCUS AND A. S. KERTES, *Ion-Exchange and Solvent Extraction of Metal Complexes*, Interscience – J. Wiley & Sons Ltd., London & New York, 1969, ix + 1037 pp., price 315 s.

Essentially, this is a physico-chemical monograph, in which the theoretical aspects of the title are discussed in detail. Presentation of the subject matter is based on the valid reasoning that ion-exchange and solvent-extraction techniques are complementary, and that neither can be applied to full advantage unless the behaviour of molecules in aqueous and organic media are clearly understood.

The first two chapters deal with electrolytes in aqueous and non-aqueous solutions; complex formation in solution is covered in Chapter 3. This is followed by a chapter on ion exchangers, and Chapter 5 and 6 discuss the cation and anion-exchange characteristics of metal complexes.

Solvent extraction is treated from a quantitative aspect in Chapter 7, and with respect to the species formed and their interactions, in Chapters 8 to 10. These three chapters deal with extractions based on compound formation, solvation, and ion-pair formation, respectively.

Synergic extraction is dealt with in Chapter 11, and Chapter 12 discusses the applications of distribution methods in studying complex formation in solutions.

The authors display a commendable knowledge of their subjects, based on first-hand experience. The book provides a fundamental basis for a detailed coverage of the chemistry of solutions and complex formation; it is supported by references, which must amount to several thousands, to published work up to 1967.

J. HIRTZ, *Les Méthodes Analytiques dans les Recherches sur le Métabolisme des Médicaments*, Masson et Cie, Paris, 1968, x+364 pp., price 98 F.

This unusual monograph presents a detailed review of the metabolic fate of a wide range of important drugs and antibiotics in which the experimental procedures used by the workers whose findings are summarized are described in some detail. The book therefore contains a wealth of information and will be of value to all workers in this field. The arrangement of the practical information will, however, make it more useful to readers seeking help in a specific and limited area than to those who require more general assistance. This could have been provided by the inclusion of summary tables or an index of experimental methods. There is an excellent bibliography covering the period to the end of 1966.

JOHANN KORKISCH, *Modern Methods for the Separation of Rarer Metal Ions*, Pergamon Press, Oxford, 1969, xii + 620 pp., price 150 s.

In presenting this publication, the author's objective was to provide the reader with up-to-date information on modern methods for separating over fifty less-common metals, by ion-exchange, liquid–liquid extraction, distillation or coprecipitation techniques, and this has been achieved by a careful selection and commendable coordination of the vast amount of scattered information available.

This broadly summarises the contents of the book's nineteen chapters, which deal with problems involving the actinide elements, rare earths, and many rarer metals of the main and transition groups of the periodic table.

The first chapter presents a short survey of the principles of modern techniques, without attempting to cover much of the experimental or theoretical information that has already been published. The remaining chapters contain information pertinent to the four separation processes, the fundamentals on which special separation principles are based, and practical problems associated with these branches of chemistry.

The book should appeal not only to the analyst with problems in this field, but to anyone engaged in related aspects of pure and applied research, because most of the procedures are discussed in great detail (there are about 4,000 references), and the relationship between the two fields is emphasised.

CONTENTS

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Short Communications

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