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Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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Publication Schedule for 1969

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

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

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Department of Chemistry,
The University,
P.O. Box 363
Birmingham 15 (Great Britain)

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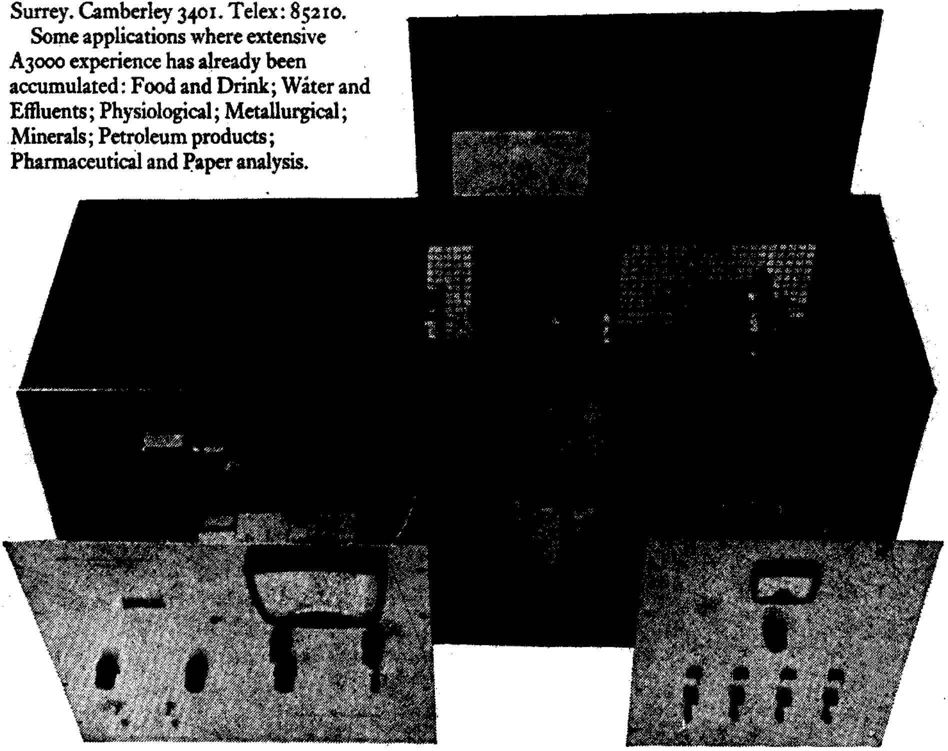

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G. Kortüm
Reflectance Spectroscopy

Principles, Methods, Applications

By Professor Dr. **G. Kortüm**, Institut für Physikalische Chemie
der Universität Tübingen
Translated from the German by Dr. **J. E. Lohr**, Philadelphia
With 160 figures. VI, 366 pages. 1969
Cloth DM 78,–

Also available in German:
G. Kortüm, Reflexionsspektroskopie
Grundlagen, Methodik, Anwendungen
Mit 160 Abbildungen
VIII, 378 Seiten. 1969
Gebunden DM 86,—

Reflectance spectroscopy differs from other spectroscopic methods in that it studies the spectral composition and angular distribution of light reflected from a surface. There are two limiting cases: regular reflectance from an ideal smooth surface and diffuse reflectance from an ideal matte surface, with all possible gradations in between.

The two main approaches of reflectance spectroscopy are fundamentally different and based upon the limiting cases. Regular reflectance relies upon dispersion theory, obtaining with the aid of the Fresnel equations two "optical constants" for the material in question: the index of refraction n and the index of absorption $\varkappa$. The use of a phase boundary between a dielectric of higher refractive index and the sample enables this method of "attenuated total reflectance" to be so far refined as to yield excellent spectra, especially in the infrared range.

Diffuse reflectance has to allow for the transfer of light within the sample by multiple scattering. There being no rigorous theory in this case, phenomenological theories of absorption and scattering in samples with close-packed particles have been developed, enabling qualitative and quantitative determinations of the coefficients of absorption and scattering to be carried out. Thus it becomes possible to obtain the spectra of solid powders and colloid solutions where there was previously no method available. The method also finds application in many problems concerned with the molecular structure of solids, adsorption and catalysis on surfaces, ligand field theory, the kinetics of solid-state and interface reactions, photochemistry and so on. It therefore represents a valuable addition to spectroscopic methods.

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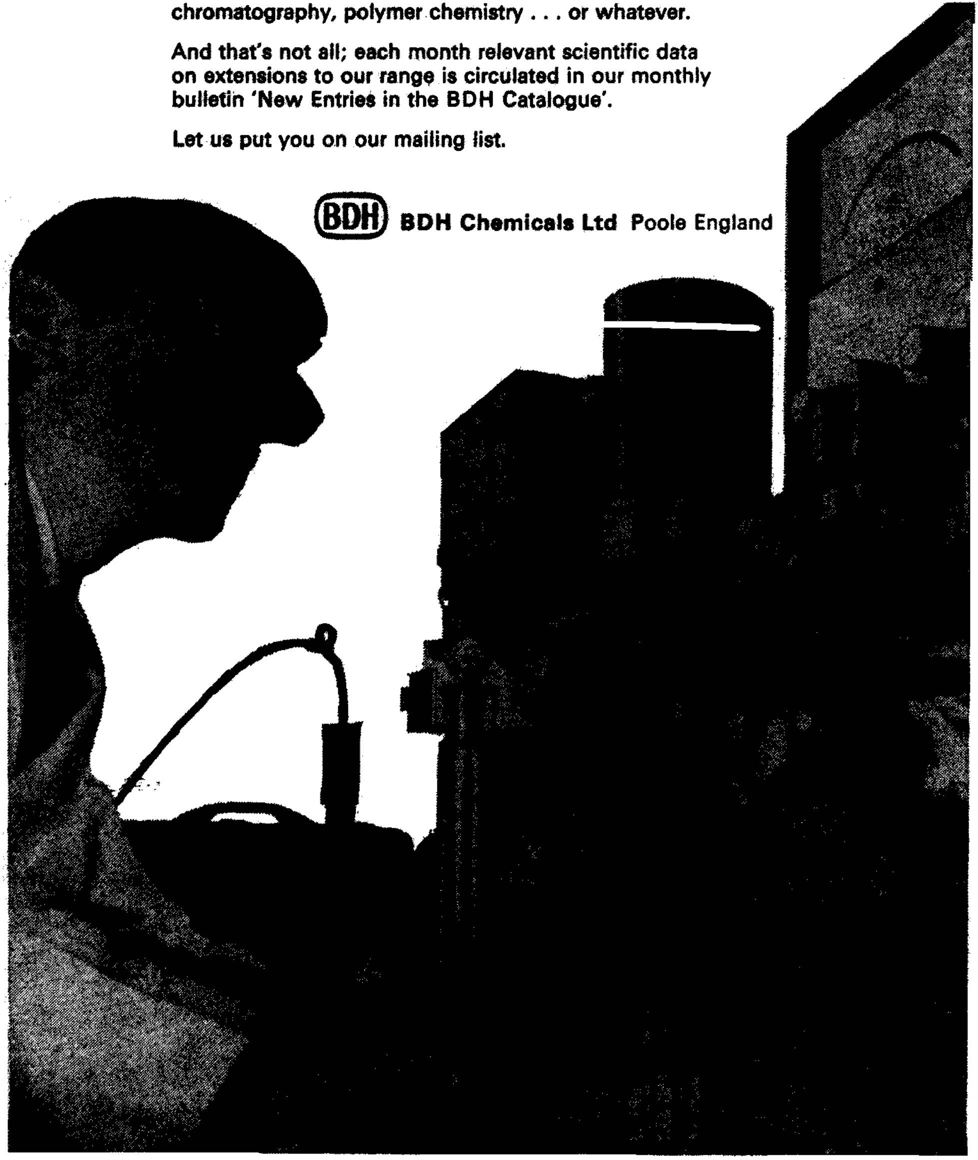

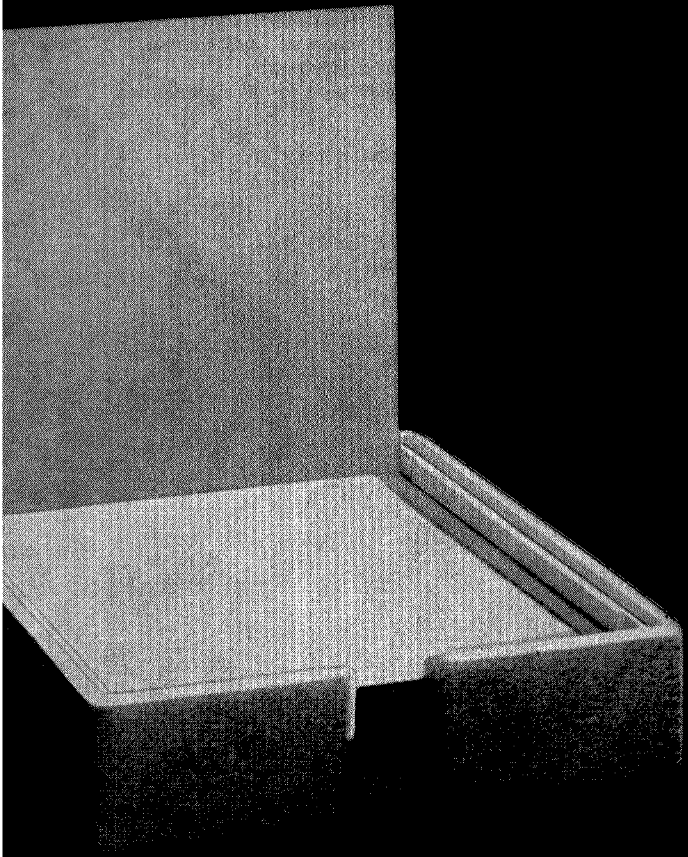

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 48, No. 1, November 1969

DETERMINATION OF IMPURITIES IN TITANIUM AND TITANIUM DIOXIDE BY NEUTRON ACTIVATION ANALYSIS

PART IV. DETERMINATION OF TRACE IMPURITIES IN TITANIUM DIOXIDE SINGLE CRYSTALS

The method is based on reactor irradiation and Ge(Li) spectrometry. An anion-exchange separation, followed by TBP solvent extractions, allows a rapid and accurate determination of up to 21 metallic impurities in titanium dioxide crystals. Of the elements investigated, only hafnium and protactinium, radioactive daughter of thorium, stayed with the matrix activity and hence could not be determined. Triplicate determinations were performed of three different samples. The sensitivity ranged from 10^{-12} g for iridium, to $5 \cdot 10^{-8}$ g for barium, for reactor irradiation at a thermal neutron flux of $5 \cdot 10^{12}$ n cm^{-2} sec^{-1} during one week.

R. Neirinckx, F. Adams and J. Hoste,
Anal. Chim. Acta, 48 (1969) 1–11

INSTRUMENTAL ACTIVATION ANALYSIS OF SILICATE ROCKS WITH EPITHERMAL NEUTRONS

The determination of some trace elements in standard rocks by epithermal neutron activation, followed by γ-ray spectrometry with a Ge(Li) detector, is described. The advantage of using this technique compared to corresponding analysis with thermal neutrons is clearly demonstrated in the case of Rb, Cs, Sr, Sb, Ta, and U. Determinations of Ba, Sm, Tb, Hf, and Th also appear to be favourable.

A. O. Brunfelt and E. Steinnes,
Anal. Chim. Acta, 48 (1969) 13–24

THE DETERMINATION OF THALLIUM IN SILICATE ROCKS, MARINE SEDIMENTS AND SEA WATER

An anion-exchange scheme has been developed for the preconcentration and almost specific separation of microgram and submicrogram amounts of thallium. It is used in conjunction with a fluorimetric method based on rhodamine B for the determination of 0.1–6 p.p.m. of thallium in silicate rocks and sediments. The method showed a coefficient of variation of 1.2% at the 6 p.p.m. level. A procedure is also described for the determination of thallium in natural waters in which the element is concentrated by anion exchange and determined by neutron activation. A sample of water from the Irish Sea was found to contain 18.7 ± 0.9 ng Tl/l.

A. D. Matthews and J. P. Riley,
Anal. Chim. Acta, 48 (1969) 25–34

Molecular Vibrations and Mean Square Amplitudes

by SVEN J. CYVIN

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

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

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

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

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

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

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

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

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THE ATOMIC FLUORESCENCE OF COPPER WITH A HIGH-INTENSITY HOLLOW-CATHODE LAMP

Copper is determined at 3248 Å by atomic fluorescence spectrometry with inexpensive, single-beam, unmodulated instrumentation with a high-intensity hollow-cathode lamp and a hydrogen/argon/entrained-air flame. The limit of detection is 0.003 μg/ml and the linear working range covers nearly five decades of concentration. Evidence is presented which suggests different fluorescence quantum efficiencies for the 3274 Å and 3248 Å fluorescence lines. In the presence of 0.01 *M* hydrochloric acid, only aluminum, phosphate and silicate give any chemical interference out of 31 species examined. An extensive study of the effect of light scattering by concomitants is presented and in favorable instances nearly 1% total dissolved solids can be tolerated. The degree of scatter was of the same order as for atomic absorption spectrometry, using low-temperature flames.

R. Smith, R. C. Elser and J. D. Winefordner,
Anal. Chim. Acta, 48 (1969) 35–43

DIRECT DETERMINATION OF ZINC IN SEAWATER BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

A direct atomic absorption spectrophotometric technique for the determination of total zinc in marine waters is described. The detection limit in a seawater matrix by this method is $2 \cdot 10^{-4}$ μg zinc, and 0.25-ml samples may be analysed without any pre-analysis preparation. Contamination problems are shown to be severe for zinc and initial attempts to evaluate the various chemical and physical forms in natural water samples have had limited success.

D. C. Burrell and G. Güner Wood,
Anal. Chim. Acta, 48 (1969) 45–49

A SINGLE-OVEN GAS CHROMATOGRAPH WITH A SIMPLE, ALL-QUARTZ, FLAME IONIZATION DETECTOR

A compact, inexpensive, single-oven gas chromatograph is described that has good stability and sensitivity. The flame ionization detector, flash chamber and column are mounted as an assembly on the oven top. The oven is constructed from a 4″ × 12″ aluminum pipe containing a continuous groove for retaining a nichrome heating wire. This design suggests the use of the apparatus on rechargeable nickel–cadmium or lead–acid batteries in field studies. The oven may be operated isothermally above 300° with low power input on either a.c. or d.c. The oven has been in continuous operation for over 3 years without maintenance. A simple flame ionization detector constructed entirely of quartz is also described. Although the gas chromatograph was constructed for glass columns in biomedical investigations, the apparatus can be used with metal columns as well as with other detectors in industrial applications. Detection of sub-microgram quantities of androgens is discussed.

S. F. Micheletti and G. T. Bryan,
Anal. Chim. Acta, 48 (1969) 51–61

SUBMICRO METHODS OF ORGANIC ANALYSIS

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

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

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

TECHNIQUES OF OSCILLOGRAPHIC POLAROGRAPHY

Second Edition, completely revised and enlarged

by R. KALVODA
Institute of Polarography, Czechoslovak Academy of
Sciences, Prague, Czechoslovakia
with a preface by Professor J. Heyrovský

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

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

TABLE OF META-STABLE TRANSITIONS FOR USE IN MASS SPECTROMETRY

by J. H. BEYNON, R. A. SAUNDERS AND A. E. WILLIAMS
Research Department, Imperial Chemical Industries Ltd.,
Manchester, Great Britain

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

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

STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Second International Symposium organized by the Chromatography
Group of the Czechoslovak Chemical Society, at Liblice
by K. MACEK AND I.M.HAIS

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

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

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A STATISTICAL STUDY OF GAS CHROMATOGRAPHIC SYSTEMS EMPLOYING FLAME IONIZATION DETECTORS

A statistically designed and interpreted series of experiments were performed with three commercially available chromatographs equipped with flame ionization detectors and operated with columns and under the conditions normally encountered in routine operation. The results in many cases agree with those previously published in studies of the detector system alone. In both cases the effect of air flow rate, polarizing voltage, and hydrogen flow rate are approximately the same. The linear range of sample size found was somewhat less than several published ranges, probably because of greater background noise. Carrier gas flow rate affected response, in contrast to the behavior of an isolated flame ionization detector. An important interaction of carrier gas flow rate and sample size was found; hydrogen flow rate–sample size, and hydrogen flow rate–carrier gas flow rate interactions were confirmed. It is suggested that additional carrier gas be added between column and detector to allow maintenance of optimum carrier flow rate. This study shows that system performance is generally less adequate than isolated component performance, being subject to various interactions which can most readily be examined by statistically designed experiments.

O. F. FOLMER, JR. AND DONALD J. HAASE,
Anal. Chim. Acta, 48 (1969) 63–78

EVALUATION OF ELECTRON SPIN RESONANCE FOR QUANTITATIVE DETERMINATIONS OF GADOLINIUM, CHROMIUM, IRON, COPPER AND MANGANESE

The use of e.s.r. as a routine quantitative analytical tool for non-destructive analysis of several metal ions in solution is examined. This application required the evaluation of numerous experimental parameters which affect the signal production. Limits of detection and analytical curves are presented for gadolinium, copper, iron, manganese, and chromium in ethanolic solution. Analytical selectivity and convenience of analysis are examined.

E. S. MOYER AND W. J. MCCARTHY,
Anal. Chim. Acta, 48 (1969) 79–85

THE DETERMINATION OF MIXTURES OF HYDRAZINE, MONOMETHYLHYDRAZINE AND 1,1-DIMETHYLHYDRAZINE

Admixtures of hydrazine and monomethylhydrazine (MMH) and of hydrazine with 1,1-dimethylhydrazine (UDMH) can be analysed by a titrimetric method in which two aliquots are titrated with potassium iodate: (*a*) directly to determine the sum of the hydrazines present, and (*b*) to determine the MMH or UDMH after selective reaction of the hydrazine with salicylaldehyde. For ternary mixtures, three aliquots are required: the sum of the hydrazines is determined with potassium iodate; the sum of MMH and UDMH is found after selective reaction of the hydrazine present with salicylaldehyde; and the UDMH content is obtained by non-aqueous solvent titrimetry after reaction of both hydrazine and MMH with acetic anhydride in dioxane.

H. E. MALONE AND D. M. W. ANDERSON,
Anal. Chim. Acta, 48 (1969) 87–91

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.

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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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THE GRAVIMETRIC DETERMINATION OF IRON WITH N-THIOBENZOYL-N-PHENYLHYDROXYLAMINE

Thiobenzoylphenylhydroxylamine (TBPHA) quantitatively precipitates iron(III) in 1 F acid solution as $Fe(C_{13}H_{10}NSO)_3$; the complex is ignited to Fe_2O_3. Aluminium, chromium, manganese and a number of common accompanying elements do not interfere. TBPHA can be used to separate copper from iron and to determine iron directly in the filtrate from the copper precipitation. Results obtained for iron standards, copper–iron mixtures, and steel and ore analyses are tabulated.

I. D. **Abraham**, J. **Abraham and** D. E. **Ryan**,
Anal. Chim. Acta, 48 (1969) 93–98

THE EXTRACTION OF LANTHANIDES AND ACTINIDES BY ALKYLPHOSPHINE OXIDES

PART V. THE EXTRACTION OF TRIVALENT ACTINIDES BY SOME DIPHOSPHINE DIOXIDES

(in French)

The distribution of trivalent actinides between an aqueous phase of constant ionic strength (2 M $NaNO_3$) and an organic solution of a diphosphine dioxide can be explained by the reaction:

$$Act^{3+}_a + 3\,NO_3{}^-_a + x(1,n\text{-DiPO})_o \rightleftharpoons Act(NO_3)_3 \cdot x(1,n\text{-DiPO})_o$$

The apparent stability constants were determined at 25° for some complexes:

$Am(NO_3)_3 \cdot 2$ (1,4-DiPO): $(3.7 \pm 0.3)\ 10^6\ M^{-2}$
$Am(NO_3)_3 \cdot 2$ (1,5-DiPO): $(8.4 \pm 0.5)\ 10^5\ M^{-2}$
$Cm(NO_3)_3 \cdot 2$ (1,5-DiPO): $(5.6 \pm 0.4)\ 10^5\ M^{-2}$
$Cf(NO_3)_3 \cdot 2$ (1,5-DiPO): $(8.7 \pm 0.5)\ 10^5\ M^{-2}$
$Am(NO_3)_3 \cdot$ (1,1-DiPO): $27 \pm 4\ M^{-1}$

J. **Goffart and** G. **Duyckaerts**,
Anal. Chim. Acta, 48 (1969) 99–106

EXTRACTION OF METALS WITH ALIPHATIC KETONES

(in German)

The extractability of a series of elements from hydrochloric acid solutions with ethyl methyl ketone, methyl propyl ketone and ethyl butyl ketone was investigated. Quantitative extraction of molybdenum(VI), iron(III), gold(III), gallium(III), indium(III), thallium(III), and arsenic(III) was obtained. Some separations are outlined. Conductometric extraction titrations established that gallium was extracted as $[GaCl_4]^-$ and molybdenum as $[MoO_2Cl_3]^-$ and $[MoOCl_5]^-$.

E. **Gagliardi and** H. P. **Wöss**,
Anal. Chim. Acta, 48 (1969) 107–114

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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CHELATES OF β-DICARBONYL COMPOUNDS AND THEIR DERIVATIVES

PART XVI. THIODIBENZOYLMETHANE AS EXTRACTION–PHOTOMETRIC AND GRAVIMETRIC REAGENT FOR COBALT

(in German)

Cobalt(II) salts react rapidly with β-monothioketones to form cobalt(III) chelates. At low temperatures and under anaerobic conditions, cobalt(II) chelates of thiothenoyltrifluoracetone and thioisobutyrylacetone can be isolated; their magnetic behaviour indicates a tetrahedral structure. The use of thiodibenzoylmethane for the extraction–photometric determination of cobalt is described. Owing to the considerable kinetic stability of the formed cobalt(III) chelate, interfering metals can be separated by reextraction with sodium hydroxide solution containing cyanide, except in the case of copper. Thiodibenzoylmethane is also suitable for the gravimetric determination of cobalt in the range 2–15 mg. In the presence of thiourea, copper and manganese do not interfere in up to 10-fold amounts; zinc can be kept in solution by means of ammonia and ammonium thiocyanate, but iron must be separated by ether extraction.

E. UHLEMANN AND H. MÜLLER,
Anal. Chim. Acta, 48 (1969) 115–122

A RAPID AND HIGHLY SENSITIVE SINGLE-SWEEP POLAROGRAPHIC METHOD OF ANALYSIS FOR ARSENIC(III) IN DRINKING WATER

A simple, rapid, and extremely sensitive method of analysis for arsenic in drinking water is presented. The method is a single-sweep polarographic technique that will determine as little as 5 p.p.b. arsenic with a relative error of 5–10% of the actual concentration. No special treatment of the sample is needed before the analysis. The method is useful in the examination of well water, spring water, and other drinking waters that contain arsenic in very low quantities (50 p.p.b. or less). The method is shown to give more reliable results on drinking water than the Gutzeit method currently used by water chemists in the analysis of arsenic at low levels.

G. C. WHITNACK AND R. G. BROPHY,
Anal. Chim. Acta, 48 (1969) 123–127

REACTION THERMAL ANALYSIS OF ORGANOPOLYSILOXANES

A new method of thermal analysis based on the reaction of the test substance with a suitable reagent under programmed temperature conditions is described. The gaseous reaction products are detected by gas chromatography. The splitting of low-molecular-weight organopolysiloxanes by sulphuric acid is used as an example to illustrate the relationship between the structure of the test substance and the temperature at which the splitting of the individual functional groups occurs. The method seems applicable for identifying chemical groups and their location in certain types of molecules.

J. FRANC AND J. POUR,
Anal. Chim. Acta, 48 (1969) 129–137

INTRODUCTION TO NUCLEAR CHEMISTRY

by D. J. Carswell

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

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

STATISTICAL THERMODYNAMICS

An Introduction to its Foundations

H. J. G. Hayman

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

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Appendices: 1. The probability integral. 2. Stirling's formula for $\ln n!$. 3. The method of variation of constants. 4. The dynamic equilibrium of a microcanonical assembly. 5. The adiabatic principle. 6. Liouville's theorem. Index.

THE STRUCTURE OF INORGANIC RADICALS

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

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

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

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Appendices: 1. The language of group theory. 2. The spin Hamiltonian. 3. Calculation of g-values. 4. Determination of spin-density distribution and bond angles. 5. Analysis of electron spin resonance spectra. Index of data. Subject index.

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THE BROMOMETRIC DETERMINATION OF BULK ENOL CONTENT OF β-DIKETONES THAT UNDERGO RAPID TAUTOMERIZATION

The bulk enol content observed for the model compound 2,4-pentanedione as determined by bromometric methods depends on the time interval between addition of bromine and quenching with phenol. The largest influence on the results was observed in polar solvents. On the assumption that bromination occurs instantaneously, discrete quench-time results were extrapolated to zero time and compared with proton magnetic resonance measurements. Good general agreement was found between the methods in all cases, although definite relative error trends were observed in the bromometric results. The technique proposed permits the use of the chemical technique in cases where proton magnetic resonance is not applicable.

C. H. LOCHMÜLLER, T. MALDACKER AND M. CEFOLA,
Anal. Chim. Acta, 48 (1969) 139–144

GRAVIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM, RHODIUM AND RUTHENIUM WITH THIOSALICYLAMIDE

Thiosalicylamide is proposed for the gravimetric and spectrophotometric determination of palladium, rhodium and ruthenium. The precipitates formed with palladium, rhodium and ruthenium can be dried at 110°–120° for direct weighing and correspond to $Pd(C_7H_7ONS)_4Cl_2$, $Rh(C_7H_6ONS)_3$ and $Ru(C_7H_6ONS)_2$ respectively. Palladium can be separated from rhodium or ruthenium in highly acidic solution; under suitable conditions, Co, Ni, Mn, Fe, Zn, Mo(VI), W(VI), Al, Ga, In, V(V), Ir, etc., do not interfere. The metal–thiosalicylamide complexes form coloured solutions in common organic solvents, so that spectrophotometric determinations are possible. The Pd complex is dissolved in 50% ethanol whereas the rhodium or ruthenium complex is extracted with a mixture of isobutyl methyl ketone and ethanol. Maximum absorbance is obtained at 350, 380 and 390 nm, and the molar absorptivities are 39,300, 7000 and 6330 for the Pd, Rh and Ru complexes, respectively. Few ions interfere.

K. SUR AND S. C. SHOME,
Anal. Chim. Acta, 48 (1969) 145–153

N-BENZOYL-N-PHENYLHYDROXYLAMINE AS A COLORIMETRIC REAGENT FOR CERIUM

N-Benzoyl-N-phenylhydroxylamine is recommended as a spectrophotometric reagent for cerium. It extracts cerium in the pH range 8–10. Beer's law is obeyed in the concentration range of 4–40 p.p.m. of CeO_2. Cerium(III) is oxidised automatically to cerium(IV) during the colour development stage. The method has been applied to samples such as lanthanum oxide, cerium glass, G-1 and carbonatites.

P. MURUGAIYAN AND M. SANKAR DAS,
Anal. Chim. Acta, 48 (1969) 155–160

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by **M. Haïssinsky** and **J.-P. Adloff**

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

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

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Appendices: The language of group theory. The spin hamiltonian. Calculation of *g*-values. Determination of spin-density distribution and bond angles. Analysis of electron spin resonance spectra. Index.

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THE PHOTOMETRIC DETERMINATION OF TRACES OF BISMUTH WITH 7-[α-(*o*-CARBOMETHOXYANILINO)BENZYL]-8-HYDROXYQUINOLINE

(in German)

The possibility of extracting trivalent metals (Al, Ga, In, Tl, Bi, La, Cr, Fe(III)) with CMAB-oxine was examined; only bismuth, indium and thallium could be extracted. Differences in the selectivities of oxine, 2-methyloxine and CMAB-oxine are discussed. The composition of the bismuth-CMAB-oxinate is 1:3. Bismuth can be extracted and determined spectrophotometrically at pH 12.2 ± 0.4; the molar absorptivity at 400 nm is $7.2 \cdot 10^3$. The method is selective and reproducible.

G. Röbisch,
Anal. Chim. Acta, 48 (1969) 161–167

GAS CHROMATOGRAPHIC QUALITATIVE AND SEMIQUANTITATIVE ANALYSIS OF APPLE AROMA BY MEANS OF RETENTION INDEXES

The components of two varieties of apples were investigated by gas chromatography. After a flash distillation method to concentrate the apple juice, aroma chromatograms were obtained in four columns of different polarity. When the values of the peak retention indexes were compared with the indexes of standard compounds, 25–26 volatile components could be identified. These constituents were semiquantitatively measured by means of peak heights. Fundamental differences in the aroma of the two apple varieties were established by this method.

J. Martín Mira,
Anal. Chim. Acta, 48 (1969) 169–176

POLAROGRAPHIC CHARACTERISTICS OF COPPER IONS IN AZIDE SOLUTIONS

The step-wise and reversible reduction of copper(II) ions in supporting electrolytes consisting of 0.5–4.0 *M* sodium azide at constant ionic strength was studied; the behaviour was different from that observed in thiocyanate solutions. The diffusion current constant for the sum of the two waves, in 4.0 *M* sodium azide supporting electrolyte, is 2.62 and is exactly twice the value for the first wave. The maximum number of azide ligands was found to be 4 and 3 for copper(II) and copper(I), respectively. No evidence was found for polynuclear species.

P. Senise and E. F. De Almeida Neves,
Anal. Chim. Acta, 48 (1969) 177–183

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.

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Proceedings of the International Symposium held in Cardiff, 1965

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DETERMINATION OF SULFIDE WITH CRYSTAL VIOLET–TETRAIODOMERCURATE(II) ION-ASSOCIATION REAGENT

(Short Communication)

J. L. LAMBERT AND D. J. MANZO,
Anal. Chim. Acta, 48 (1969) 185–186

STUDIES WITH DITHIZONE

PART XIX. A PHOTOCHEMICAL OXIDATION PRODUCT OF DITHIZONE

(Short Communication)

H. M. N. H. IRVING AND D. C. RUPAINWAR,
Anal. Chim. Acta, 48 (1969) 187–188

SOME CHEMICAL INTERFERENCES IN THE ATOMIC ABSORPTION SPECTROPHOTOMETRY OF CALCIUM

(Short Communication)

J. Y. HWANG AND L. M. SANDONATO,
Anal. Chim. Acta, 48 (1969) 188–191

DETERMINATION OF RHENIUM AND MOLYBDENUM AND THEIR SEPARATION FROM EACH OTHER AND OTHER IONS BY INTERNAL ELECTROLYSIS

(Short Communication)

A. K. MAJUMDAR AND GOURI BHOWAL,
Anal. Chim. Acta, 48 (1969) 192–195

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.

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

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DETERMINATION OF IMPURITIES IN TITANIUM AND TITANIUM DIOXIDE BY NEUTRON ACTIVATION ANALYSIS

PART IV. DETERMINATION OF TRACE IMPURITIES IN TITANIUM DIOXIDE SINGLE CRYSTALS

R. NEIRINCKX, F. ADAMS AND J. HOSTE
Institute for Nuclear Sciences, Ghent University, Ghent (Belgium)

(Received July 22nd, 1969)

Titanium dioxide crystals are distributed widely in nature, and are usually present in the form of fine particles in other minerals. Large crystals seldom occur; large rutile crystals can be found in Norway, but most crystals are produced artificially, usually by the VERNEUIL and CZOCHRALSKI methods. These are used as rubies in watches and recently, because of their hardness and high refractive index, as gems.

The recent literature mentions only one article on the analysis of rutile single crystals and doped rutile single crystals by spectrometry of 0.007–0.7% of iron, magnesium, aluminium and silicon[1]. In the present work a procedure is elaborated for a rapid determination of 21 metallic impurities in titanium dioxide crystals. The method consists of a reactor irradiation of the sample and subsequent γ-spectrometry with a high-resolution detector, after some simple group separations.

Nuclear data and interferences

Pertinent nuclear data for reactor irradiation of titania are summarized in Table I. The only important radioactive titanium isotope, ^{51}Ti, can only interfere in

TABLE I

NUCLEAR DATA OF THE ISOTOPES, FORMED BY REACTOR IRRADIATION OF TITANIA

Reaction	*Activation cross-section (barn)*	*Half-life of the reaction product*	*Decay and energy (MeV)*
^{50}Ti(n,γ)^{51}Ti	0.14	5.8 min	β^- 2.13 γ 0.3200; 0.6084; 0.9285
^{46}Ti(n,p)^{46}Sc	$8 \cdot 10^{-3}$	84 d	β^- 0.357 γ 0.8894; 1.1203
^{47}Ti(n,p)^{47}Sc	$15 \cdot 10^{-3}$	3.44 d	β^- 0.439 γ 0.1600
^{48}Ti(n,p)^{48}Sc	$4 \cdot 10^{-3}$	1.83 d	β^- 0.65 γ 0.9835; 1.0376; 1.3118
^{46}Ti(n,2n)^{45}Ti	$5 \cdot 10^{-6}$	3.07 h	β^+ 1.02; E.C. γ 0.718; 1.238; 1.408
^{50}Ti(n,α)^{47}Ca $\xrightarrow{\beta^-}$ ^{47}Sc	$4 \cdot 10^{-7}$	4.7 d	β^- 0.67 γ 1.2969 (^{47}Ca)

the determination of short-lived species. The cross-section for the ^{46}Ti(n,2n)^{45}Ti reaction is too small to give rise to an important activity. Calcium and scandium can hardly be determined quantitatively in titanium compounds by means of reactor irradiation and subsequent γ-ray spectrometry, as the only long-lived γ-ray emitting calcium isotope ^{47}Ca, is also formed by the ^{50}Ti(n,α)^{47}Ca reaction. This reaction gives rise to an apparent calcium concentration of 300 p.p.m. if we assume the thermal-to-fast neutron flux ratio to be 10, which is quite reasonable in the irradiation conditions used, and the cross-section of the (n,α) reaction to be $4\cdot10^{-7}$ barn[2]. If this cross-section is assumed to be $4\cdot10^{-6}$ barn, as was estimated by Roy and Hawton[3], then the interference on the calcium determination is 3,000 p.p.m. The ^{46}Sc isotope, used for the determination of scandium by reactor irradiation, is also formed by (n,p) reaction on the stable ^{46}Ti isotope. Hence, scandium cannot be determined accurately in titanium compounds, unless an irradiation with and without cadmium is applied. For the determination of the long-lived isotopes, long irradiation and cooling periods are introduced and the radioactive scandium isotopes will constitute the major activity. A chemical separation from scandium is thus required.

The nuclear data of the radionuclides, produced from the trace constituents in titanium dioxide crystals by reactor irradiation, are shown in Table II. A list of the γ-rays used for the quantitative determinations of these elements is included[4].

In a previous publication[5], the importance of the self-shielding effect was calculated to be negligible in the case of titania powder. However, the density of the titanium dioxide crystals is much higher than for the powder, resulting in a higher self-shielding effect.

TABLE II

IMPURITIES IN TITANIUM DIOXIDE CRYSTALS—NUCLEAR DATA

Target nuclide	*Abundance (%)*	*Reaction product*	*Activation cross-section (barn)*	*Half-life*	*γ-Radiation used (MeV)*
^{109}Ag	48.2	^{110m}Ag	2.8	270 d	0.6578; 0.8845; 0.9372
^{197}Au	100	^{198}Au	96	2.7 d	0.4118
^{130}Ba	0.10	^{131}Ba	8.8	11.6 d	0.1242; 0.2161; 0.3731
^{140}Ce	88.5	^{141}Ce	0.5	32.5 d	0.1454
^{59}Co	100	^{60}Co	36	5.2 y	1.1731; 1.3324
^{50}Cr	4.31	^{51}Cr	11	27.8 d	0.3200
^{63}Cu	69.1	^{64}Cu	3.0	12.8 h	0.5110; 1.3455
^{151}Eu	47.8	^{152}Eu	1,700	13 y	0.1218; 0.3442; 1.4074
^{58}Fe	0.33	^{59}Fe	0.9	45.1 d	1.0986; 1.2915
^{71}Ga	39.6	^{72}Ga	3.4	14.2 h	0.6301; 0.8341; 2.2014
^{191}Ir	37.3	^{192}Ir	960	74 d	0.2958; 0.3165; 0.4679
^{41}K	6.9	^{42}K	1.1	12.4 h	1.5247
^{139}La	99.9	^{140}La	8.9	40.2 h	0.3286; 0.4868; 1.5954
^{98}Mo	23.8	^{99}Mo	0.13	67 h	0.1406; 0.1809; 0.7399
^{23}Na	100	^{24}Na	0.54	14.8 h	1.3684; 2.7536
^{58}Ni	67.9	^{58}Co	0.105	71 d	0.8103
^{121}Sb	57.2	^{122}Sb	3.7	2.8 d	0.5640; 0.6925; 1.1405
^{152}Sm	26.72	^{153}Sm	216	47 h	0.0696; 0.1032
^{181}Ta	99.99	^{182}Ta	19	111 d	0.0677; 0.1003; 1.1212; 1.2216
^{186}W	28.4	^{187}W	34	23.9 h	0.1343; 0.4793; 0.6857
^{64}Zn	48.9	^{65}Zn	0.25	254 d	1.1154

The ratio of the medium value of the neutron flux throughout the material to the flux through the standards can, for a cylindrical sample with radius R, be calculated by the equation

$$f = 1 - \frac{8}{3}\frac{\sigma NR}{\pi} + \frac{1}{2}(\sigma NR)^2 - \frac{32}{45}\frac{(\sigma NR)^3}{\pi} + \frac{1}{12}(\sigma NR)^4$$

assuming the neutron flux to be perpendicular to the cylinder axis. The absorption cross-section for titanium is 5.6 barn, and the number of titanium atoms cm^{-3} is $3.2 \cdot 10^{22}$. The calculated decrease of the neutron flux throughout the material is 1.8%. The error from self-shielding was therefore neglected.

Dissolution of the sample

Titanium dioxide is very resistant to chemical attack. Boiling concentrated sulfuric acid or hydrofluoric acid only allows a very slow dissolution of even very finely ground titanium dioxide crystals. Fusion with potassium hydrogen fluoride has the inconvenience of losing volatile compounds of some elements (*e.g.* As, Se and Ge), but has the advantage of speed; 50-mg samples of a crystal can be dissolved in 500 mg of potassium hydrogen fluoride within 30 min. The titanium dioxide single crystals are only very slowly soluble by pressure-tube attack; when 50-mg amounts of the finely ground sample are heated in a 10-ml pyrex tube with 4 ml of 12 M hydrochloric acid at 225°, only 50% is dissolved after 24 h. Longer reaction times cannot be applied to the irradiated sample in view of the short half-life of several isotopes used for the analysis. Pressure-tube attack at temperatures above 225° resulted in a sharp increase in the frequency of explosion of the reaction tube. Although the dissolved fraction could easily be determined by activity measurements, the pressure-tube method was not applied, as there was uncertainty about the possible preferential leaching of some impurities from the crystal surface by the hydrochloric acid solution.

Separation scheme

The potassium fluoride cake, spread over the inside of the platinum crucible after the potassium hydrogen fluoride fusion, can easily be dissolved in water, or dilute acid. The previously discussed procedure[5], used for the separation of the impurities in titania powder from the scandium isotopes, could not be applied as it starts with an elution from a strongly basic anion exchanger, with dilute hydrofluoric acid; the potassium fluoride remaining after the fusion forms a buffer system with the weakly acidic hydrofluoric acid. Even with 10 M hydrofluoric acid, the pH of a 40-ml solution of the potassium fluoride, remaining from 500 mg of flux, is 1.4. Experiments showed that scandium and antimony hydrolyze partially in this condition, so that their separation from the elements with low K_D-values on an anion exchanger in hydrofluoric acid, is unsatisfactory.

To keep the pH of the solution low, the potassium fluoride cake must be dissolved in a solution of a strong acid, *e.g.* 9 M hydrochloric acid. In this medium scandium and titanium have a very low distribution constant on an anion-exchange resin. The decomposition of 500 mg of potassium hydrogen fluoride yields 6.25 mmoles of potassium fluoride and this will be almost completely converted to hydrofluoric acid on addition of hydrochloric acid. This results in 40 ml of solution which is 8.85 M in hydrochloric acid, 0.15 M in hydrofluoric acid and 0.15 M in potassium chloride.

The column is washed with 9 *M* hydrochloric acid. The behaviour on an anion-exchange resin of the most important metallic impurities in these working conditions were checked and are summarized in Table III. A number of elements, *i.e.* the rare earths, the alkali and alkaline earth metals, chromium, silver, protactinium and hafnium, are eluted, together with the scandium activity, while Au, Co, Cu, Fe, Ga, Ir, Mo, Sb, Ta, W, Zn are retained by the resin. In order to obtain a better sensitivity for the elements eluted together with scandium, an additional separation is necessary. This can be performed by tri-*n*-butyl phosphate (TBP) extraction from a 12 *M* hydrochloric acid solution. Scandium is extracted in this way[6], while a number of elements remain in the aqueous solution. The results of the tracer experiments for this separation are shown in Table III. Chromium, the light rare earths, the alkali and the alkaline earths can be separated by two successive extractions with TBP. Heavy rare earths are partially extracted, but backwashing with hydrochloric acid allows an almost quantitative recovery, whereas scandium remains in the organic layer. Silver can be recovered by stripping the TBP fraction with a small volume of 14 *M* nitric acid. Scandium remains in the organic phase[6]. The nitric acid fraction is then added to the 12 *M* hydrochloric acid fraction, in order to collect all the silver in one group. Table III also lists the tracer experiments for these operations. It appears that among the tested elements, only hafnium and the protactinium daughter of thorium stay with the scan-

TABLE III

BEHAVIOUR OF THE MOST IMPORTANT METALLIC ELEMENTS ON ANION-EXCHANGE RESIN IN HYDROCHLORIC ACID MEDIUM AND ON EXTRACTION WITH TRIBUTYL PHOSPHATE FROM HYDROCHLORIC AND NITRIC ACID

Element	*Anion exchange*		*Extraction*			
			From 12 M HCl		*From 14 M HNO_3*	
	Resin fraction (%)	*Eluate (%) (total of 80 ml)*	*Aq. layer (%)*	*Org. layer (%)*	*Aq. layer (%)*	*Org. layer (%)*
Sc		99.9	0.3	99.7		99.5
Ag		>99.4	60	40	>97	
Au	>99.5					
Ba		>96	>98			
Ce		>97	97	3		
Co(Ni)	>98.8					
Cr		>98	99.1	0.9		
Cu	>99.2					
Fe	>99.7					
Ga	>99.99					
Hf		>99.8	3	97		>99.7
Ir	>98.5					
K		>99.5	>99			
Mo	>99.6					
Na		98.8	>99.7			
Pa(Th)		>98		>99	2	98
Sb	>99.2					
Ta	>99					
W	>99.6					
Zn	>99					
Lu		>99.6		12	45	55

dium activity after the successive separation steps. Consequently, hafnium and thorium cannot be analyzed with a high sensitivity. After the separations two groups remain to be measured on the high-resolution detector:

1. The resin fraction, containing over 99% of the total amount of Au, Co, Cu, Fe, Ga, Ir, Mo, Sb, Ta, W and Zn.

2. A nitric–hydrochloric acid fraction (40 ml), containing chromium, silver, the rare earths, the alkalis and the alkaline earths.

γ-Ray spectra of both fractions for one of the samples (crystal) are shown in Figs. 1 and 2. Figure 3 shows the spectrum of an unseparated sample, demonstrating that non-destructive analyses were impossible.

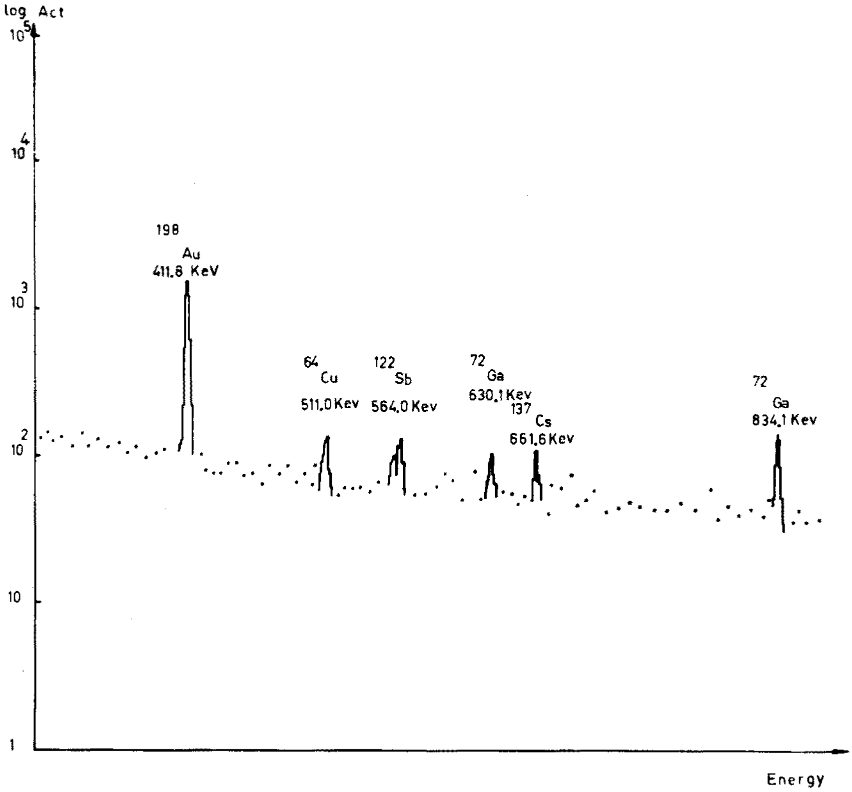

Fig. 1. γ-Spectrum of the resin fraction.

EXPERIMENTAL

Instrumental

Two Ge(Li) spectrometers were used. One was an 18-cm^3 detector, coupled to a Tennelec (TC 200) amplifier, an Intertechnique analog to digital converter (CA 13) and a BM 96 4096-channel memory unit. The other was a 40-cm^3 detector coupled to an Ortec (440A) amplifier, an Intertechnique C 42 X ADC and a Didac 4000-channel memory unit. Integration and differentiation time constants were 1.6 μsec for counting rates not exceeding 1,000 counts sec^{-1}, whereas a doubly differentiated pulse

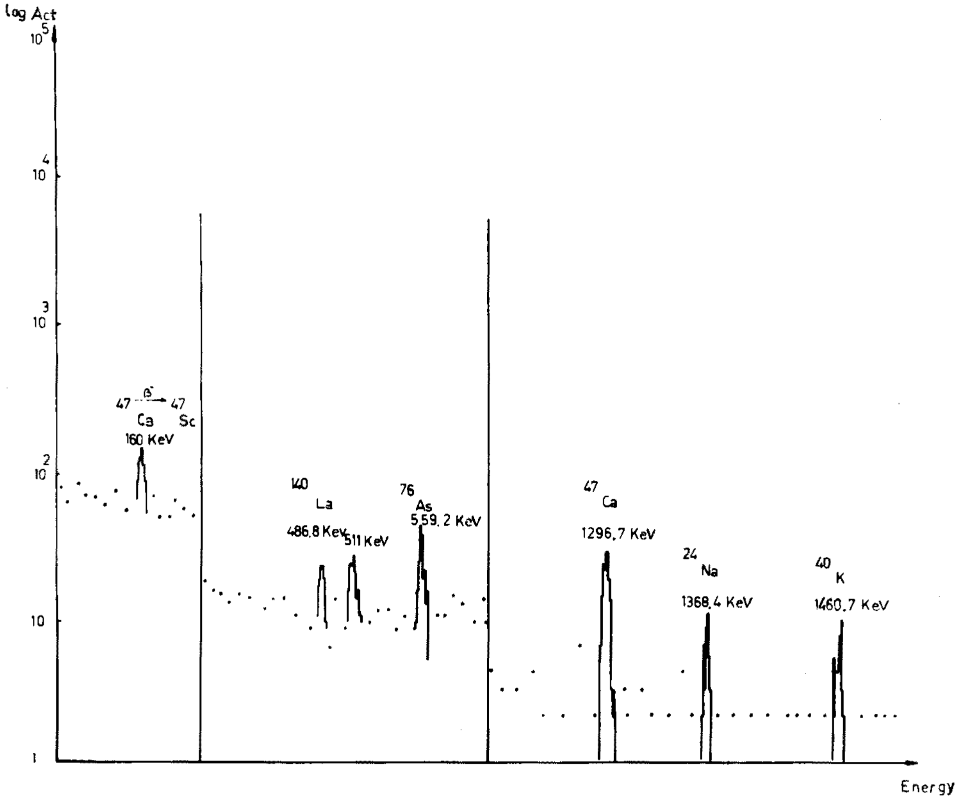

Fig. 2. γ-Spectrum of the nitric–hydrochloric acid fraction.

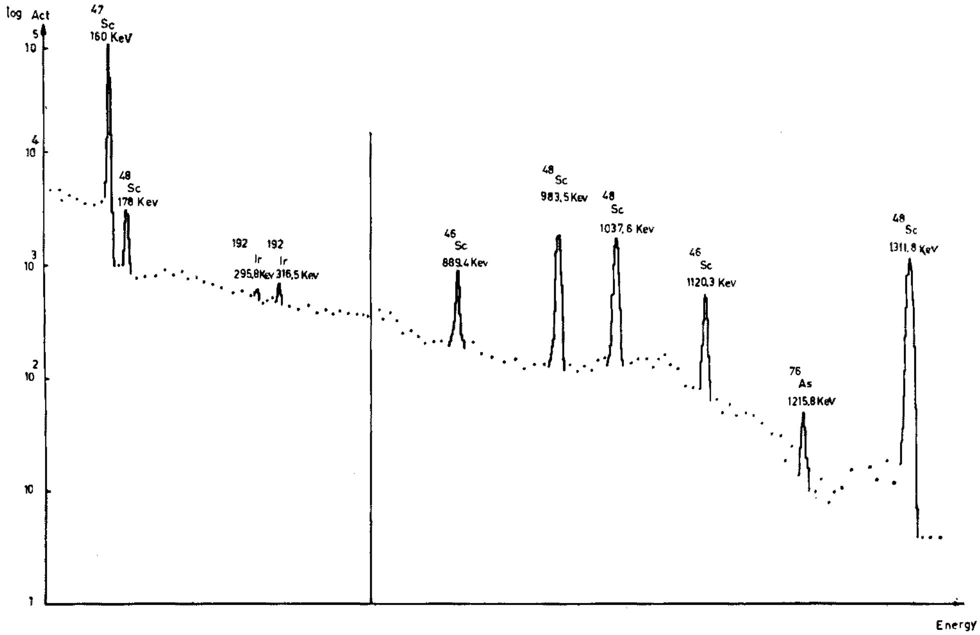

Fig. 3. γ-Spectrum of an unseparated sample.

shape was chosen to insure a symmetrical peak and to prevent any errors caused by pulse pile-up in the case of higher count rates. In the Didac 4000 spectrometer, count-rate effects were eliminated by using pole-zero cancellation and base line restoration.

Preparation of the standards

As 21 elements were determined quantitatively, it was hardly possible to enclose each of the standards in a separate quartz tube and reserve enough space for a number of samples in the irradiation container. On the basis of their solubilities, the standards were divided into seven groups. Co–Al alloy, ZnO, Ga_2O_3, CuO, Fe, NiO, Cr, $CaCO_3$ and $BaCO_3$ were dissolved in 6 *M* hydrochloric acid; the oxides of the rare earths were separately dissolved in 6 *M* hydrochloric acid; Na_2CO_3, K_2CO_3 and $AgNO_3$ were dissolved in dilute nitric acid; $Na_2WO_4 \cdot 2H_2O$, $(NH_4)_6\ Mo_7O_{24} \cdot 4H_2O$ and Sb_2O_3 in 6 *M* ammonia solution, to which ammonium tartrate was added; Ta_2O_5 was fused with potassium hydrogen sulfate, precipitated with ammonia solution and dissolved in 5% oxalic acid; gold was treated with aqua regia, while iridium was brought into solution by a pressure tube method with hydrochloric and nitric acids. A suitable concentration of these elements was chosen so as to insure that in the γ-spectrum the peak areas of the main γ-rays were of comparable heights. The concentration of each element is shown in Table IV; 10 μl of each solution was pipetted and evaporated in a quartz tube. After irradiation, the standards were dissolved in a suitable solvent and counted in the same geometrical conditions as the corresponding sample fractions.

TABLE IV

CONCENTRATION OF THE STANDARD SOLUTIONS

Solvent	*Element*	*Concentration (μg/10 μl)*	*Solvent*	*Element*	*Concentration (μg/10 μl)*
6 *M* HCl	Ba	2,000[a]	Dilute HNO_3	Na	1
	Ca	2,000[a]		K	100
	Co	10		Ag	20
	Cr	20			
	Cu	20	$KHSO_4$ fusion dissolved in 5% oxalic acid	Ta	1
	Fe	3,000[a]			
	Ga	2			
	Ni	3,000[a]			
	Zn	20	Aqua regia	Au	0.1
6 *M* HCl	Ce	5	Pressure tube ($HCl + HNO_3$)	Ir	0.1
	Eu	0.1			
	La	5			
	Sm	1			
6 *M* NH_4OH + NH_4-tartrate	Mo	10			
	Sb	5			
	W	1			

[a] Added in solid form after evaporation of the solution of the other standards.

Irradiation conditions

Samples were enclosed in quartz tubes and irradiated in the BR-2 reactor at the S.C.K. (Mol) at a flux of $5 \cdot 10^{12}$ n cm^{-2} sec^{-1} during one week. The short-lived isotopes cannot be determined in this way, because of the long waiting period, caused by the transfer time (24 h) from Mol to Ghent.

Separations

Place the 50-mg sample on the bottom of a platinum crucible, cover with 500 mg of potassium hydrogen fluoride and heat over a low flame during 30 min. Dissolve the potassium fluoride cake in 10 ml of water and add 30 ml of 12 *M* hydrochloric acid. Transfer to a Dowex 1-X8 anion-exchange column (height: 13 cm, diameter: 1 cm) and elute with an additional 40 ml of 9 *M* hydrochloric acid. Measure the γ-ray spectrum of the resin for Au, Co(Ni), Cu, Fe, Ga, Ir, Mo, Sb, Ta, W and Zn. Evaporate the eluate almost to dryness in a plastic beaker. Add 10 ml of 12 *M* hydrochloric acid and evaporate twice more to expel all hydrofluoric acid. Add 20 ml of 12 *M* hydrochloric acid. Extract twice with 10 ml of TBP equilibrated with 12 *M* hydrochloric acid. Wash the organic phase with 10 ml of 12 *M* hydrochloric acid. Strip the organic phase with 10 ml of 14 *M* nitric acid. Combine all the aqueous phases and count for Ag, Ba, Ce, Cr, Eu, K, La, Na and Sm.

Calculation of the results

The concentrations were calculated from the ratios of the photo peak areas for samples and standards. A computer program searched for every statistically significant peak, after data smoothing and differentiation. The net photo peak activity was then calculated[7].

TABLE V

CONCENTRATION OF IMPURITIES IN TITANIUM DIOXIDE CRYSTALS
(All concentrations are given in p.p.m.)

Element	*Analysis 1*	*Analysis 2*	*Analysis 3*	*Median value* $\bar{x}$	*Error*(%)
Crystal 1					
Ag	<0.07				
Au	0.00016	0.00019	—	0.00017	
Ba	<4				
Ce	<0.4				
Co	<0.005				
Cr	0.52	0.49	0.50	0.50	2
Cu	0.54	0.62	0.56	0.57	4
Eu	<0.004				
Fe	<3				
Ga	<0.03				
Ir	<0.00004				
K	<4				
La	0.0063	—	—	0.0063	
Mo	<0.5				
Na	0.32	0.68	—	0.50	
Ni	<2				
Sb	<0.0005				
Sm	<0.003				
Ta	<0.006				
W	0.029	0.039	0.032	0.033	9
Zn	<0.1				
Ca[a]	7,700	7,000	8,040	7,580	5

TABLE V (Continued)

Element	*Analysis 1*	*Analysis 2*	*Analysis 3*	*Median value* $\bar{x}$	*Error*(%)
Crystal 2					
Ag	<0.08				
Au	<0.00006				
Ba	<3				
Ce	<0.4				
Co	<0.003				
Cr	0.32	0.37	0.31	0.33	4
Cu	1.50	1.03	1.44	1.32	11
Eu	<0.002				
Fe	<3				
Ga	0.015	0.020	0.022	0.019	11
Ir	0.0006	0.0027	0.0016	0.0016	30
K	<3				
La	0.0052	0.0055	0.0061	0.0056	5
Mo	<0.5				
Na	0.20	0.25	0.27	0.24	10
Ni	<1				
Sb	<0.001				
Sm	<0.01				
Ta	0.005				
W	0.022	0.020	0.026	0.023	6
Zn	0.1				
Ca[a]	6,180	6,160	5,830	6,060	1.5
Crystal 3					
Ag	<0.07				
Au	0.0017	0.0014	0.0016	0.0016	5
Ba	<2				
Ce	<0.4				
Co	<0.006				
Cr	0.063	0.064	0.042	0.056	13
Cu	0.23	0.21	0.26	0.24	7
Eu	<0.003				
Fe	<6				
Ga	0.121	0.115	0.129	0.122	3
Ir	<0.0001				
K	<2				
La	0.0058	0.0092	0.0061	0.0070	15
Mo	<0.5				
Na	0.40	0.37	0.29	0.35	9
Ni	<1				
Sb	0.0014	0.0019	0.002	0.0016	
Sm	<0.008				
Ta	<0.005				
W	<0.005				
Zn	<0.1				
Ca[a]	6,580	7,200	6,450	6,740	3

[a] Apparent calcium content including $^{50}Ti(n,\alpha)^{47}Ca$ reaction.

For the calculation of the lower limits, the number of counts, s, above the background, at the energy region of the photo peak, was compared with the square root of the total number of counts in the background[8], N. If this ratio was higher than 4.65, a quantitative determination was made. For ratios below 4.65, a detection limit ($L_D = 4.65\sqrt{N}$) was calculated and a lower concentration limit (C_D) derived from this value.

RESULTS

Three titanium dioxide crystals were analyzed in triplicate. The search for 21 different elements resulted in a detection of Au, Cr, Cu, Ir, La, Na, Sb, and W in at least one of the samples. For the other elements lower concentration limits were calculated.

For these lower limits only the lowest values are listed, because the values depend on the counting time and decay time of the sample. The results are summarized in Table V.

DISCUSSION

The total separation procedure takes about 4 h. However, several samples can easily be treated at the same time. The number of simultaneous analyses was mainly determined by the measurement time, as for several nuclides it is impossible to introduce a long waiting period. With two Ge(Li) detectors, it was possible to analyze nine samples at a time.

The results were reproducible within the limits of counting statistics. The sensitivity of the method ranged from 10^{-12} g (0.03 p.p.b. in 50 mg of sample) for iridium, up to 10^{-7} g for barium, for a reactor irradiation in a thermal neutron flux of $5 \cdot 10^{12}$ n cm^{-2} sec^{-1} during one week.

The titanium dioxide crystals turned out to be highly pure. They were also submitted to emission spectrography to determine whether calcium was present in a high concentration or not. No calcium could be detected, although the lower limit was 150 p.p.m. The apparent calcium concentration, induced by the $^{50}Ti(n,\alpha)^{47}Ca$ reaction, was some 7,000 p.p.m., in our irradiation conditions. As the thermal-to-fission flux ratio can be estimated at about 10, the cross-section for the $^{50}Ti(n,\alpha)^{47}Ca$ reaction should have a value of approximately 10^{-5} barn. This estimate lies closer to the value estimated by ROY AND HAWTON[3], than to the value experimentally determined by MELLISH *et al.*[2].

Thanks are due to the "Instituut voor Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw" for financial support to one of us (R.N.) and to R. K. MACCRONE, from the Rensselaer Polytechnic Institute, New York for donation of the samples.

SUMMARY

The method is based on reactor irradiation and Ge(Li) spectrometry. An anion-exchange separation, followed by TBP solvent extractions, allows a rapid and accurate determination of up to 21 metallic impurities in titanium dioxide crystals. Of the elements investigated, only hafnium and protactinium, radioactive daughter of thorium, stayed with the matrix activity and hence could not be determined. Triplicate determinations were performed of three different samples. The sensitivity ranged from 10^{-12} g for iridium, to 10^{-7} g for barium, for reactor irradiation at a thermal neutron flux of $5 \cdot 10^{12}$ n cm^{-2} sec^{-1} during one week.

RÉSUMÉ

La méthode est basée sur l'irradiation au réacteur et spectrométrie Ge(Li). Une séparation par échangeur d'anions, suivie d'extraction dans solvant TBP, permet un dosage rapide et précis de 21 impuretés métalliques dans des cristaux de dioxyde de titane. Parmi les éléments recherchés, seuls hafnium et protactinium, fille radioactive du thorium, restent avec l'activité de la matrice et par conséquent ne peuvent pas être dosés. Une triple détermination a été effectuée pour 3 échantillons différents. La sensibilité est comprise entre 10^{-12} g pour l'iridium et 10^{-7} g pour le baryum, pour irradiation au réacteur à un flux de neutrons thermiques de $5 \cdot 10^{12}$ n cm^{-2} sec^{-1} pendant une semaine.

ZUSAMMENFASSUNG

In Titandioxid-Einkristallen werden Spuren Verunreinigungen durch Anregung mit Neutronen im Reaktor und anschliessender Ge(Li)-Spektrometrie bestimmt. Die Trennung an einem Anionenaustauscher und die Extraktion mit TBP erlauben eine schnelle und genaue Bestimmung von bis zu 21 metallischen Verunreinigungen. Von den untersuchten Elementen verbleiben nur Hafnium und Protaktinium, eine radioaktive Tochter des Thoriums, bei der Matrixaktivität und können deshalb nicht bestimmt werden. Die Empfindlichkeit reicht von 10^{-12} g für Iridium bis 10^{-7} g für Barium bei einwöchiger Bestrahlung mit einem thermischen Fluss von $5 \cdot 10^{12}$ n cm^{-2} sec^{-1}.

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INSTRUMENTAL ACTIVATION ANALYSIS OF SILICATE ROCKS WITH EPITHERMAL NEUTRONS

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Instrumental reactor neutron activation analysis has proved to be a useful technique for the determination of a number of elements in geological material. With NaI(Tl) detectors[1,2], six to eight elements can usually be determined in silicate rocks without serious interferences. With the introduction of Ge(Li) detectors[3,4], the number of elements which can be determined is increased to about twenty-five. For several of these elements, the precision which can be obtained in routine analysis with the Ge(Li) detector systems available at present, is not entirely satisfactory.

In order to extend the number of elements to be determined, and to obtain better data for those already determinable, at least two ways could be tried. Firstly, the quality of data could be improved by the use of detectors with better resolution, or by the introduction of more sophisticated systems of measurements such as $\gamma\gamma$-coincidence circuits. Secondly, the activation process itself might be altered in some way, to change the formation rate for certain radionuclides relative to others. In the present paper, the second alternative has been attempted, based on activation with epithermal neutrons.

As test material for this investigation, five U.S. Geological Survey standard rocks, listed in Table II, were selected. These rocks have previously been extensively analyzed for minor and trace elements in the authors' laboratories, and were also used by GORDON *et al.*[4] in their instrumental analysis of standard rocks by thermal neutron activation and Ge(Li) detectors. As the counting equipment used in the present work is quite similar to that used by GORDON *et al.*, a direct comparison of results obtained in these two investigations has been found useful when the possible advantage of using epithermal activation is to be discussed for each of the elements investigated.

EPITHERMAL NEUTRON ACTIVATION

The theoretical aspects of epithermal neutron activation have been previously discussed in the literature[5-7]. Nuclides that can be more favourably determined by epithermal neutron activation than by corresponding activation in the total reactor neutron spectrum, are those having high resonance activation integrals compared to their thermal activation cross-sections.

BRUNE AND JIRLOW[5], discussing the feasibility of epithermal activation, have defined an "advantage" factor expressed as the ratio $(R_{\mathrm{Cd}})_{\mathrm{d}}/(R_{\mathrm{Cd}})_{\mathrm{D}}$, where R_{Cd} is the cadmium ratio, and d and D denote the interfering nuclide and the nuclide under investigation, respectively. If the advantage of using epithermal activation for the determination of one or more elements in a certain matrix is to be established, the cadmium ratios have to be determined for the nuclides upon which the analysis is based, as well as for nuclides giving rise to major activities in the sample. This can be done either experimentally or by calculation. If the cadmium ratio of a standard nuclide, usually ^{197}Au, has been determined for the actual irradiation position, the corresponding R_{Cd} for another nuclide can be determined by means of the following formula[6]:

$$R_{\mathrm{Cd}} = 1 + \frac{\sigma_0}{\sigma_0{}^{\mathrm{Au}}} \cdot \frac{0.44\,\sigma_0{}^{\mathrm{Au}} + I^{\mathrm{Au}}}{0.44\,\sigma_0 + I} (R_{\mathrm{Cd}}{}^{\mathrm{Au}} - 1)$$

where σ_0 means the thermal neutron activation cross-section, and I the resonance activation integral excluding the $1/v$ contribution.

Applications of instrumental resonance neutron activation analysis have been demonstrated for the determination of manganese in biological material[8] and of molybdenum in steel[5]. This technique should be favourable also for geological material, because most of the nuclides leading to major activities in a silicate matrix by thermal neutron activation, *i.e.* ^{23}Na, ^{45}Sc, ^{58}Fe, ^{59}Co, ^{139}La and ^{151}Eu, have resonance integrals which are low compared to their thermal neutron activation cross-sections. Recent experience[9,10] in the laboratory of one of the present authors clearly emphasized this point. A more extensive study in this area, based on instrumental activation analysis with a Ge(Li) detector, was therefore initiated. This work has been restricted to nuclides with more than 2 days' half-life.

EXPERIMENTAL

Preliminary investigations

Inspection of all those nuclides giving rise to γ-emitters with half-lives above 2 days upon thermal neutron irradiation, regarding their cross-section data and abundance in geological material, indicated the following to be most promising as far as epithermal neutron activation is concerned: ^{121}Sb, ^{123}Sb, ^{133}Cs, ^{152}Sm, ^{159}Tb, ^{168}Yb, ^{180}Hf, ^{181}Ta, ^{232}Th, and ^{238}U. During the experiments with standard rocks, it became evident that the nuclides ^{84}Sr, ^{85}Rb, and ^{130}Ba also represented advantageous cases, a fact which could not be predicted because data on the resonance activation integrals of these nuclides were not available in the literature.

In order to permit a quantitative discussion in terms of "advantage" factors, it was necessary to know the cadmium ratios of the nuclides involved, in the actual irradiation position. As the cross-section data of several of the nuclides are questionable, it was decided to determine all cadmium ratios experimentally. In addition to the nuclides mentioned above, the standard nuclide ^{197}Au and the following nuclides giving rise to major activities in silicate rock samples, were included: ^{23}Na, ^{45}Sc, ^{46}Ca, ^{58}Fe, ^{59}Co, ^{139}La and ^{151}Eu.

The samples used in the cadmium ratio measurements were aliquots of dilute solutions, evaporated to dryness on small sheets of aluminium foil. One set of samples was irradiated in a small cadmium box as described below, while an identical set of samples was irradiated simultaneously at a distance of 10 cm from the cadmium box, both sets of samples being included in the same aluminium container. The data obtained were corrected for the difference in thermal neutron flux of these two positions when no cadmium was present, which was of the order of 5%. The activity measurements were carried out in the same way as for the standards used in the rock analysis, correcting for activity induced in the aluminium foil by means of blanks irradiated together with the samples.

If possible from available literature data, the cadmium ratios were also determined by calculation.

In Table I, a comparison of calculated and experimentally determined cadmium ratios is shown. For a substance following the $1/v$ law closely, the R_{Cd} would be about 80 under the actual conditions. As can be seen from Table I, the agreement between calculated and experimental values is reasonable in those cases where comparison is possible.

TABLE I

CADMIUM RATIOS FOR THE MOST IMPORTANT NUCLIDES INVOLVED IN THE PRESENT WORK (Cd-thickness = 1.0 mm)

Nuclide	σ_0[a] *(barn)*	$0.44\,\sigma_0 + I$[a] *(barn)*	*Cadmium ratio*	
			Calculated	*Observed*
^{197}Au	99	1550	Basis for calculation	3.2
^{85}Rb	0.50	—	—	3.1
^{84}Sr	0.88	—	—	3.4
^{121}Sb	6.2	143	2.5	2.5
^{123}Sb	3.4	183	1.6	—
^{133}Cs	30	470	3.2	3.3
^{130}Ba	11	—	—	2.5
^{152}Sm	210	2800	3.6	3.3
^{159}Tb	30	630	2.6	2.7
^{168}Yb	3200	—	—	9.0
^{180}Hf	12.6	22	21	17
^{181}Ta	22	580	2.3	2.3
^{232}Th	7.4	84	4.0	3.5(^{233}Pa)
^{238}U	2.72	280	1.33	1.49(^{239}Np)
^{23}Na	0.53	0.31	59	60
^{46}Ca	0.25	—	—	27
^{45}Sc	22	10.2	75	74
^{58}Fe	1.23	1.15	38	32
^{59}Co	37	71	19	18
^{139}La	8.8	14	23	26
^{151}Eu	5000	—	—	45(12 y ^{152}Eu)

[a] Preferred literature values.

Counting equipment

The Ge(Li) detector used in this work was an ORTEC 24-cm^3 coaxial detector 8002-20 SP with a resolution of 3.2 keV (FWHM) for the 1331-keV peak of ^{60}Co. The associated electronics were also ORTEC products: a preamplifier 118 A, a selectable

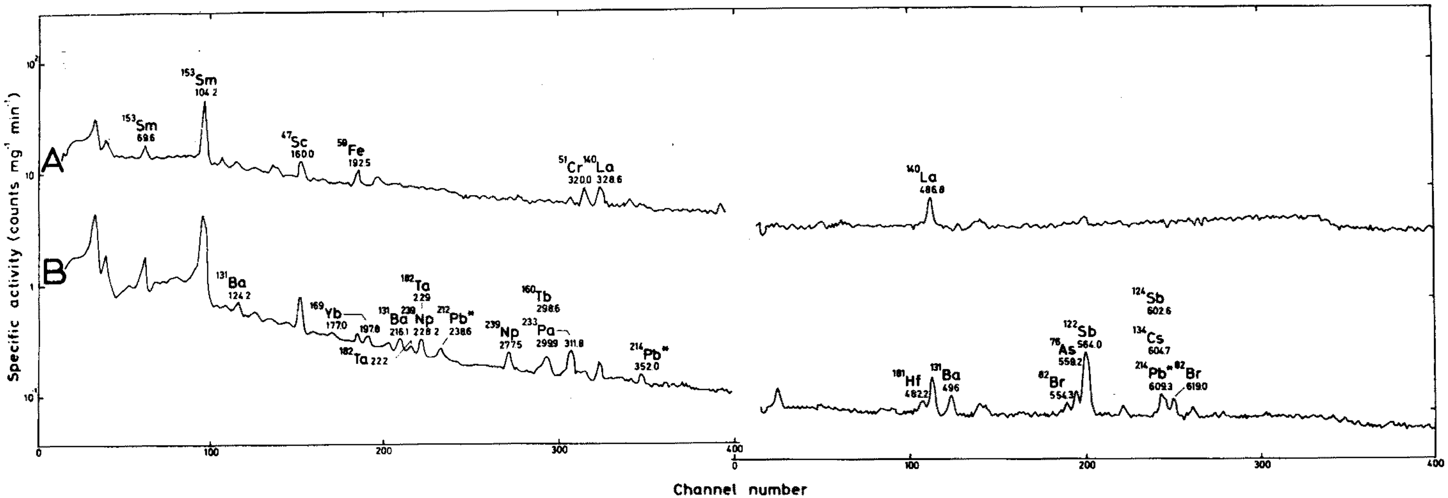

Fig. 1. γ-Ray spectra of diabase W-1. These spectra were obtained 7 days after end of irradiation. (A) Thermal neutron activation, weight of sample *ca.* 10 mg, counting time 30 min; (B) epithermal neutron activation, weight of sample *ca.* 100 mg, counting time 300 min. Peaks from natural background activities are denoted by an asterisk.

active filter amplifier 440 A, a biased amplifier 408 and a pulse stretcher 411. For the pulse-height analysis an "Intertechnique SA-40B" 400-channel analyzer was used.

Treatment of samples and standards for irradiation

Rock samples of about 100 mg were wrapped in 30 × 30 mm sheets of aluminium foil for irradiation. Standards were prepared by carefully evaporating aliquots of dilute solutions on the same sort of aluminium sheets. Corresponding blanks of the aluminium foil were also prepared. The approximate amount of each element used as standard was as follows: 1 μg of Sb, Cs, Sm, Tb, Ta, Th, U; 10 μg of Rb, Yb, Hf; 100 μg of Ba, Sr.

For each irradiation, five standard rock samples, twelve standards and two aluminium blanks were placed in a 1.0-mm thick cylindrical cadmium box, of 14-mm internal diameter and 10-mm internal height. The box was irradiated for 2 days in a vertical isotope channel of the JEEP-II reactor (Kjeller, Norway), in a fixed position where the thermal neutron flux was about $1.5 \cdot 10^{13}$ n cm^{-2} sec^{-1} and the cadmium ratio for ^{197}Au was 3.2.

Before the activity measurements, the rock samples were accurately weighed into new sheets of aluminium foil.

Activity measurements

The γ-spectrometric measurements were started 5 days after the end of the irradiation. For optimal utilization of the high-resolution detector, the actual energy interval was divided into four parts of 400 channels each. These intervals were about 65–450 keV, 450–800 keV, 800–1150 keV, and 1150–1400 keV. In the first measurements, taken after 5–7 days, γ-activity from the nuclides ^{122}Sb, ^{153}Sm and ^{239}Np was registered. A second series of measurements was performed after 20–25 days, in which the rest of the activities in question were recorded. Measurement times were 30–600 min.

In Fig. 1, γ-spectra of two samples of W-1, recorded 7 days after the irradiation, are shown. One of the samples was irradiated in a cadmium box, while the other was activated simultaneously without cadmium cover. In Fig. 2, γ-spectra of the same samples after 20 days are presented. The relative enrichment of several activities is clearly indicated in the spectra.

The peaks used for the determination of each element are listed in Table II, the energies being taken from the tabulation of DAMS AND ADAMS[11]. Peak areas were calculated according to the method of COVELL[12], by selecting the number of channels used in the calculation high enough to include a major part of the total peak area. In some cases, corrections for interfering γ-rays had to be performed, as indicated in Table II. When measurements at high count rates were performed, the areas calculated by the COVELL procedure gave low results, as previously reported by YULE[13]. Counting at low dead-times, in most cases below 3–4%, was therefore employed.

As no shielding was used round the detector, peaks from natural background activities were observed in the spectra, as indicated in Fig. 2. None of these peaks, however, seemed to interfere significantly in the analysis.

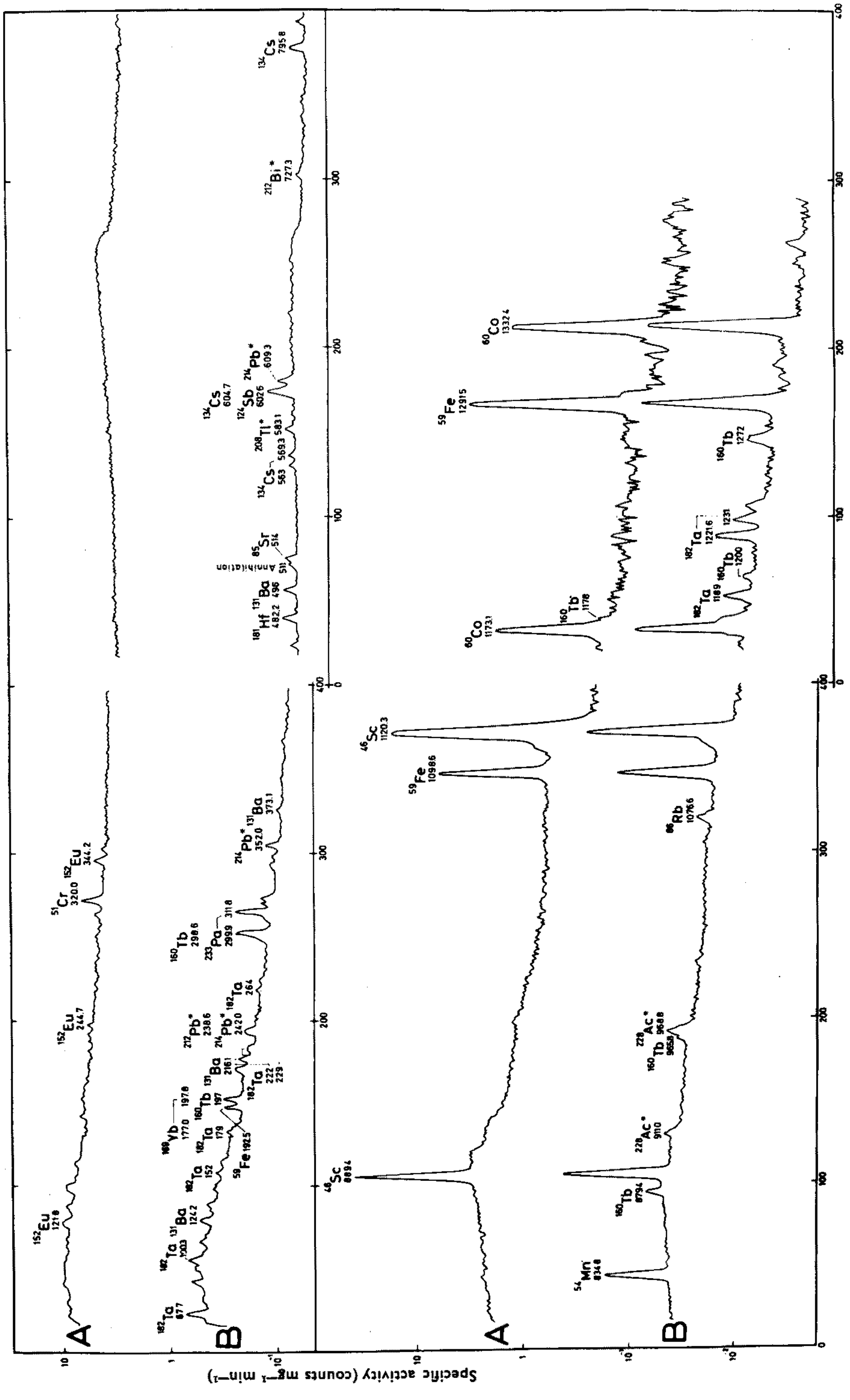

Fig. 2. γ-Ray spectra of diabase W-1. These spectra were obtained about 20 days after end of irradiation. (A) Thermal neutron activation, weight of sample *ca.* 10 mg, counting time 90 min; (B) epithermal neutron activation, weight of sample *ca.* 100 mg, counting time 900 min. Peaks from natural background activities are denoted by an asterisk.

RESULTS AND DISCUSSION

The data presented in this paper were obtained in three different irradiations (A–C), and are summarized in Table II. In Table III, the mean values of the present work are compared with some neutron activation data obtained by other workers for the same standard rocks. The "recommended values" for W-1[16] have also been included in the Table; for this rock, no attempt has been made to include all previous neutron activation data, for these have already been collected in a series of compilations[14–16], together with results obtained by other analytical techniques. Correspondingly, results from techniques different from neutron activation also exist for a number of the actual elements in the four new standard rocks, and can be found in the compilation by FLANAGAN[17].

In the following text, the advantage of epithermal activation compared to thermal activation is discussed. For this purpose, reference is made to the thermal neutron activation work of GORDON *et al.*[4]. The results are not directly comparable, because the error limits reported by GORDON *et al.* were estimated from counting statistics and errors associated with the corrections made, rather than the observed spread of replicate determinations.

Rubidium

This element could not be determined in the basic standard rocks by GORDON *et al.*; this is probably due mainly to the high ^{46}Sc activity in these samples. By epithermal activation, an enrichment factor of 24 was found for rubidium relatively to scandium, and in accordance with this, rubidium could be determined without difficulty in the present work. The agreement with the radiochemical neutron activation values previously reported is good, especially with those by ATHAVALE[21].

Strontium

The determination of strontium was not reported by GORDON *et al.* By the present irradiation technique, however, the 514-keV peak of ^{85}Sr could easily be detected in all the samples. Difficulties may be encountered in samples with low contents of strontium, owing to incomplete resolution of the 514-keV γ-ray and the 511-keV annihilation peak.

Antimony

For antimony, the advantage of using epithermal activation is again evident. GORDON *et al.* were able to establish approximate values for this element using the 1691-keV γ-ray of ^{124}Sb. In this work, satisfactory results were obtained from the 564-keV peak of ^{122}Sb as well as the 603-keV peak of ^{124}Sb. The former γ-ray is preferable due to the apparent absence of interfering γ-rays.

Caesium

The precision obtained in this work appears to be significantly improved compared to the work of GORDON *et al.* This improvement could also have been predicted from examination of the resonance activation data. Again the agreement with the data of ATHAVALE[21] is good.

TABLE II

RESULTS OBTAINED FOR FIVE U.S.G.S. STANDARD ROCKS (p.p.m.)

Element	*Radioisotope measured*	*γ-Energy used (keV)*	*Interfering γ-rays (keV)*	*Andesite AGV-1*		
				A	*B*	*C*
Rb	^{86}Rb	1076.6	—	74	61	61
Sr	^{85}Sr	514.0	Annihilation 511.1	—	595	616
Sb	^{122}Sb	564.0	^{134}Cs 569.3	4.35	4.27	4.17
	^{124}Sb	602.6	^{134}Cs 604.7	4.21	3.98	4.07
Cs	^{134}Cs	795.8	—	1.24	1.31	1.27
Ba	^{131}Ba	496	—	—	1061	1081
Sm	^{153}Sm	103.2	^{233}Pa 98.4, ^{182}Ta 100.3 ^{239}Np 106	5.94	5.87	5.22
Tb	^{160}Tb	298.6	^{233}Pa 299.9	0.58	—	0.54
Yb	^{169}Yb	177.0	^{182}Ta 179	1.60	0.99	1.74
Hf	^{181}Hf	482	^{131}Ba 486	4.25	5.13	4.86
Ta	^{182}Ta	152	—	0.85	—	0.70
	^{182}Ta	222.1	—	0.80	—	0.85
	^{182}Ta	1189	—	0.93	—	0.78
	^{182}Ta	1221.6	—	0.84	—	0.74
	^{182}Ta	1231	—	0.77	—	0.77
Th	^{233}Pa	311.8	^{169}Yb 308	5.89	6.02	5.72
U	^{239}Np	277.5	—	1.93	1.99	1.78

[a] Corrections have been applied for the underlined γ-rays.

Barium

For this element the advantage of epithermal activation is perhaps best demonstrated in the case of W-1. While GORDON *et al.* were not able to determine barium in this rock, no difficulty was encountered in this work.

Samarium

The 103-keV peak of ^{153}Sm is likely to be exposed to interference from ^{233}Pa, ^{239}Np and probably ^{182}Ta. This interference is not expected to be much different in thermal and epithermal activation analysis, since the radionuclides involved are all formed from parent nuclides with low cadmium ratios. The interfering peaks will mainly appear near the boundaries of the samarium peak, which is expected to result in slightly low results by the use of the COVELL method. This seems to be supported by the fact that the present results are about 7% lower on average than the corresponding epithermal activation results obtained by one of the present authors[9] by measuring the 41-keV X-ray of ^{153}Sm in the NaI(Tl) spectra. The latter method has few interferences which can be fairly easily controlled, and should hence give reasonably accurate results.

The main advantage of epithermal activation in the case of ^{153}Sm seems to be the high advantage factor of 18 compared to ^{24}Na.

Terbium

^{160}Tb has high energy peaks at 879.4 keV and 1272 keV which become essentially free of interferences in samples irradiated by epithermal neutrons, owing to the enrichment of this nuclide compared to ^{152}Eu and ^{154}Eu, which interfere by thermal neutron activation. The results presented in Table III, however, have been calculated from the 299-keV peak, because of the better counting statistics obtained. Although the

Basalt BCR-1			*Granite G-2*			*Granodiorite GSP-1*			*Diabase W-1*		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
49	43	45	174	151	157	246	216	220	22.8	21.4	22.3
—	362	275	—	419	400	—	203	182	—	163	161
0.62	0.59	0.57		—		2.95	3.02	3.06	0.82	0.94	1.06
0.42	0.41	0.49		<0.07		3.27	3.10	2.64	0.75	0.95	0.84
0.98	1.02	0.98	1.40	1.25	1.34	0.88	0.91	0.98	1.06	0.84	0.96
—	567	582	—	1704	1701	—	1187	1198	—	188	185
6.10	6.19	6.13	6.91	7.30	6.39	—	25.2	24.2	3.09	3.27	3.12
1.00	—	0.91	0.40	—	0.55	1.47	—	1.34	0.59	—	0.55
3.77	3.44	3.36	0.86	0.67	1.27	0.69	1.15	1.11	1.67	2.06	1.67
4.60	4.78	4.77	8.28	7.46	7.17	13.7	13.7	14.4	2.32	2.58	2.46
0.75	—	0.86	0.73	—	0.70	0.88	—	0.78	0.34	—	0.43
0.69	—	0.83	0.69	—	0.71	0.99	—	0.86	0.50	—	0.50
0.73	—	0.73	0.73	—	0.77	0.84	—	0.64	0.42	—	0.44
0.78	—	0.78	0.76	—	0.75	0.81	—	0.71	0.45	—	0.43
0.74	—	0.70	0.79	—	0.78	0.96	—	0.59	0.40	—	0.37
5.46	5.57	5.78	23.7	22.3	24.0	105	97	101	2.00	2.19	2.14
1.79	1.69	1.91	2.01	1.90	1.89	—	2.01	2.09	0.60	0.58	0.60

interference from ^{233}Pa with this peak is not appreciably reduced by epithermal activation, the conditions should still be favourable, because of the enrichment of ^{160}Tb compared to the major activities responsible for the Compton continuum in the 300-keV region.

Ytterbium

The determination of ytterbium by this technique is difficult owing to serious interference from other nuclides affecting all the prominent peaks of ^{169}Yb. The peak least disturbed was estimated to be the one at 177 keV, but even in this case the 177-keV γ-ray of ^{182}Ta interfered appreciably. The results obtained were not satisfactory, and no advantage seems to be gained for ytterbium by the use of epithermal activation.

Hafnium

Although the determination of hafnium by thermal neutron activation is fairly good[4], there seems to be evidence that slightly better results can be obtained by the present technique, with the 482-keV peak.

Tantalum

This seems to be a case where definite advantage is obtained by epithermal activation. GORDON *et al.* were able to determine this element using the low energy peaks at 67 keV and 100 keV. In the present work, tantalum was determined independently by means of five other γ-rays, which would scarcely be observed in the spectra after thermal activation. The results obtained from different peaks are in good agreement, thus indicating that results of good accuracy are attainable.

Thorium

Although the formation of ^{233}Pa is enhanced by epithermal activation com-

TABLE III

MEAN VALUES OF THE PRESENT WORK COMPARED WITH PREVIOUS DATA (p.p.m.)

Rock		*Rb*	*Sr*	*Sb*	*Cs*	*Ba*	*Sm*	*Tb*	*Yb*	*Hf*	*Ta*	*Th*	*U*
AGV-1	This work	65	606	4.18	1.27	1071	5.68	0.56	1.4	4.75	0.80	5.88	1.90
	GORDON *et al.*	61	—	5.2	1.3	1180	5.4	0.77	1.6	5.4	1.0	7.0	—
	Other literature values	71[20] 68[21]	612[22]	4.35[18]	1.22[20] 1.13[21] 1.2[23]	1060[22]	6.6[2] 6.08[9]	0.75[29]	1.91[29]	3.7[24] 6.6[25]	0.32[24]	6.47, 6.4[26] 8.1[27]	2.17, 1.9[26] 1.93[10] 2.09[27], 1.46[28]
BCR-1	This work	46	318	0.52	0.99	575	6.14	0.96	3.5	4.72	0.75	5.60	1.80
	GORDON *et al.*	<105	—	1.1	1.5	650	5.9	1.0	3.2	4.7	0.9	6.7	—
	Other literature values	53[20] 50[21]	327[22]	0.579[19]	1.08[20] 0.95[21] 0.91[23]	625[22]	7.4[2] 6.61[9]	1.22[29]	3.69[29]	3.3[24] 5.4[25]	0.86[24]	6.00, 6.1[26] 7.6[27]	1.81, 1.6[26] 1.94[10] 1.80[27], 1.42[28]
G-2	This work	161	410	<0.07	1.33	1703	6.87	0.48	0.9	7.64	0.73	23.3	1.93
	GORDON *et al.*	129	—	<0.6	1.4	1800	8.7	0.52	0.8	7.8	1.0	25.9	—
	Other literature values	185[20] 178[21]	445[22]	0.063[19]	1.27[20] 1.27[21] 1.1[23]	1627[22]	7.3[2] 7.66[9]	0.51[29]	0.86[29]	6.1[24] 7.7[25]	0.82[24]	24.1, 25.7[26] 24.6[27]	2.16, 2.1[26] 2.06[10] 2.07[27], 1.64[28]
GSP-1	This work	227	193	3.01	0.92	1193	24.7	1.41	1.0	13.9	0.81	101	2.05
	GORDON *et al.*	255	—	4.1	0.8	1110	23.2	1.3	2.0	13.7	1.4	125	—
	Other literature values	272[20] 240[21]	224[22]	3.09[19]	1.07[20] 0.92[21] 1.2[23]	1137[22]	33[2] 25.8[9]	1.31[29]	1.93[29]	11[24] 9.7[25]	0.77[24]	106[26] 116.4[27]	1.7[26] 2.15[10] 2.68[27], 1.80[28]
W-1	This work	22.2	162	0.89	0.95	187	3.16	0.57	1.8	2.45	0.42	2.11	0.59
	GORDON *et al.*	<30	—	—	0.83	<200	2.8	0.57	2.2	3.0	0.67	2.6	—
	Other literature values	22[20]	193[22]	0.90[18]	1.06[20] 0.90[23]	167[22]	3.2[2] 3.31[9]	0.71[29]	2.29[29]	1.4[24]	0.55[24]	3.5[27]	0.61[10] 0.62[27]
	Recommended value[16]	22	180	1.1	1.0	180	4	0.8	2.2	2	0.7	2.4	0.5

pared to the major activities, the potentialities of the determination of thorium by the two techniques should not be very different, because this element is also easily determined by thermal activation. The present results for this element appear to be slightly lower than those obtained by GORDON *et al.* Good agreement is observed, however, with the values by MORGAN AND HEIER[25], based on radiochemical activation analysis and measurements of natural radioactivity, respectively.

Uranium

It is not possible to determine this element purely by γ-spectrometry after thermal neutron activation. The exceptionally high advantage factor for ^{239}Np compared to the major activities, however, enables determination of uranium with good precision and accuracy after epithermal activation. The 278-keV peak, which is virtually free of interference, was used for this determination. The 229-keV peak, which was also tried, gave high results, probably due to interference from the 229-keV γ-ray of ^{182}Ta.

The epithermal activation determination of uranium by means of 23-min ^{239}U has recently been demonstrated by STEINNES AND BRUNE[10]. The agreement between the results from these two investigations based on epithermal activation, is very satisfactory. Also for uranium, the agreement with the work of MORGAN AND HEIER[26] is good.

The present technique, as demonstrated in this work, should be attractive for earth science applications; in several cases, elements which are geochemically related can be determined by one single measurement. This applies to rubidium and caesium, barium and strontium, and also uranium and thorium. Moreover, the good precision and accuracy which can evidently be obtained for the elements antimony, hafnium and tantalum, should facilitate increased effort in the geochemical studies of these trace elements, which are difficult to determine by analytical techniques other than neutron activation. Determination of rare earth distributions, on the other hand, is probably more properly performed by the use of thermal neutron activation.

There seems to be no reason for assuming the introduction of additional errors by the present technique compared to the corresponding thermal neutron activation procedure. The most important difference is probably the possibility of errors caused by resonance neutron shielding effects. It can be calculated, however, that even for ^{152}Sm, which has by far the highest resonance integral of the nuclides investigated, such effects are negligible in the actual samples.

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SUMMARY

The determination of some trace elements in standard rocks by epithermal neutron activation, followed by γ-ray spectrometry with a Ge(Li) detector, is described. The advantage of using this technique compared to corresponding analysis with thermal neutrons is clearly demonstrated in the case of Rb, Cs, Sr, Sb, Ta, and U. Determinations of Ba, Sm, Tb, Hf, and Th also appear to be favourable.

RÉSUMÉ

On décrit un dosage de traces dans des roches standards par activation neutronique épithermique, suivie d'une spectrométrie aux rayons γ avec détecteur Ge(Li). On démontre clairement les avantages de cette technique comparée à l'analyse à l'aide de neutrons thermiques pour Rb, Cs, Sr, Sb, Ta et U. Des dosages de Ba, Sm, Tb, Hf et Th semblent également favorables.

ZUSAMMENFASSUNG

Die aktivierungsanalytische Bestimmung einiger Spurenelemente in Standardgesteinen mit epithermischen Neutronen und anschliessender γ-Spektrometrie mit einem Ge(Li)-Detektor wird beschrieben. Der Vorteil gegenüber der Verwendung von thermischen Neutronen wird am Beispiel folgender Elemente demonstriert: Rb, Cs, Sr, Sb, Ta und U. Die Bestimmung von Ba, Sm, Tb, Hf und Th scheint ebenfalls günstig zu sein.

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THE DETERMINATION OF THALLIUM IN SILICATE ROCKS, MARINE SEDIMENTS AND SEA WATER

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The determination of thallium in most rocks and minerals (other than its ores) is a difficult task on account of the low crustal abundance of the element (average *ca.* 1.0 p.p.m. in igneous rocks[1]). Conventional spectrographic procedures employing d.c. arc excitation have a sensitivity for the element of *ca.* 0.5 p.p.m.[2-4]. However, the detection limit can be reduced to as low as 0.05 p.p.m. by the use of specialized excitation techniques such as the double arc[5]. Further enhancement in the sensitivity of spectrographic procedures has been attained by the use of preconcentration techniques such as ion exchange[6] or solvent extraction[7,8]. Flame photometric procedures are also rather lacking in sensitivity, although it has been claimed[9] that 0.2 p.p.m. of thallium can be detected if a preliminary concentration technique is employed. Although the technique of neutron activation analysis has a relatively high sensitivity for thallium, and has been used for the analysis of silicates containing 0.02–1.3 p.p.m.[10,11], it demands facilities which are available to comparatively few laboratories. Several colorimetric procedures have been described for the determination of the element in ores and concentrates but, perhaps because of a dearth of sufficiently sensitive reagents, only one such procedure[12], using brilliant green, has been employed for the analysis of igneous rocks.

Very little is known about the occurrence of thallium in natural waters. Its concentration even in mineral waters is several orders of magnitude lower than in rocks and a preconcentration stage is essential before the element can be determined. Coprecipitation with mercury(I) chloride[13] and extraction techniques[8,14] have been used for this purpose in the examination of non-saline waters. BROOKS[15] has used a combination of chloro-anion exchange and spectroscopy in an unsuccessful attempt to detect thallium in sea water.

The present paper describes methods for the determination of thallium in rocks, sediments and sea water. The preconcentration stage, a modification of that used by BROOKS[15], is common to both procedures. A fluorimetric method involving rhodamine B with a sensitivity of *ca.* 0.01 μg Tl is used for the examination of rocks and sediments. Neutron activation is used for its determination in sea water because of its extremely low concentration.

Preparation of samples

Sea water. Studies were made radiochemically with ^{204}Tl to determine the optimum conditions for storage of sea water samples. In agreement with the observations of ROBERTSON[16] it was found that filtered samples stored in high-density polythene

TABLE I

PERCENTAGES OF ELEMENTS ORIGINALLY RETAINED BY DEACIDITE FF COLUMN AND PRESENT IN VARIOUS ELUATES

	ml	Ag^+	Au^{3+}	Bi^{3+}	Cd^{2+}	Fe^{3+}	Ga^{3+}	In^{3+}	Mn^{2+}	Mo^{6+}	Pb^{2+}	Pt^{6+}	Sb^{3+}	Sn^{4+}	Re^{7+}	Zn^{2+}	V^{5+}
Retained by resin	—	100	100	99	79	16	9	19	3	98	54	87	73	92	99	59	10
Water	25	0	0	0	79	7.5	0.8	12	3	7	13	1.7	20	6	0	30	0
Nitric acid (2 *N*)	55	0	0	0		5.0		7	0		41			67		24	10
Water	25	0	0	0		1.5		0	0		0			19		4	0
Sulphur dioxide soln.	35	0.0	0.0	0.0	0.0	1.0	8.0	0.0	0.0	0.0	0.0	0.0	1.9	0.0	0	1.2	0

bottles for 2–3 months lost only 3–4% of their thallium content. Even this loss could be prevented if the samples were rendered 0.1 *N* with respect to hydrochloric acid before storage.

Silicates. Because of the volatility of thallium it is difficult to bring siliceous materials into solution without loss. Radiochemical tests with ^{204}Tl showed that prolonged fuming of the solution after decomposition of such samples with hydrofluoric acid and either sulphuric[9,11] or perchloric acids could lead to the volatilization of up to 40% of the thallium present. Quantitative recoveries of the element could be obtained if the sample was decomposed with a mixture of hydrofluoric and nitric acid and then evaporated several times with nitric acid to eliminate fluoride. This technique was used in all subsequent work.

Preconcentration and separation of thallium

Since thallium occurs at low concentrations in both sea water and geochemical samples, it is necessary to carry out a preliminary separation to concentrate it and to separate it from major elements. A survey of the literature suggested that this separation might be most readily achieved by anion exchange. KRAUS AND NELSON[17] have shown that thallium(III) is very strongly held from 2 *M* hydrochloric acid medium by strongly basic anion-exchange resins. Of the other elements, only Au^{3+}, Pb^{2+}, Sn^{4+}, Bi, Cd, Zn, Mo^{6+}, Re^{7+}, In and the platinum metals can be successfully concentrated by this technique. BROOKS and co-workers have applied this procedure to the analytical separation of thallium and a number of other trace elements from the major elements of silicates[18] and sea water[15].

The uptake of thallium by 0.3 cm^2 × 7.5 cm columns of Deacidite FF resin (50–100 mesh) was studied radiochemically with ^{204}Tl. It was observed that 0.05 µg of the element was retained with an efficiency of >99.9% from both 500 ml of 0.1 *M* hydrochloric acid and 10 l of sea water made 0.1 *M* with respect to hydrochloric acid, provided that a trace of bromine was present to ensure that thallium was present in the 3+ oxidation state. Unlike most of the other elements forming strong chlorocomplexes, thallium was not eluted from the resin by passage of 55 ml of 2 *M* nitric acid. However, it could be quantitatively eluted by means of 35 ml of a saturated aqueous solution of sulphur dioxide. It appeared likely therefore that if the column was first eluted with 55 ml of 2 *M* nitric acid to remove other elements, thallium could then be separated specifically by elution with 35 ml of sulphur dioxide solution. In order to test whether this was the case, 500-ml aliquots of 0.1 *M* hydrochloric acid containing *ca*. 5 µg of possible interfering elements were spiked with radio-isotopes of the elements concerned. The solutions were treated with 5 ml of bromine water and allowed to flow through 0.3 cm^2 × 7.5 cm columns of Deacidite FF. The columns were then eluted successively with 25 ml of water, 55 ml of 2 *M* nitric acid, 25 ml of water and 35 ml of sulphur dioxide solution. The activity of each eluate was then determined with a scintillation counter. It was found (Table I) that thallium could be separated efficiently from most of the other elements examined. However, appreciable amounts of iron, gallium, antimony and zinc were found in the sulphur dioxide water eluate. Although these would not cause interference in the determination of thallium in sea water, interference would be experienced, particularly from iron, in the analysis of silicate rocks. Further experiments were therefore carried out which showed that interference from these elements could be completely prevented if the exchange column was eluted consecutively with 350 ml of 0.5 *M* nitric acid and 250 ml of 0.5 *M* hydrochloric acid. Under these conditions only tin (*ca.* 2%) was present in the sulphur dioxide eluate. This procedure was therefore used in subsequent work on the analysis of rocks and sediments. However, elution with 55 ml of 2 *M* nitric acid was adopted for the removal of other elements in the analysis of sea water to reduce the danger of contamination.

Determination of thallium by neutron activation analysis

Since the concentration of thallium in sea water is very low it was decided to determine it by neutron activation after concentrating it by the ion-exchange process described above. Naturally occurring thallium consists of two isotopes ^{203}Tl (29.5%) and ^{205}Tl (70.5%) which have thermal neutron capture cross sections of 8 and 0.1 barns respectively. When these isotopes are irradiated with thermal neutrons the following nuclear reactions occur:

$$^{203}\text{Tl} \xrightarrow{n,\gamma} {}^{204}\text{Tl}\ (t_{\frac{1}{2}}=4.1\text{ years}) \begin{array}{l} \xrightarrow{\beta^-(98\%)} {}^{204}\text{Pb} \\ \qquad\qquad\quad \text{stable} \\ \xrightarrow{\text{EC}(2\%)} {}^{204}\text{Hg} \\ \qquad\qquad\quad \text{stable} \end{array}$$

$$^{205}\text{Tl} \xrightarrow{n,\gamma} {}^{206}\text{Tl}\ (t_{\frac{1}{2}}=4.19\text{ min}) \xrightarrow{\beta^-} {}^{206}\text{Pb}\ \text{stable}$$

MORRIS AND KILLICK[10] have used ^{204}Tl in neutron activation analysis for thallium in rocks. A slightly modified version of their separation procedure has been used to process the irradiated concentrate from sea water. After spiking with a known amount of inert thallium the element is extracted from 0.1 *M* hydrobromic acid medium instead of from 4 *M* hydrochloric acid, since a much more selective separation can be obtained[19]. With equal volumes of 0.1 *M* hydrobromic acid and ether, the efficiency of extraction of thallium exceeded 98%. Under these conditions less than 0.01% of the following were extracted As^{3+}, Au^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ga^{3+}, In^{3+}, Mo^{6+}, Ni^{2+}, Sb^{3+}, Sb^{5+}, Se^{4+}, Se^{6+}, Sn^{2+}, Sn^{4+}, Te^{6+}, V^{5+}, Zn^{2+}; of the elements examined only mercury was appreciably extracted (58.3%). Thallium is recovered from the ether extract by evaporation with dilute sulphuric acid. After removal of bromide, the analysis is completed as described by MORRIS AND KILLICK[10]. Thallium is purified by precipitation as the iodide and by scavenging with lanthanum hydroxide. It is finally converted to thallium(III) chromate for determination of chemical yield and β-counting. The overall chemical field was found to be *ca.* 80%.

Fluorimetric determination of thallium in rocks and sediments

A review of the literature suggested that none of the published colorimetric procedures[12,14,20–23] is sufficiently sensitive for the precise determination of 0.1–1 μg of thallium. It appeared that the desired sensitivity might be attained by fluorimetry. Microgram and submicrogram amounts of thallium have been determined by means of its fluorescence in hydrochloric acid medium[24,25] or that of its rhodamine B complex[26-28]. The process with rhodamine B was selected for investigation. It depends on the reaction of thallium(III) with rhodamine B in hydrochloric acid medium to yield a complex of the formula $(RH)TlCl_4$ (where R is rhodamine B) which exhibits a violet fluorescence when extracted into benzene. Gold(III), gallium and antimony(V) also form extractable fluorescent complexes under rather similar conditions.

Attempts were made to determine thallium under the conditions recommended by ONISHI[26] but it was found that reagent blanks were very high owing to extraction of much rhodamine B. The extraction of rhodamine B and its complexes with metals is known to depend on the hydrochloric acid concentration of the solution from which the extraction is made. A study was therefore made to determine the optimum acid concentration for the extraction of the thallium complex. Aliquots (5 ml) of hydrochloric acid of the appropriate molarity containing 0.5 μg of thallium and 0.5 μCi of ^{204}Tl were treated with 1 ml of bromine water. The mixture was heated to 70° until the excess bromine was removed. The solution was transferred to a separating funnel with a further 5 ml of hydrochloric acid of the same molarity and 2 ml of a 0.1% solution of rhodamine B in the same strength of acid was added. The rhodamine B complex was extracted by shaking for 2 min with 5 ml of benzene. The thallium which had not been extracted was assessed by comparing the β-activity of the aqueous phase with that of a similar solution which had not been extracted. Corresponding blank extractions were carried out in the same manner except that the thallium was omit-

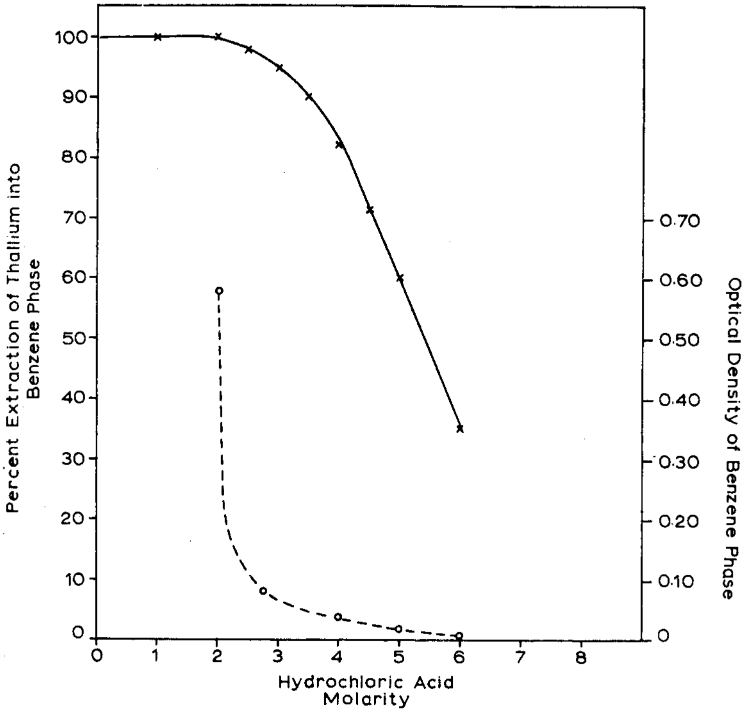

Fig. 1. Percentage extraction of thallium as its rhodamine B complex with benzene at various hydrochloric acid molarities (continuous line), and extraction of rhodamine B by benzene under the same conditions (expressed as optical density at 560 nm in 1-cm cell) (broken line).

ted. In these instances, the optical densities of the benzene phases were measured at 560 nm in a 1-cm cell in order to give an estimate of the amount of rhodamine B extracted. The results of these experiments are shown diagrammatically in Fig. 1. At hydrochloric acid strengths below *ca.* 2 *M*, thallium is completely extracted by benzene. However, at higher acidities the efficiency of extraction falls rapidly. Considerable amounts of rhodamine B itself are extracted at acidities below 2.7 *M*. To produce a workable method it was therefore necessary to accept a somewhat less than quantitative extraction of thallium in order to keep the blank as small as possible. All subsequent work was carried out at a total hydrochloric acid concentration of 2.7 *M*, when 97% of the thallium was extracted. This molarity is considerably greater than that employed by ONISHI (*ca.* 1 *M*).

Under the conditions described in the EXPERIMENTAL section below, the response of the fluorimeter was linear up to at least 1.5 μg of thallium. The sensitivity, expressed as 3 times the standard deviation of the blank was 0.01 μg. The coefficient of variation measured at the 1.0-μg level was ±1.5%. The interferences of a number of elements in the determination of 0.5 μg of thallium were investigated at the 10-μg level. No interference was experienced from Sb^{3+}, Ga^{3+}, Fe^{3+} or V^{5+}. The fluorescence caused by thallium was approximately halved by the presence of 10 μg of gold(III) and was completely suppressed by 100 μg of this element. Geochemical samples frequently contain considerable quantities of elements which may interfere in the fluorimetric analysis. Although all of these should be removed during the specific preliminary anion-exchange process, as a precaution thallium is extracted selectively as its chloride by means of ether before determination by fluorimetry.

EXPERIMENTAL

All water, acids and solvents used in the analysis were purified by distillation through a silica still.

β-Counting of thallium(I) chromate precipitates was carried out with an end-window Geiger tube coupled to an ECKO preamplifier (type N558) and scaler (type N530F).

Determination of thallium in sea water

Immediately after collection, filter the sea water sample (10 or 20 l) through a 0.5-μ membrane filter and make it 0.1 *M* with respect to hydrochloric acid by addition of 15.4 ml of the redistilled 6.5 *N* acid per litre. On return to the laboratory, treat the sample with a sufficient quantity of saturated bromine water to give 10 p.p.m. of bromine and allow it to pass through a 7.5 × 0.3 cm^2 column of Deacidite FF purified as described below. Wash the column with 20 ml of water. Elute adsorbed ions, other than thallium, with 55 ml of 2 *M* nitric acid, again wash the column with 25 ml of redistilled water, and then elute thallium with 35 ml of a saturated solution of sulphur dioxide into a silica beaker. Evaporate this eluate to small volume after addition of 0.2 ml of 6.5 *M* hydrochloric acid. Transfer the solution quantitatively to a silica irradiation capsule and evaporate it in an oven at 90°, taking care to prevent contamination. Seal the capsule with an oxy–hydrogen torch after cooling the sample in liquid nitrogen to prevent loss of thallium by volatilization. Irradiate the sample in a reactor with thermal neutrons at a flux of $5 \cdot 10^{12}$ n cm^{-2} sec^{-1} for 1 month.

Remove the capsule from the reactor and allow short-lived activities to disintegrate for 2 days. After opening the capsule, add as a carrier 20 mg of thallium as thallium(I) nitrate. Transfer to a silica beaker with 1 *M* hydrobromic acid saturated with bromine. Evaporate to dryness on the water bath and repeat the evaporation with two 5-ml aliquots of 1 *M* hydrobromic acid saturated with bromine. Dissolve the residue in 1.5 ml of the same reagent, make up to 15 ml with distilled water, and extract thallium with two 25-ml aliquots of diethyl ether which has been previously saturated with 0.1 *M* hydrobromic acid. Combine the extracts and wash them twice with 0.1 *M* hydrobromic acid saturated with ether. Extract the combined washings with 5 ml of ether. Add this extract to the main extract and evaporate down with 10 ml of 1 *M* sulphuric acid on the water bath. Continue the evaporation on the hot plate until *ca.* 2 ml of liquid remains. Add 10 ml of a 40:60 (v/v) mixture of concentrated nitric and sulphuric acids and heat on a hot plate at a low setting to remove bromide and most of the nitrate ions; do not allow white fumes to form. Dilute the solution with water to *ca.* 30 ml and reduce thallium to the monovalent state by bubbling sulphur dioxide into the hot solution.

Precipitate thallium iodide by addition of 0.1 ml of 0.5 *M* potassium iodide to the warm solution. Cool, centrifuge and discard the supernatant liquid. Wash the precipitate by decantation with 10 ml of water. Add 0.5 ml of concentrated nitric acid to the precipitate and heat until the colour of iodine has disappeared. Dilute to 20 ml and bubble sulphur dioxide into the solution for a few seconds to ensure that thallium is in the monovalent state. Add 4 drops of 1% (w/v) lanthanum nitrate solution, neutralize by dropwise addition of 10 *M* ammonia solution and then add 1 ml excess of the ammonia solution. Centrifuge and discard the precipitate. Add 5 ml of 10% (w/v) potassium chromate to the supernatant liquid. Allow to stand for 5 min, add 1 drop of Teepol and filter onto a weighed 1.7-cm diameter Whatman GF/B filter. Wash the precipitate of thallium(I) chromate with 10 ml of water and with two 5-ml aliquots of methanol. Place the filter on a weighed planchette, and dry in an oven at 110° for 10 min. When cool, weigh the planchette and precipitate to determine the chemical yield of the separation process. Count the ^{204}Tl β-activity of the precipitate using an end-window Geiger tube. Confirm the identity of the activity by plotting an aluminium absorption curve.

Carry out a reagent blank, by allowing the same quantity of hydrochloric acid and bromine water that was added to the sample to pass directly through the column of Deacidite FF and eluting as described above. Thallium was found to be held quantitatively from 6.5 *M* hydrochloric acid. The method is standardized by irradiating 0.1 μg and 0.03 μg of thallium (as nitrate) in sealed ampoules along with the samples. These standards and a blank are processed and counted in the same manner as the samples.

Determination of thallium in rocks and sediments

A Turner Model III fluorimeter was used for all measurements of fluorescence. Excitation was carried out with a UV lamp and primary filter (maximum transmission at 546 nm). The secondary radiation was screened with a Wratten 22 filter (maximum transmission at 600 nm).

Standard thallium solutions. Dissolve 0.1303 g of thallium(I) nitrate in 1 l of water; the resultant solution contains 100 μg Tl/ml. Prepare working standards from it containing 0.5 μg Tl/ml which are 2.7 *M* with respect to hydrochloric acid.

Rhodamine B. Dissolve 0.1 g of rhodamine B in 100 ml of 3.5 *M* hydrochloric acid.

Ion-exchange resin. Wash Deacidite FF resin (50–100 mesh) with a current of redistilled water to remove "fines" and then digest it twice on the water bath with 2 *N* hydrochloric acid. Wash well with water and pack a 0.6-cm diameter ion-exchange column to a depth of 7.5 cm with the resin.

Method

Weigh into a 50-ml PTFE beaker sufficient of the sample to give 0.05–1.5 μg of thallium. Add 10 ml of electronic-grade hydrofluoric acid and 5 ml of concentrated nitric acid. Heat the covered beaker overnight on the water bath. On the following day remove the cover and evaporate the acid on the water bath. Evaporate the residue twice to dryness with further 10-ml aliquots of concentrated nitric acid, stirring occasionally with a platinum rod. Remove nitrate ion by evaporating to dryness twice with 6.5 *M* hydrochloric acid.

To the residue add 7.7 ml of 6.5 *M* hydrochloric acid and 20 ml of water and warm until it has all dissolved. Dilute the solution to 500 ml with redistilled water and add 5 ml of saturated bromine water. Allow the resultant solution to pass through the ion-exchange column at a flow rate not exceeding 3 ml/min. Wash the column with 20 ml of water and elute interfering elements with 350 ml of 0.5 *M* nitric acid followed by 250 ml of 0.5 *M* hydrochloric acid. Wash again with 25 ml of water and elute thallium with 35 ml of a saturated aqueous solution of sulphur dioxide. Collect the eluate in a silica beaker, and add 1 ml of 6.5 *M* hydrochloric acid. Evaporate to *ca.* 15 ml on the water bath, and oxidize any sulphur dioxide remaining by warming with 4 ml of bromine water. Cool and add 3 ml of bromine water. Transfer the solution quantitatively to a 50-ml separating funnel, using 5 ml of 0.3 *M* hydrochloric acid for washing. Extract thallium with 15-ml aliquots of redistilled diethyl ether. Wash the ether extract twice with 5-ml aliquots of 0.3 *M* hydrochloric acid. Run the ether extract into a silica beaker containing 5 ml of 2.7 *M* hydrochloric acid. Gently warm to evaporate the ether. Oxidize thallium to the trivalent state by addition of 1 ml of bromine water and warm gently to remove the excess of reagent (the temperature should not exceed 70°). Transfer the solution to a 50-ml separating funnel with the aid of 5 ml of 2.7 *M* hydrochloric acid. Add 2 ml of rhodamine B solution, mix well and extract for 2 min with 5 ml of benzene. Measure the fluorescence of the extract. Determine the reagent blank as described above but omitting the sample.

To calibrate the fluorimeter, dilute known amounts of thallium in the range 0.05–1.5 μg to 10 ml with 2.7 *M* hydrochloric acid and add 1 ml of bromine water. Carry out the extraction and fluorimetry as described above.

RESULTS

Rocks and sediments

In order to check the accuracy of the fluorimetric procedure, 1.0-g samples of a deep sea clay and the U.S. Geological Survey Standard andesite AGV-1 were analyzed both alone and after spiking with thallium. These analyses showed (Table II) that satisfactory recoveries of thallium were obtained. The precision of the method was estimated by carrying out 5 replicate analyses on a red clay from the Pacific Ocean

TABLE II

RECOVERY OF THALLIUM ADDED TO 1.00-g SAMPLES OF SILICATES

Sample	*Tl added (μg)*	*Tl found (μg)*	*Recovery (%)*
Andesite AGV-1	0.00	0.39	—
	0.61	1.00	100
	0.92	1.30	99
	1.22	1.60	99
Red Clay	0.00	1.75	—
	0.61	2.37	102
	1.22	2.96	99

TABLE III

DETERMINATIONS OF THALLIUM IN U.S. GEOLOGICAL SURVEY STANDARD ROCKS

Rock	*Reference no.*	*Position*	*Split*	*Thallium (p.p.m.)*		
				Present work	WAHLER[30]	CHAMP[31]
Andesite	AGV-1	27	27	0.39	0.27	1.6
Basalt	BCR-1	8	26	0.59	0.36	—
Dunite	DTS-1	3	41	0.13	< 0.05	—
Granite	G-2	32	105	1.02	0.85	1.3
Granodiorite	GSP-1	4	21	1.87	0.71	1.6
Peridotite	PCC-1	31	27	0.35	< 0.05	—

(Lat. 22° 07′S, Long. 115° 10′W). This was found to contain 5.73 ± 0.06 p.p.m. of thallium. Duplicate analyses were carried out on the six new series U.S. Geological Survey Standard Rocks[29], with the results shown in Table III. For comparison, analyses of these samples by pulse-polarographic[30] and optical spectrographic[31] methods are also included in Table III.

Sea water samples

The precision of the neutron activation method was tested by carrying out 5 replicate analyses on 10-l aliquots of a water sample from the Irish Sea ($\mathrm{Cl} = 34.2\,^{0}/_{00}$). These showed an average thallium content of 18.7 ng/l with a coefficient of variation of ± 5%. The identity of the $^{204}\mathrm{Tl}$ was confirmed by plotting an aluminium absorption curve. Analyses of two further 10-l aliquots of the same water which had been spiked with 67 and 134 ng of thallium showed total recoveries of 70 ng and 127 ng respectively corresponding with recoveries of added thallium of 104% and 95% respectively.

SUMMARY

An anion-exchange scheme has been developed for the preconcentration and almost specific separation of microgram and sub-microgram amounts of thallium. It is used in conjunction with a fluorimetric method based on rhodamine B for the determination of 0.1–6 p.p.m. of thallium in silicate rocks and sediments. The method showed a coefficient of variation of 1.2% at the 6 p.p.m. level. A procedure is also described for the determination of thallium in natural waters in which the element is concentrated by anion exchange and determined by neutron activation. A sample of water from the Irish Sea was found to contain 18.7 ± 0.9 ng Tl/l.

RÉSUMÉ

Une méthode de préconcentration à l'aide d'échangeur d'anions est mise au point; elle permet une séparation presque spécifique de teneurs en thallium de l'ordre du microgramme et du submicrogramme. Elle est utilisée en complément d'un procédé fluorimétrique au moyen de rhodamine B pour le dosage de 0.1 à 6 p.p.m. de thallium dans des silicates et des sédiments. Cette méthode fournit un coefficient de variation de 1.2% pour 6 p.p.m. Un procédé est également décrit pour le dosage du thallium dans les eaux naturelles avec concentration par échangeur d'anions et détermination par activation neutronique. Un échantillon d'eau de mer a donné un résultat de 18.7±0.9 ng Tl/l.

ZUSAMMENFASSUNG

Für eine Vorkonzentration und nahezu spezifische Abtrennung von Mikrogrammen und Submikrogrammen Thallium wurde ein Anionenaustauscher-Schema entwickelt. Es wird in Verbindung mit einer fluorimetrischen Methode verwendet, die auf der Bestimmung von 0.1 bis 6 p.p.m. Thallium in Silikatgesteinen und Sedimenten mit Rhodamin beruht. Im 6 p.p.m.-Bereich besitzt die Methode einen Variationskoeffizienten von 1.2%. Es wird weiterhin ein Verfahren zur Bestimmung von Thallium in natürlichen Wässern beschrieben, bei dem das Element mit einem Anionenaustauscher angereichert und mit der Neutronenaktivierungsanalyse bestimmt wird. Eine Probe aus der irischen See enthielt 18.7±0.9 ng Tl/l.

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THE ATOMIC FLUORESCENCE OF COPPER WITH A HIGH-INTENSITY HOLLOW-CATHODE LAMP

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Atomic fluorescence spectrometry (a.f.s.) provides a very sensitive method of analysis for easily volatilized metals having simple spectra. For these elements, it is possible to obtain limits of detection which are one or more orders of magnitude lower than those obtained by atomic absorption (a.a.s.). Furthermore, the range of linearity, in a.f.s., is usually at least one order of magnitude greater than in a.a.s., as a result of the lower detection limits in a.f.s. Finally it is possible to obtain these results with low-cost monochromators and extremely unsophisticated electronics.

The use of electrodeless discharge tubes as excitation sources for a.f.s. has recently been described[1], and there is little doubt that these are the most satisfactory general light sources available today. However, the electrodeless discharge tubes of a few elements have poor lifetimes and operating characteristics because the metal of interest attacks or diffuses into the quartz wall of the tube when under the influence of a microwave field. As a result, electrodeless discharge tubes of the alkaline earth and "copper group" metals have short lifetimes (less than 100 h) and unsatisfactory operating characteristics. WEST AND WILLIAMS[2,3] have investigated the atomic fluorescence characteristics of magnesium[2] and silver[3] in detail with high-intensity hollow-cathode lamps as excitation sources. Similarly, MANNING AND HENEAGE[4] have obtained limits of detection in a.f.s. and a.a.s. for several elements with these lamps. Their results show a limit of detection for copper which is five-fold lower than that obtained by atomic absorption and, therefore, suggest a more detailed examination of the a.f.s. characteristics of copper.

EXPERIMENTAL

Apparatus

ASL (Atomic Spectral Lamps, Australia) high-intensity hollow-cathode lamp for copper was used as the excitation light source at a primary current 20 mA, booster current 400 mA and filament current 4.5 A.

A Jarrell-Ash Hetco total-consumption burner was used for all the flames examined, the detailed examination being carried out with a hydrogen/argon flame (see Table I).

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TABLE I

LIMITS OF DETECTION (μg/ml) OF COPPER IN VARIOUS FLAMES

Flame	*Detection ($\mu g/ml$)*	*Fuel (l/min)*	*Aspirant (l/min)*	*Uptake (ml/min)*	*Slit*[a] *(mm)*
H_2/argon	0.003	14.0	6.4	1.25	1.0
H_2/air	0.02	14.8	7.5	1.67	1.5
H_2/N_2O	0.03	15.2	7.2	1.50	1.0
H_2/O_2	0.1	14.0	6.7	1.37	0.5
H_2[b]	0.5	—	16.0	0.94	1.0

[a] Entrance slit-width given, the exit slit-width is one half of this value.

[b] Hydrogen/entrained-air flame obtained by supplying fuel to the aspirant gas port on the burner.

The fluorescence emission was focused onto the slit of a Bausch and Lomb compact monochromator, having a range 2000 to 4000 Å, blazed at 2000 Å with a speed of f-3.5, dispersion 3.5 Å/mm and a grating having 2700 lines/mm.

An RCA 1P 28 photomultiplier tube operated at 900 V was used as detector in conjunction with an inexpensive d.c. nanoammeter[5], based on solid-state operational amplifiers and having exceptional stability and gain. A Texas Instruments Recti-Riter galvanometric recorder was used for readout.

Reagents

A stock solution of copper (10,000 μg/ml) was prepared by dissolving 15.61 g of $CuSO_4 \cdot 5H_2O$ in deionized, distilled water and diluting to 1 l. All solutions were kept in polyethylene containers in order to eliminate surface adsorption effects.

Procedure

The d.c. detection system does not permit compensation for any atomic emission arising as a result of thermal excitation by the flame. In order to compensate for this, measurements of the atomic fluorescence of sample, blank and water were made with and without the excitation light beam shut-off by means of a simple shutter. The thermal emission of copper, however, was never detectable at the same amplification used to measure fluorescence.

Measurements were made at 3248 Å with the flame conditions and slit-widths stated in Table I, lamp parameters given previously, and a height of measurement of 12 cm above the burner.

EXPERIMENTAL PARAMETERS

Wavelength of measurement

The largest fluorescence emission signal was obtained at 3248 Å corresponding to the $^2P_{1\frac{1}{2}}^0$–$^2S_{0\frac{1}{2}}$ resonance transition and was the wavelength used for analysis. The atomic fluorescence signal for the $^2P_{0\frac{1}{2}}^0$–$^2S_{0\frac{1}{2}}$ resonance transition at 3274 Å was 0.38 of that at 3248 Å. The intensity of the excitation light from the hollow-cathode lamp was measured spectrographically and the emission at 3274 Å was found to be 0.83 of the intensity at 3248 Å. As the absorption oscillator strengths for copper are 0.16 at both wavelengths[6], this suggests a difference in the quantum efficiencies of fluorescence for the two transitions. With high quenching rates, typical of flames, the ratio of the two quantum efficiencies should be approximately that of their statistical weight/oscillator strength products (0.64 at 3248 Å and 0.31 at 3274 Å)[6], and it would be interesting to verify this experimentally by measuring quantum efficiencies at the two wavelengths.

Atomic fluorescence could not be detected on aspiration of solutions containing 10 μg/ml of copper at any of the other characteristic wavelengths between 2000 Å and 4000 Å (the range of the monochromator), although all of the lower wavelength atomic resonance lines could be identified in the spectrum of the high-intensity hollow-cathode lamp.

Flame type and flow rate

Five commonly used turbulent flames were examined for their suitability for the a.f.s. of copper (Table I). Variations in gas flow rates also result in a drastic change in the shape of the flame; consequently the independent parameters of height of measurement and flow rates of fuel and aspirant gases were evaluated in conjunction with one another. Optimum signal-to-noise ratios were obtained when the atomic fluorescence was measured just above the visible portion of the flame. A height of 12 cm above the burner was found to be the most convenient for the flames used. With the hydrogen/nitrous oxide flame and hydrogen/entrained-air flame, measurements were made within the flame because of the greater length of visible portion.

The most suitable flame for the atomic fluorescence of copper was found to be a hydrogen/argon flame which gave a limit of detection of 0.003 μg/ml. All further work was carried out on this flame.

Lamp parameters

In the high-intensity hollow-cathode lamp, the primary current controls the rate of metal sputtering from the hollow cathode and the lamp intensity is controlled

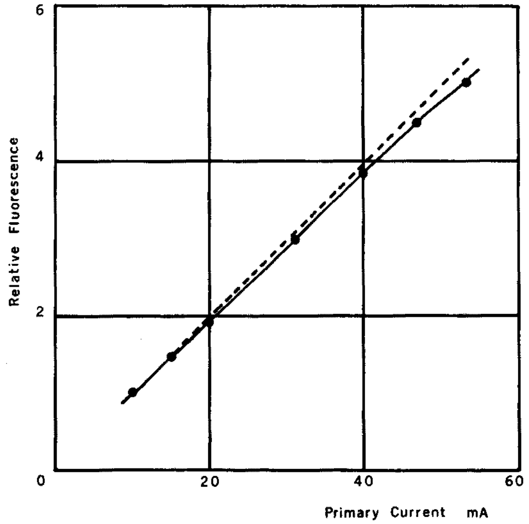

Fig. 1. Variation of fluorescence intensity (relative units) of 0.1 μg/ml Cu with change in primary (sputtering) current of the high-intensity hollow-cathode lamp.

by both the primary and secondary (booster) currents. In a.a.s., the lamp parameters are usually optimized by plotting working curves and using the lamp currents which give the greatest linearity. In a.f.s., self-absorption by the metal vapor of the lamp is less important than in a.a.s. Consequently, increased signals may be obtained in a.f.s. by running the lamp at currents in excess of those recommended for a.a.s.

Lamp warm-up was sufficiently complete for a.f.s. 4 min after the secondary discharge was initiated. The lamp had less than 1% noise after this time but had a long-term drift which was of the order of −10% per hour over the first 2 h. This necessitates the frequent use of standards and would be expected to be even more serious in a.a.s. with single-beam instrumentation.

The atomic fluorescence signal of 0.5 μg/ml of copper at 3248 Å was increased by about 20-fold in changing the lamp secondary current from 0 to 200 mA. Above this current, there was very little increase (*ca.* 5%) in fluorescence up to 500 mA, the maximum current allowable from the power supply. In all subsequent measurements, the maker's maximum recommended current of 400 mA was used.

Alteration of the lamp primary current gave rise to marked increases in the atomic fluorescence of copper as shown in Fig. 1. The a.f.s. signal was almost linear with lamp primary current and, although the lamp could have been operated at 50 mA, this would have reduced its effective lifetime and the recommended current of 20 mA was used in subsequent measurements; at 50 mA the signal is increased by more than two-fold.

Slit-width, gain, etc.

The variation of signal-to-noise ratio and was not critical between entrance slit-widths of 0.5 to 2.5 mm. Outside this range the signal-to-noise ratio decreased appreciably. The exit slit was always set at half the width of the entrance slit because of a reduction in image size within the monochromator.

The photomultiplier dark current was of the order of 1 nA and the peak-to-peak, dark current noise equivalent to 0.05 nA, when measured with a recorder-limited time constant of 0.3 sec. The flame background with 1-mm entrance slit and 0.5-mm exit slit was equivalent to 10 nA and the atomic fluorescence signal from 0.5 μg/ml copper was equivalent to 10–15 nA depending on daily variations in the aspirator and lamp intensity. The values given represent the true photoanodic current from the photomultiplier in nanoamperes.

RESULTS AND DISCUSSION

Range of determination

Limits of detection for various flames are listed in Table I and were taken as the solution concentration producing a signal equal to twice the peak-to-peak fluctuation on aspiration of water only. For each limit of detection, five duplicate measurements (copper solution and water) were made with a time constant of 5 sec, 30 sec being taken for each measurement, for a concentration approaching the limit of detection within a factor of at least five.

The limit of detection was found to be 0.001 μg/ml of copper when the hollow cathode lamp was run with a primary current of 50 mA and 0.003 μg/ml at the recommended maximum current of 20 mA.

Figure 2 shows double logarithmic plots of the fluorescence signal of copper *vs.* solution concentration. The range of linearity extends from the limit of detection to about 20 µg/ml. Between 50 and 500 µg/ml the bending is considerable and independent of solution concentration. Beyond 500 µg/ml the double logarithmic curve has a negative slope as would be expected from theory[7,8]. This corresponds to increasing absorption of the excitation light and re-absorption of fluorescence as the concentration is increased. The slope of the working curve at very high concentrations has a *theoretical* slope of −0.5; however, an experimental slope of −0.26 was found. The deviation from the theoretical could be explained by incomplete volatilization of the analyte at high concentrations and differences between the practical and theoretical models.

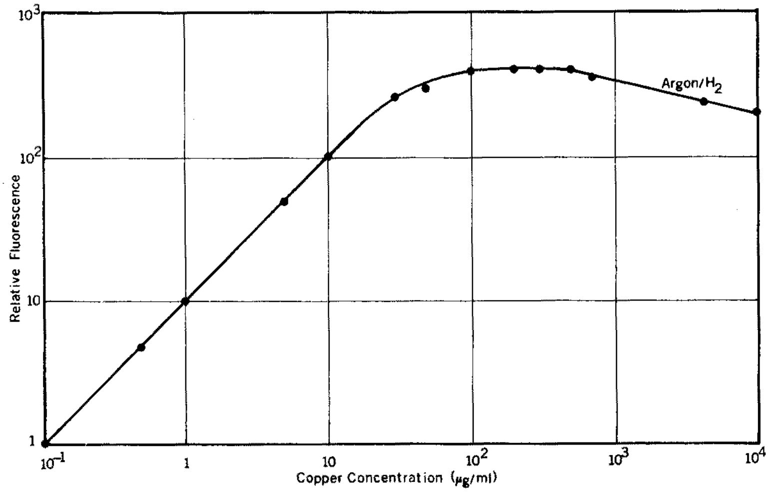

Fig. 2. Analytical working curve of fluorescence intensity (relative units) *vs.* concentration of copper in solution aspirated into flame.

At concentrations higher than 500 µg/ml, the atomic emission of copper became increasingly noticeable and was about one half of the fluorescence signal at 10,000 µg/ml. Below 300 µg/ml the atomic emission was not appreciable relative to the atomic fluorescence signal. The increasing importance of atomic emission at high concentrations would be expected in accordance with theory[7].

Interferences

The effect of concomitant elements was investigated by preparing solutions containing 0.5 µg/ml of copper together with 500 µg/ml of the foreign element. Blanks were made up containing no copper and the value of the blank was subtracted from the signal obtained with copper. This procedure indicated the presence of chemical interferences. A recovery of greater than 105% or less than 95% was taken as an interference.

Chloride was found to give an enhancement of about 20% in the copper signal when present in greater than five-fold molar excess over copper. However, the fluorescence intensity was independent of the chloride concentration beyond this point as shown in Fig. 3. Subsequent studies were carried out in the presence of 0.01 M hydrochloric acid, which successfully buffered out the effect of additional chloride in the solution.

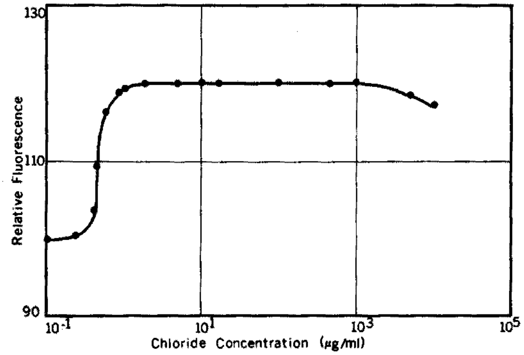

Fig. 3. Effect of added hydrochloric acid on the fluorescence intensity (relative units) of 0.1 µg/ml copper present as $CuSO_4$.

In the presence of 0.01 M hydrochloric acid, the following cations gave *no interference*: Ag, Ca, Cd, Co, Cr, Fe, Ga, Ge, Hg, In, K, Li, Mg, Mn, Mo, Na, NH_4^+, Ni, Sr, Te, Tl, and Zn. Also the following anions gave *no interference* when the hydrochloric acid molarity was more than five times the foreign anion molarity: bromide, carbonate, ethylenediaminetetraacetate, iodide, nitrate and sulphate. The presence of ascorbic acid in an ammonia–ammonium chloride buffer at pH 9 is known to reduce copper(II) to copper(I). However, no interference was noted from this source. The presence of a 1000-fold excess of aluminum reduced the atomic fluorescence of copper by 42%, phosphate by 56% and silicate by 20%. Depressions in signal were noted also when the concentration of other anions: carbonate, nitrate and sulphate, exceeded one fifth of the hydrochloric acid molarity. This effect could easily be overcome by ensuring a large excess of hydrochloric acid at all times or by chelating the copper with 0.001 M EDTA at pH 2–10.

Because of the wide slits employed, the spectral band-width of the monochromator was about 64 Å and, in certain cases, high blanks were noted as a result of atomic emission from concomitants. In particular the elements Li, Na, K, Ag and Cd showed this behavior. However, this could be easily compensated by making measurements with and without the excitation radiation. This enables a satisfactory compensation to be made and this procedure is usually carried out whenever a.f.s. measurements are made on unmodulated systems. Complete compensation for up to 1000 µg/ml of these elements was made when the d.c. amplifier was replaced by an a.c. amplifier (Oak Ridge Amplifier MkVII) and a mechanical chopper operating at 300 hz.

Scattering of excitation light

To date, no detailed studies have been carried out concerning the light scattering which may arise from the presence of large amounts of dissolved solids which are incompletely evaporated in the flame. Unlike atomic emission, *instrumental compen-*

sation can not be made for light scatter, which appears as an increase in the fluorescence signal and which can only be compensated for by the use of suitable blanks.

Before any solutions were used for the scattering experiments, they were analyzed for copper by a.a.s. with an air–acetylene flame and were found to contain less than $1 \cdot 10^{-4}\%$ copper relative to the amount of dissolved solid present. Where necessary a very small correction was made for this. Compensation was also made for any atomic emission occurring. As the atomic fluorescence and scatter signals are both proportional to the intensity of the light source, the most suitable way of recording the light scattering signal is as μg/ml equivalents to the copper a.f.s. signal. For example, if 1000 μg/ml of an element gives a scatter of 10 scale divisions and the a.f.s. signal of 0.1 μg/ml of copper is also 10 divisions, then 1000 μg/ml of the element is equivalent to 0.1 μg/ml of copper. In order to cover several orders of magnitude the results are plotted on double logarithmic scales. Figure 4 shows the results of this study.

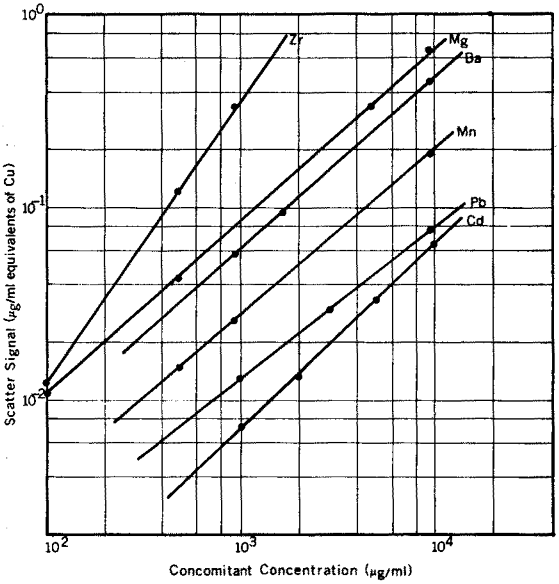

Fig. 4. Scatter caused by high concentrations of dissolved solids expressed as μg/ml of copper required to give the same fluorescence signal.

Despite the criticisms which have been levelled at a.f.s., because of the possibility of light scattering, these results are surprising in that they show scattering of the same order as has been obtained by BILLINGS[9] for a.a.s. with a propane–air flame. Therefore, it would appear that the prevalence of scatter in a.f.s. results more from the use of low-temperature flames, than from any inherent shortcoming in the technique.

CONCLUSIONS

The results of this study show that copper down to 0.003 μg/ml may be determined by AFS with inexpensive apparatus. This result compares with a value of

0.001 μg/ml obtained by MANNING AND HENEAGE[4] with a modified atomic absorption spectrometer and a similar excitation light source. Although little better than the a.a.s. detection limits obtainable on sophisticated double-beam instruments[10] (0.005 μg/ml), the a.f.s. detection limits are considerably better than can be obtained in a.a.s. with low-cost, single-beam instruments[9] (0.02 μg/ml). Conversion of low-cost a.a.s. instruments to a.f.s. operation would therefore appear to be advantageous.

The use of high-intensity hollow-cathode lamps as excitation sources for the a.f.s. of copper has been shown to give limits of detection which are similar to those reported[1] for electrodeless discharge tubes. However, more stable operation and longer lamp life is possible with high intensity hollow-cathode lamps. The development of stable electrodeless discharge tubes of even moderate intensity could be expected to reduce the detection limits quoted here by a factor of ten.

Despite the serious interferences found in the hydrogen/argon flame in the atomic emission of calcium[11], very little interference was found in the a.f.s. of copper because of the greater height of measurement and more favorable volatilization characteristics of this element. Measurements must be carried out, however, with an excess of chloride present or in EDTA solution.

Finally, a study was made of the effect of light scattering by solid particles in the flame and in favorable cases about 1% total solids could be tolerated depending on the concentration of copper being measured and the nature of the dissolved solid. The degree of scatter was found to be little different from that reported for a.a.s.[8] with low-temperature flames.

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SUMMARY

Copper is determined at 3248 Å by atomic fluorescence spectrometry with inexpensive, single-beam, unmodulated instrumentation with a high-intensity hollow-cathode lamp and a hydrogen/argon/entrained-air flame. The limit of detection is 0.003 μg/ml and the linear working range covers nearly five decades of concentration. Evidence is presented which suggests different fluorescence quantum efficiencies for the 3274 Å and 3248 Å fluorescence lines. In the presence of 0.01 M hydrochloric acid, only aluminum, phosphate and silicate give any chemical interference out of 31 species examined. An extensive study of the effect of light scattering by concomitants is presented and in favorable instances nearly 1% total dissolved solids can be tolerated. The degree of scatter was of the same order as for atomic absorption spectrometry, using low-temperature flames.

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DIRECT DETERMINATION OF ZINC IN SEAWATER BY ATOMIC ABSORPTION SPECTROPHOTOMETRY*

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The importance of the trace transition metals in natural water systems is well established. There is, however, a serious lack of data, particularly for seawater, upon which distribution surveys and more specialized studies may be based. Thus, much interest has recently been shown in the role of zinc in marine biota[1] and in marine water–sediment exchange[2] but published values for the ocean system are highly sporadic and biased heavily in favor of certain areas. HOGDAHL[3] has compiled all data available for zinc and other trace metals up to 1963 and more recent work has been incorporated by GOLDBERG[4].

The commonly accepted mean abundance figure[4] for the world's oceans of 10 μg/l is below the detection limit of most conventional instrumentation employed for water analysis, and many techniques require sophisticated pre-analysis concentrations. RILEY[5] has thoroughly summarized the methods utilized by many pioneers in this field. Any lengthy analytical treatment must, however, now be suspect in view of the almost inevitable potential contamination problems, unless most stringent precautions are taken.

Neutron activation analysis and specialized polarographic techniques have been used successfully to determine the zinc contents of seawater without benefit of subsidiary concentrating treatments. However, the procedure developed by HOOD *et al.*[6] requires pre-activation separation of the transition metals from the major interferents, notably sodium and the halides. SCHUTZ AND TUREKIAN[7] have directly irradiated and analysed salt freeze-dried from seawater for many trace metals including zinc. This procedure involves a lengthy post-irradiation cooling period and complex radiochemical separations. The multidimensional γ-spectrometric technique of PERKINS *et al.*[8] allows direct determination of the activation products simultaneously and also eliminates the need for post-irradiation chemistry. These latter techniques provide a total analysis of all species of the test element. Zinc is a most suitable candidate for analysis by anodic stripping voltammetry[9] and some differentiation of the chemical forms of the metal present is potentially possible. ZIRINO AND HEALY[10] have reported data for marine waters by this technique.

The history of the application of atomic absorption spectrophotometry to trace metal analysis of seawater is essentially that of the development of pre-analysis

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* This work was presented in part at the Seventh National Fall Meeting of the American Geophysical Union, San Francisco, December 1968. This is contribution No. 57 from the Institute of Marine Science.

concentration methodology. Coprecipitation[11], chelation and solvent extraction[12,13] and resin column concentration[14,15] are the more successful procedures commonly used to bring the trace metal contents of seawater to within the range of standard equipment, namely, 0.1–1.0 mg/l. The common nebulizer–burner system of conventional atomic absorption equipment is chiefly responsible for limiting the sensitivity of such analyses. Minor modifications to improve flame shape and stability, and various higher temperature combustion mixtures have marginally increased detection limits. However, the basic requirement of continually introducing sample solution in a form suitable for atomization of the test element has severely limited the possibility of any major improvement in this area. As much as 80% of the sample fails to reach the flame and there are physical limitations to the rate at which the liquid sample may be continuously introduced. The "sampling boat" system introduced by KAHN *et al.*[16] avoids these difficulties for certain elements by atomizing a discrete quantity of sample very rapidly. This report describes the development of this method for the determination of zinc in seawater. This procedure is of such intrinsic simplicity and rapidity that detailed, statistically significant surveys are now potentially obtainable.

EXPERIMENTAL

Small quantities of sample, accurately measured with a non-metallic micrometer gauge syringe, were added to the standard tantalum sample boat, dried and atomized in the optical path of a Perkin–Elmer 303 spectrophotometer. The standard sample volume employed was 0.25 ml, but since the analysis time is, within reasonable limits, the same regardless of the amount of sample in the boat, increased sensitivities are easily obtained. The peak areas recorded are linearly related to the quantity of zinc in the sample and concentration values are conventionally assigned by direct comparison with standards similarly treated. For simple solutions—standards and samples of low ionic strength—integration is unnecessary, and peak heights yield acceptable data.

It was found that natural seawater samples produced a pronounced irregular tailing effect on the chart record compared with simple solutions. This appeared to indicate the possibility of differential volatilization of the zinc from the sea-salt surface or the presence of distinct chemical forms. Either possibility would have required determination of the "tail" area. However, additional tests confirmed that the initial absorption peak represented the total zinc content of the water and that the high salt content was superimposing an interference signal. The practical detection limit established by this work was $2 \cdot 10^{-4}$ μg of zinc. Precision for zinc standards in double distilled water and in marine water was ±0.04 and 0.15 μg Zn/l respectively.

RESULTS AND DISCUSSION

Contamination

The determination of trace metals in the μg/l range—as in seawater—necessitates the most stringent precautions against possible contamination. This would seem to be particularly important for zinc, which appears to be a ubiquitous contaminant. It should be noted that the most severe problems in this respect occur during shipboard collection and storage[17]. ROBERTSON[18] has examined many typical containers and handling materials commonly used during trace metal analysis for several metals. This latter work, however, consisted of a total analysis of the test materials, which could yield misleading information. We have elected to determine the amount of zinc removed by contacting known volumes of pure water over varying periods. All commonly used filter membranes, synthetic tubing and dialysis membrane materials readily contaminate samples unless most carefully treated. Table 1 reproduces some of the contamination values obtained for filters treated in several ways. The worst offender was consistently the coarse glass frit used to support the test membranes.

TABLE I

CONTAMINATION DATA FOR FILTER MATERIAL (47 mm DISCS)

(μg Zn/100 ml double distilled water ± 0.004)

Test no.	*Filter*	*Treatment*[a]	*Successive filtrate aliquots (100 ml)*			
			1	*2*	*3*	*4*
1	Millipore—coarse glass frit	c	0.26[b]			
2	Millipore—coarse glass frit	d	0.11			
3	Millipore—coarse glass frit	e	0.01	0.00	0.00	
4	Millipore—type HA—plain	a	0.06	0.01	0.01	0.00
5	Millipore—type HA—plain	a	0.08	0.05	0.02	0.03
6	Millipore—type HA—plain	a	0.10	0.01	0.01	0.06
7	Millipore—type HA—plain	d	0.00	0.00	0.00	0.00
8	Millipore—type HA—plain	d	0.00	0.00	0.00	0.00
9	Millipore—type HA—plain	d	0.00	0.00	0.00	0.00
10	Millipore—type HA—grid	a	0.08[b]	0.03[b]	0.03[b]	0.02
11	Millipore—type HA—grid	b	0.05			
12	Millipore—type HA—grid	b	0.06			
13	Gelman—type H—glass fiber	a	0.19			
14	Gelman—type H—glass fiber	a	0.13	0.04	0.02	
15	Gelman—type H—glass fiber	d	0.09	0.02	0.09	0.01
16	Gelman—type H—glass fiber	d	0.02	0.00		
17	Gelman—type H—glass fiber	d	0.03[b]	0.02	0.00	0.00
18	Selas—type FM 47—silver	a	0.22			
19	Selas—type FM 47—silver	a	0.21	0.03	0.02	
20	Selas—type FM 47—silver	d	1.13	0.06	0.20	0.01
21	Selas—type FM 47—silver	d	0.03	0.02		
22	Selas—type FM 47—silver	d	0.11	0.02	0.04	0.03

[a] Treatment scheme: a = untreated; b = rinsed with double distilled water; c = rinsed with 10% HCl and double distilled water; d = soaked overnight in 10% HCl and washed with double distilled water; e = soaked in aqua regia and washed with double distilled water.

[b] Mean of duplicate samples.

Chemical speciation

The above-noted problems have added greatly to the difficulty of determining the chemical form of the metal in the marine environment. Thus removal of particulate material as conventionally defined for ocean waters by a 0.45–0.5 μ filter was not attempted. The analysis technique is capable of determining the zinc content of the sediment component of sea samples in addition to that fraction held in solution. Thus particulate zinc data are possible by re-analysing the water after removal of the sediment by centrifugation. Minimal sample handling is thus necessary. The present work has shown that in Alaskan coastal waters rich in suspended glacial sediment, soluble zinc constitutes typically only about 5% of the total metal present. These data thus appear to confirm the observation that zinc is effectively scavenged from seawater by clay adsorption and subsequent sedimentation[2,19,20].

RONA *et al.*[21] suggested from dialysis experiments that some zinc in Gulf of Mexico waters is organically complexed. It has been found exceedingly difficult to remove heavy metal contamination from the dialysis membranes, but initial values by this method indicate some 10% of the total soluble fraction of Alaskan estuarine samples to be non-dialyzable. A fuller evaluation of the role of organically-bound zinc in seawater has been given elsewhere[22].

Analysis of seawaters

A general survey of the total zinc contents of Chukchi Sea waters by means of the technique described here, gave a mean value of 2.5 μg/l zinc for 35 samples for 13 stations. It thus appears likely that reported data for zinc by other methods in some open ocean waters may have been overestimated by up to an order of magnitude. In view of the almost insurmountable difficulties with potential contaminants, such inaccuracies would not be surprising. However, it is not suggested that data from this one area should be regarded in any way as typical. Most zinc is apparently adsorbed onto suspended particles in the water, but the "boat sampling" method of atomic absorption analysis is very suitable for either fraction.

The boat accessory, as currently utilized, does not attain the temperature of the conventional air–acetylene flame[16] and therefore only metals atomized at relatively low temperatures may be analysed by this method at present. Zinc has been shown to be particularly suitable; work is currently progressing on silver and lead.

This work was principally supported by Atomic Energy Commission Contract #AT-(04-3)-310. Samples were collected on cruises sponsored by Office of Naval Research Contract NOOO 14-67-A-3017-001 and National Science Foundation Grant GP 5115. We are grateful to several members of the Institute of Marine Science for collecting many of the samples analysed, and also to the officers and crew of the U.S.C.G.C. NORTHWIND.

SUMMARY

A direct atomic absorption spectrophotometric technique for the determination of total zinc in marine waters is described. The detection limit in a seawater matrix by this method is $2 \cdot 10^{-4}$ μg zinc, and 0.25-ml samples may be analysed without any pre-analysis preparation. Contamination problems are shown to be severe for zinc and initial attempts to evaluate the various chemical and physical forms present in natural water samples have had limited success.

RÉSUMÉ

On décrit une méthode directe par spectrophotométrie par absorption atomique pour le dosage du zinc dans des eaux de mer. La limite de détection est de $2 \cdot 10^{-4}$ μg zinc; il est possible d'utiliser des échantillons de 0.25 ml sans préparation spéciale. On examine les problèmes de contamination et les diverses formes chimiques et physiques présentes dans les eaux naturelles.

ZUSAMMENFASSUNG

Es wird eine direkte atomabsorptionsspektralphotometrische Technik zur Bestimmung des gesamten Zinks im Seewasser beschrieben. Proben von 0.25 ml können ohne vorherige Behandlung direkt analysiert werden. Die Nachweisgrenze im Seewasser beträgt bei dieser Methode $2 \cdot 10^{-4}$ μg Zink. Es wird gezeigt, dass Verunreinigungen für die Bestimmung des Zinks von Bedeutung sind. Anfängliche Versuche zur Bestimmung solcher verschiedener chemischer und physikalischer Arten in natürlichem Seewasser hatten begrenzten Erfolg.

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A SINGLE-OVEN GAS CHROMATOGRAPH WITH A SIMPLE, ALL-QUARTZ, FLAME IONIZATION DETECTOR

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(Received June 1st, 1969)

Numerous gas chromatographs have been evolved since the onset of gas liquid chromatography. TOUCHSTONE AND DOBBINS[1] have shown the feasibility of a single-oven gas chromatograph with an on-column argon detector. The unit described here, however, contains an on-column flame ionization detector that can be operated at high temperatures.

WILHITE AND BURNELL[2] have designed a lunar gas chromatograph, as part of Surveyor scientific payload, to do many complex functions on command from earth. The analytical oven in the complex module operates at less than 50 W of heating power. However, most commercial gas chromatographic ovens operate in excess of 500-W heating power, and air mixing is attained by conventional blowers. The compact gas chromatograph unit presented below represents a significant reduction in weight, volume and power requirements. These features suggest use of the instrument in field studies with battery power.

Since the introduction of the flame ionization system by RYCE AND BRYCE[3] and by MCWILLIAM AND DEWAR[4], excellent papers have been published by numerous investigators[5-8] on the theory, applications, effects of design and operational parameters of the detector. The purpose of this paper is to discuss the construction of (*a*) a compact, single-oven gas chromatograph with good stability and sensitivity, (*b*) an inexpensive, all-quartz, flame ionization detector of simple design, and (*c*) a column conditioning oven.

EXPERIMENTAL

Gas chromatograph

The gas chromatograph, shown in Fig. 1, consists of a single oven for both the detector and column. The on-column detector, flash chamber and injection port are mounted on the top assembly as shown in the exploded view in Fig. 2. The top for the oven (assembly) is made of aluminum for rigidity and insulated with 3/8" Transite on the bottom side and 2" Marinite 36 (Johns-Mansville) on the top side. The flash chamber is completely recessed into the insulation to minimize heat loss.

A 4" × 12" aluminum pipe is used for the oven as shown in Fig. 3. The aluminum pipe is machined to contain a continuous triangular groove, four turns per inch, of sufficient depth to contain a nichrome resistance wire. Asbestos-insulated, 20-gauge, nichrome heating wire is wrapped in the groove. The aluminum pipe (oven) is then insulated with conventional 2″ fiberglass. An outer shell, constructed of aluminum, forms a stand for the apparatus (Fig. 1).

The temperature of the oven as well as the flash chamber is regulated with proportional temperature controllers containing thermistors (Texas Instruments, Klixon, Model 10CT3-3, 125 W, 60 hz, 120 V a.c.). Oven heat is distributed by a circulating fan located on the bottom cover of the oven, as shown in Fig. 1. The fan blade is coupled to the exterior motor by a 3/16″ × 4″ shaft. A 2″ × 5″ circular block of Marinite 36 insulates the bottom of the oven and the blower motor.

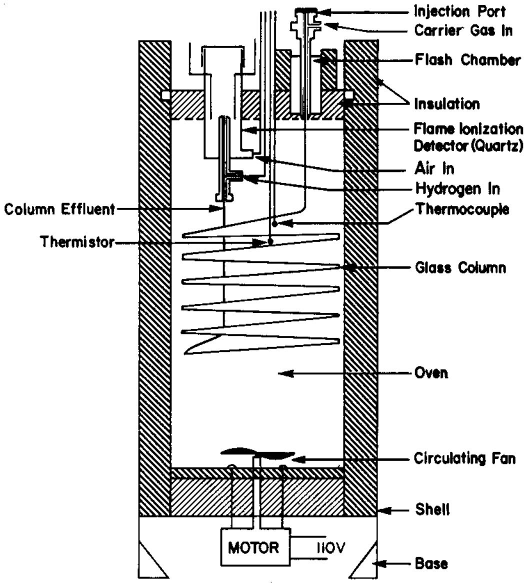

Fig. 1. Schematic drawing of the gas chromatograph.

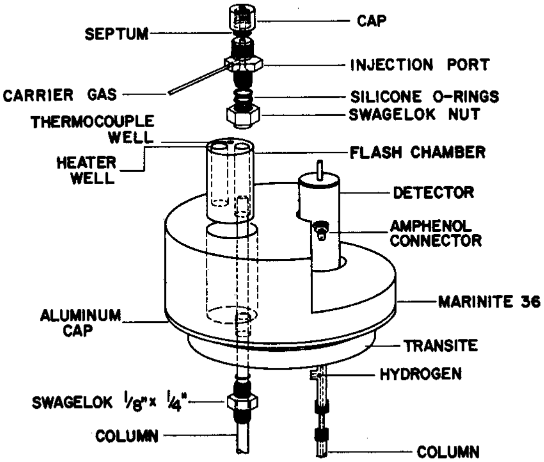

Fig. 2. Detailed drawing of the top assembly.

The flash chamber and injection port are of a simple design as shown in the exploded view in Fig. 2 and in Fig. 4. The chamber is constructed from 1-1/2″ × 2″ aluminum stock drilled to allow passage of an arm of a coiled glass analytical column. Heat is applied to the flash chamber with a Chromalox, 85-W, 120-V cartridge heater contained in a 3/8″ × 1-3/4″ heater well. An additional hole is drilled to a depth of 1-3/4″ to retain conveniently a 20-gauge iron–constantan thermocouple. Temperature in the oven as well as the flash chamber is indicated with a pyrometer, Model # 561 (Assembly Products, Inc.).

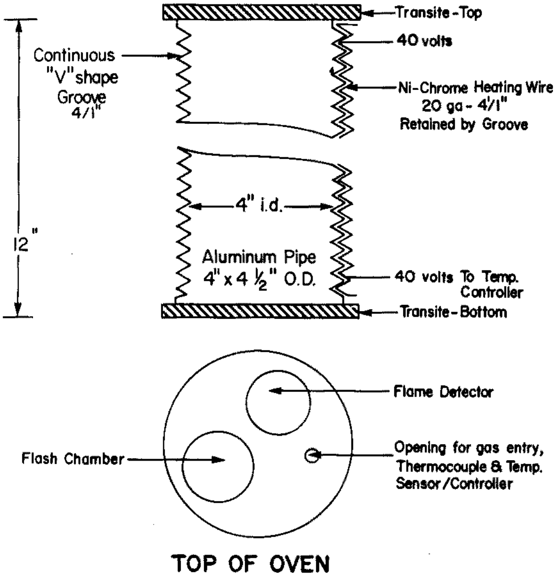

Fig. 3. Design of the oven.

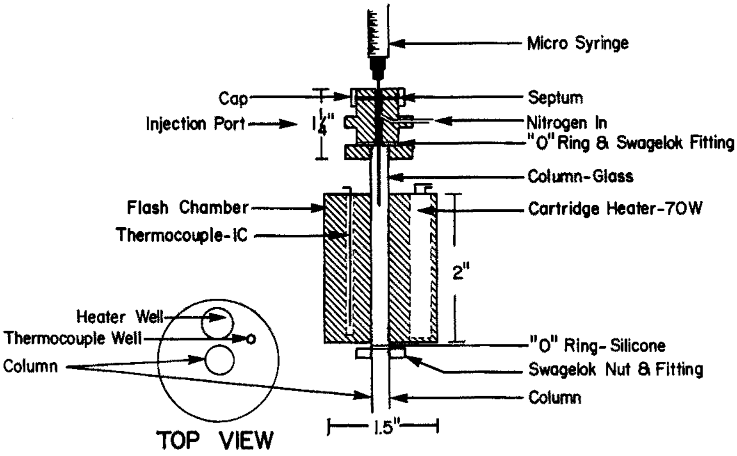

Fig. 4. Detailed drawing of the injection port and flash chamber.

The injection port, as shown in Figs. 2 and 4, is constructed from stainless steel stock with 1/4″ male pipet thread on one end and a 1/4″ Swagelok tube connection on the other end. A 0.06″ hole is drilled through the center of the stainless steel stock to allow passage of a 27-gauge, 2″ hypodermic needle (Hamilton # 701) for injection into the column.

Carrier gas enters the injection port by means of a 1/8″ o.d. × 0.04″ i.d. stainless steel line welded to an inner orifice. The glass analytical column is connected to the Swagelok tube end of the injection port by means of a 1/4″ nut and silicone rubber O-rings.

Microregulators, Model # 11-101-003 (C. A. Norgren & Co.) are used to regulate air, hydrogen and carrier gases to the detector and column. A 2″ × 1/16″ × 0.02″ restrictor is used in the air flow, while a 2′ × 1/16″ × 0.02″ restrictor is used in the hydrogen line for easy flow control.

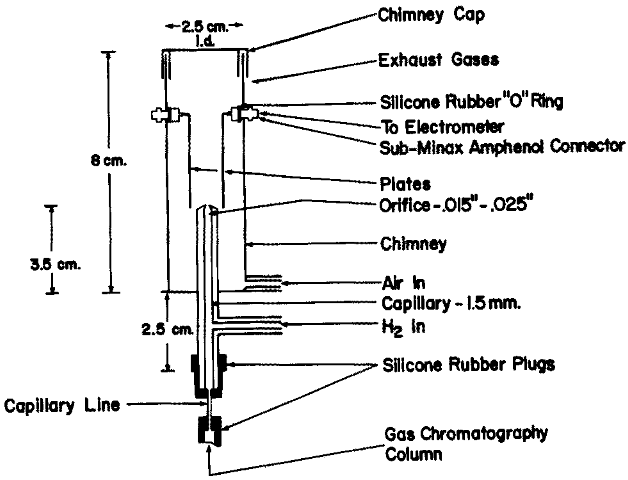

Fig. 5. Diagram of the all-quartz flame ionization detector.

The detector is mounted on the gas chromatography column in the same oven as the column by means of a 1/2″ stainless steel tubing (Figs. 1, 2). The design of the detector is shown in Fig. 5. The detector chimney is fabricated from quartz tubing of 2.5–2.8-cm inside diameter and 8.0-cm length. Hydrogen enters just below the base of the chimney as one leg of a capillary tee. This tee extends into the chimney for a distance of about 3.5 cm and terminates in a fine orifice (0.015″–0.030″) where the column effluent is burned. The capillary tee extends below the base of the chimney for a distance of 2.5 cm and is connected to the gas chromatography column with silicone rubber sleeves and 1/2″ × 0.04″ capillary stainless steel transfer line. Air to the chimney enters the base through a capillary quartz tube sealed at a tangent. This design creates a cylindrical air flow around the base of the burner and turbulence is minimized.

The cap to the detector is also made of quartz. It is a double cap, concentric in design, fitting against the inner and outer walls of the chimney. Sufficient clearance is provided for exhausting excess air and combustion products from the burner. The detector contains parallel plates for maximum collection of electrical species and it can be used at temperatures in excess of 300° with either glass or metal columns.

The chimney contains sub-minax Amphenol (# 17-9) connectors for removing the parallel plates for easy cleaning. The connectors are mounted firmly to the chimney by use of O-rings or Teflon ferrules. The plates are made of stainless steel, 1/16″ × 1/2″ × 1-1/4″. The plates are installed parallel to the burner jet 4 mm apart.

Three different types of air injection systems may be used with variation in the installation of the polarizing and collecting plates. In Fig. 6A, air is diffused around the base of the burner through a coarse frit. The parallel plates are mounted on a ceramic or quartz cap. The grooved cap is fixed to the chimney by springs. In Fig. 6B, air is diffused at the base of the burner through a concentric, doughnut-shaped tube. Air holes in the upper surface of the ring direct the air flow parallel to the plates, thereby maintaining a laminar flow. In Fig. 6C, air enters the base of the chimney through a capillary quartz tube sealed to the chimney at a tangent. This design creates an upward, cylindrical direction of air around the burner, maintaining a laminar flow. The detachable parallel plates are connected to a ceramic seal by means of slip-joint connectors. A standard taper joint provides an air seal which is necessary when collecting exhaust gases for subsequent analysis.

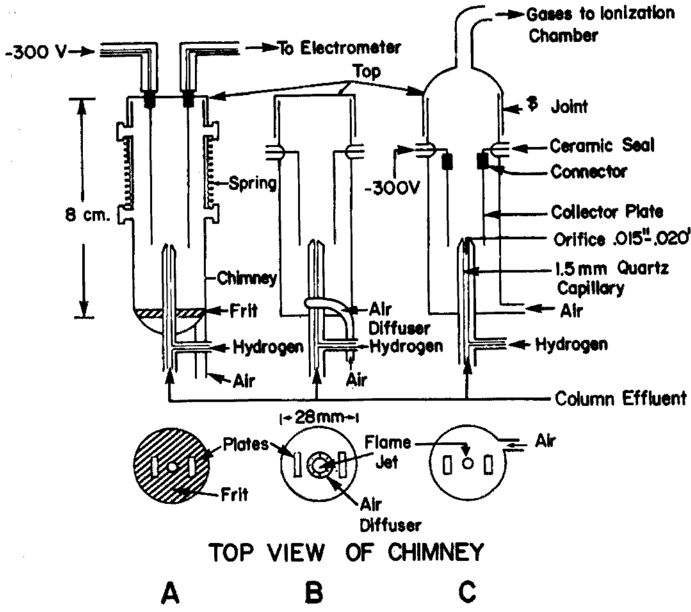

Fig. 6. Variations of detector design.

Conditioning oven

The oven used for conditioning columns is also heated by means of a 20-gauge nichrome resistance wire wrapped around a 10″ × 4″ grooved aluminum pipe, similar in design to the analytical oven. For simplicity of design, the air circulating fan is excluded and temperature in the oven is allowed to equilibrate to the desired temperature by using a Variac. The bottom of the oven as well as the top is also insulated with 2″×4″ Marinite 36. The top of the oven contains a 1/4″ hole to allow passage of one arm of a glass coiled column, and gas flow to the column is attained by means of a Swagelok fitting and silicone O-rings. The effluent of the column contains a one-hole silicone plug. A stainless steel transfer line extends from this plug through the top of the oven. During column conditioning flow rate can then be accurately regulated. A thermometer or a thermocouple is provided to indicate the temperature of column conditioning. The oven can be operated at temperatures greater than 400°.

For the entire evaluation of the gas chromatograph, a Hamilton #701, 10-μl syringe was used for injection. The detector signal output was amplified by a Barber-Colman line operated electrometer Model #5040. The output signal of the electrometer was used to drive a Leeds and Northrup 1-mV, 1-sec response, gas chromatograph recorder. The polarizing voltage to the detector was supplied by an Eveready #493, 300-V battery.

The compressed gases to the detector were dried with molecular sieves. In all studies a 6′×1/4″ coiled, silanized glass column packed with a 2% neopentyl glycol succinate on 80–100 mesh Gas Chrom Q solid support was used. Before use the packed column was conditioned for 12–16 h at 240° with a nitrogen flow of 15 ml/min.

RESULTS

In order to demonstrate the symmetry and efficiency of the parallel plate collection system the gas flows to the detector were optimized for maximum sensitivity. The polarizing voltage was then set at −300 V. Normal procedure was followed for introducing a sample to the column. The sample consisted of a synthetic mixture of steroids as their trimethylsilyl ether derivatives. The polarizing voltage was then reversed and again the synthetic mixture was charged. The results of this study are shown in Table I. The area percent of the individual steroids as the trimethylsilyl derivatives was calculated by assuming that the entire injected sample was eluted from the column. These data show that good symmetry exists in the collection system, and either negative or positive species may be collected with equal efficiency.

TABLE I

EFFECT OF REVERSING POLARITY OF PARALLEL PLATES ON EFFICIENCY OF SPECIES COLLECTION

	Area	
Polarizing voltage (300 V)	*Negative voltage*	*Positive voltage*
Pregnanediol (TMS)	22.3	21.8
Androsterone (TMS)	21.6	21.8
Etiocholanolone (TMS)	21.8	20.5
Dehydroisoandrosterone (TMS)	10.5	10.6
Epicoprostanol (TMS)	8.6	9.6
Pregnanetriol (TMS)	15.2	15.8
Total	100.0	100.0

To evaluate the gas chromatograph for sensitivity and linearity at low concentrations a synthetic mixture (1.0 μg/μl) of steroids was prepared. The mixture consisted of androsterone (A), etiocholanolone (E), dehydroisoandrosterone (DHIA), pregnanediol (P-diol), pregnanetriol (P-triol), and epicoprostanol (Epi-Cop) dissolved in alcohol. Trimethylsilyl ethers (TMS) of this mixture were prepared by the usual method of reacting 0.3 ml of hexamethyldisilazane and 0.1 ml of trimethylchlorosilane overnight[9]. Lower concentration was obtained by diluting aliquots of the synthetic mixture with tetrahydrofuran. The curves for pregnanediol and pregnanetriol in this study are shown in Fig. 7. Peak area measurements were made in triplicate by plani-

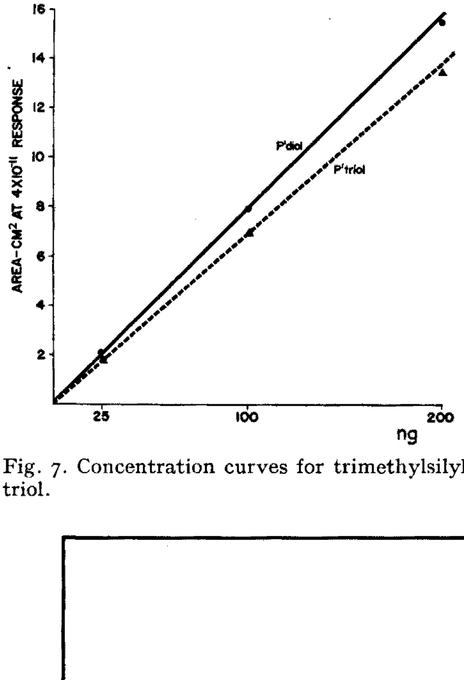

Fig. 7. Concentration curves for trimethylsilyl ether derivatives of pregnanediol and pregnanetriol.

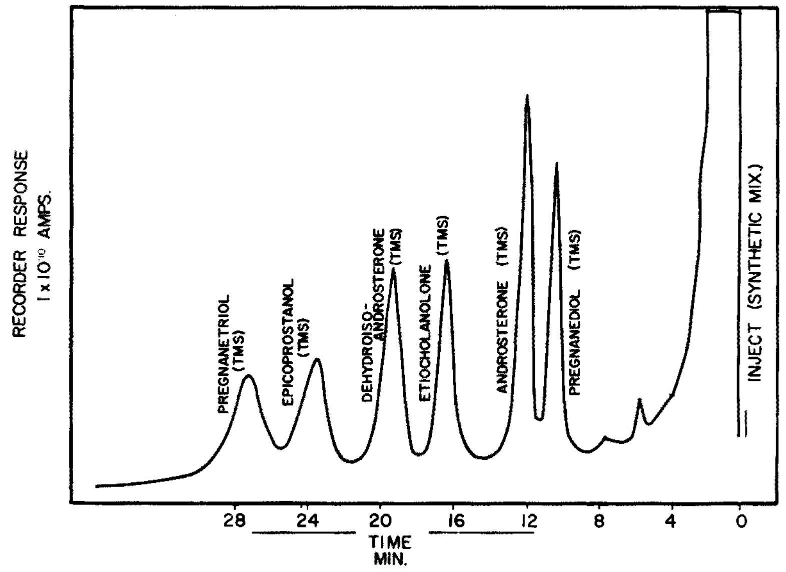

Fig. 8. Chromatogram of trimethylsilyl ether derivatives of synthetic 17-keto steroids, pregnanediol and pregnanetriol. Instrumental conditions: column 6′×0.25″ 2% NGS on 80–100 mesh Chrom Q. Column and detector temperature 207°, flash chamber temperature 240°.

metry and adjusted to one sensitivity ($4 \cdot 10^{-11}$ A). Good reproducibility of sample injection was achieved with practice. The concentration curve for androsterone followed very closely the slope of pregnanediol, while the concentration curves for etiocholanolone, epicoprostanol (internal standard) and dehydroisoandrosterone followed closely the slope of pregnanetriol. The curves show that there is no obvious

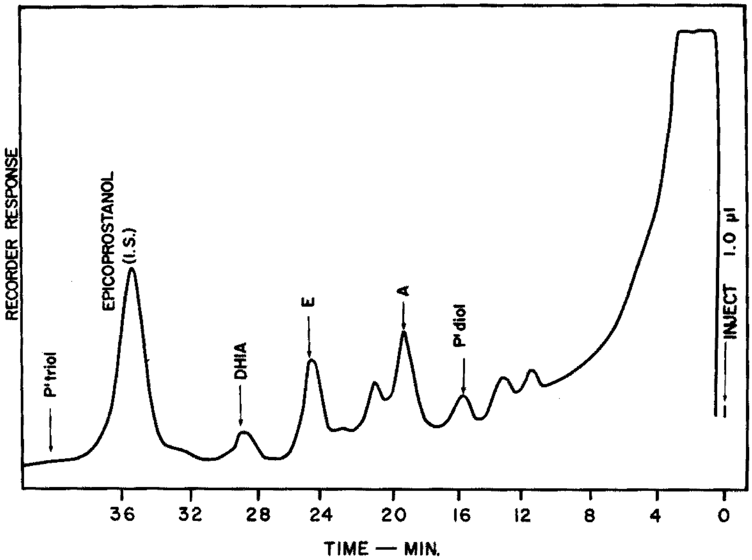

Fig. 9. Chromatogram of TMS derivatives from urine of normal subject. Mixture as trimethylsilyl ether derivatives.

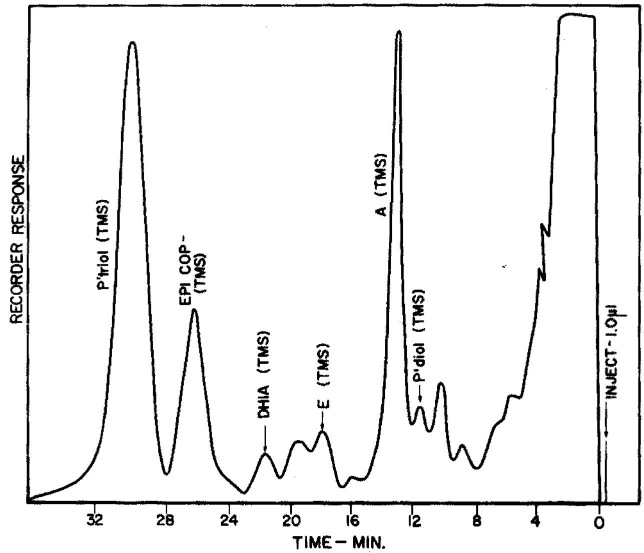

Fig. 10. Chromatogram of TMS derivatives from urine of patient with congenital adrenal hyperplasia. Mixture as trimethylsilyl ether derivatives.

loss of steroids in the chromatography procedure at low concentration levels. Linearity of the calibration curves was maintained to 25 ng.

Figure 8 shows the separation and detection of a synthetic steroid mixture as trimethylsilyl ether derivatives at a concentration of approximately 1.0 $\mu g/\mu l$. At sensitivity of $1 \cdot 10^{-10}$ A (1 mV full scale recorder deflection), the drift of the gas chromatography system is less than 1.0%/h with no detectable noise, while at $2 \cdot 10^{-11}$ A the noise is less than 2.0%.

The chromatograms shown in Figs. 9 and 10 are those of a normal and an abnormal endocrine patient respectively. In each analysis a 20-ml aliquot of a 24-h urine specimen was incubated with β-glucuronidase and the steroids were then extracted with ethyl acetate. To the mixture was added a known quantity of epicoprostanol which was used as an internal standard (I.S.). The internal standard eliminates the necessity of injecting an accurate volume of sample into the gas chromatograph. Each individual area of a steroid of an unknown concentration is compared with a known quantity of epicoprostanol (I.S.) of a given area. No detectable quantity of pregnanetriol is noticed in the chromatogram in Fig. 9. However, an excessive amount of pregnanetriol is easily detected as shown in Fig. 10. This patient (R.Q.) was diagnosed as having congenital adrenal hyperplasia.

DISCUSSION AND PROPOSED APPLICATIONS

A single-oven design for both the detector and column renders the gas chromatography unit ideal for isothermal operation, while the unique method of heating the oven minimizes hot and cold spots. Less than 50 W of heating power is needed for stable operation at 225°; therefore, the oven may utilize rechargeable nickel–cadmium batteries or lead–acid batteries of the proper ratings.

Heat loss in the detector chimney is minimized by preheating the hydrogen and supporting air before they enter the detector. The various designs for introducing air to the detector maintain a laminar flow and minimize turbulence. These designs enhance combustion and efficiently remove combustion products from the chimney. Increased flame stability and ion collection is therefore achieved. Thus the simplicity of design, the superior collection of a charged species, and the absence of thermionic emission and electrical leakage make this detector ideal in a gas chromatography system.

The flame ionization detector, shown in Fig. 6C, can be used for radiotracer studies in biomedical and industrial fields. Normally, when a flame ionization detector is used in a chromatography system, a fraction of the column effluent is taken (effluent split) for subsequent radioactive counting. This is accomplished by passing the unchanged effluent over copper oxide at temperatures above 800°. The product of combustion, labeled carbon dioxide and water, is dried and the activity measured by suitable means. This technique, even though widely used, is time consuming, expensive, and requires bulky equipment. Furthermore, since a fraction of the eluted stream is taken, maximum sensitivity is not realized. By using the all-quartz, flame ionization detector, as shown in Fig. 6C, the entire organic material eluting from a gas chromatography column is combusted in the flame without the need of an effluent split as follows:

$$H_2 + O_2 + \text{volatile organic} \rightarrow CO_2 + H_2O + \text{ions and electrons}$$

It is then possible to collect quantitatively and record charged particles representing a chromatographic peak and subsequently monitor radioactive combustion products such as $^{14}CO_2$ by using a suitable flow-through cell or a flow-through counting chamber. Other methods of gas collection may be used conveniently. For example, condensation at liquid nitrogen temperature and adsorption in molecular sieve traps or trapping the $^{14}CO_2$ in caustic solution are all possible.

Thus, for example, if degradation of labeled benzene is to be followed in an industrial process, or if a labeled steroid is to be studied in a biological system, the all-quartz, flame ionization detector may be desirable.

The all-quartz flame ionization detector could be adapted for measuring organic sulfur and phosphorus compounds eluted from a gas chromatography column. The feasibility of measuring the emission spectra of these compounds in a hydrogen-in-air detector has been disclosed by a German patent[10] in 1962 and was later applied to the specific detection of sulfur- and phosphorus-containing compounds eluted from a gas chromatography column by BRODY AND CHANEY[11] and GETZ[12]. Since the detector chimney as well as the burner is entirely of quartz, and since the collecting and polarizing electrodes are mounted as parallel plates, it is feasible with modifications not only to measure ionization currents but simultaneously to detect flame emission photometrically.

The unit can be used in the field for study of water pollution where oil is discharged into waterways from the petrochemical industry and from ships in harbors or intracoastal canals. The unit should also prove valuable in gas and oil well studies and geological surveys for the analysis of trace gases and hydrocarbons. The gas chromatography unit is not limited to the use of the flame ionization detector alone. Other detectors can be mounted on the top assembly by suitable modifications.

Development of this instrument was supported by DHEW Grants 5MOl FR-00073 and 5ROl AM-07616, Division of Research Facilities and Resources, National Institutes of Health. The assistance of Miss CAROLYN CORN, (the late) Mr. CARL SCHUSTER, (the late) Mr. MELVIN NEELY and Mrs. RUTH MCBEE is gratefully acknowledged.

SUMMARY

A compact, inexpensive, single-oven gas chromatograph is described that has good stability and sensitivity. The flame ionization detector, flash chamber and column are mounted as an assembly on the oven top. The oven is constructed from a 4″ × 12″ aluminum pipe containing a continuous groove for retaining a nichrome heating wire. This design suggests the use of the apparatus on rechargeable nickel–cadmium or lead–acid batteries in field studies. The oven may be operated isothermally above 300° with low power input on either a.c. or d.c. The oven has been in continuous operation for over 3 years without maintenance. A simple flame ionization detector constructed entirely of quartz is also described. Although the gas chromatograph was constructed for glass columns in biomedical investigations, the apparatus can be used with metal columns as well as with other detectors in industrial applications. Detection of sub-microgram quantities of androgens is discussed.

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A STATISTICAL STUDY OF GAS CHROMATOGRAPHIC SYSTEMS EMPLOYING FLAME IONIZATION DETECTORS

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(Received July 12th, 1969)

In the last nine years, many studies concerning the flame ionization detector have been published. Most of these are concerned with the detector alone; no partitioning column was used and the sample was introduced into the detector in a constant stream. In attempts to use chromatographs equipped with flame ionization detectors for routine analyses, the behavior obtained proved to be quite different from that expected on the basis of published work. For this reason a study of some gas chromatographic systems using flame ionization detectors was carried out. Because of the number of variables to be studied and the strong possibility of complex interactions among them, it was decided to use statistical methods in planning the experiments and in interpreting the results.

The planned work was limited in scope to the use of the three brands of chromatographs equipped with flame ionization detectors which were available in our laboratory. The important factor of detector geometry was considered only by noting differences among the three instruments. This limitation was considered justifiable because most workers now buy commercial instruments and use them as received rather than construct their own detectors. Thus, the purpose of this work was to study the gas chromatographic system as a whole, for commercially available instruments.

Although the particular instrument models used in this work are now obsolete, this does not affect the validity of the statistical methods of investigation and interpretation of data. The reporting of these methods is the aim of this paper; it is not the aim of this paper to report comparative test results on different instrument models.

Literature survey

Most of the published work on the flame ionization detector was performed under conditions most suitable for the study of the detector alone[1–14]. These generally were not the conditions which would be encountered if the flame ionization detector were placed in a chromatograph to act as a detector in actual analyses. It seems likely that, since conditions are different in the two cases, and since the quantity labelled "response" is different, the relation between the operating parameters and "response" might be different in the two cases. In fact, it has been suggested that such a difference would exist[2].

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In order to determine what such differences might be, it is first necessary to consider very carefully the reported results obtained under non-chromatographic conditions. In the studies of the detector alone, where sample flows continuously, response is measured as electrical current flowing through the detector circuit in amperes. Response arising from injection of sample slugs is usually measured as peak area, which is equivalent to coulombs or amp-sec. In this paper where response arising from continuously flowing sample is meant, the term "response (amperes)" will be used; where response from injected samples is meant, the term "response (coulombs)" will be used. The word response alone will mean both types of response.

One of the most frequently studied parameters of the flame ionization detector is the hydrogen flow rate. Several authors[1,3,4,6,9,10,12,13] have shown that there is an optimum hydrogen flow for which maximum response (amperes) is obtained. Several authors[15-18], working with "chromatographic" conditions have found similar results, although DURRETT *et al.*[19] report a decrease in response (coulombs) with increased hydrogen flow; but it may be possible that they studied a smaller range of hydrogen flow (for their detector) than the other authors. BRUDERRECK *et al.*[2] report a response (amperes) which increases with hydrogen flow rate to a certain point, whereupon the response shows little further increase with increased hydrogen flow. The comment made on the work of DURRETT *et al.* may apply to the work of BRUDERRECK *et al.*; or, as suggested in the latter paper, the different effect of hydrogen flow rate may be due to the geometry of their detector.

Another frequently studied parameter is polarizing voltage; and again there is agreement among a large number of authors[2,4-6,9,10-13] that response (amperes) increases with increasing voltage up to a point. Beyond this point, further increase in voltage results in little change in response. Of course, if the voltage is made high enough, "breakdown" ionization of the gases in the detector occurs; signal increases very rapidly with voltage increase, and actual arcing can occur. Workers[15,16,19] using chromatographic conditions also find that response (coulombs) is affected in a similar way by polarizing voltage.

The effect of air flow rate, according to several authors, in both chromatographic[15,19] and non-chromatographic conditions[2,6,9,13] is similar to that of polarizing voltage. At first, response increases with an increase in air flow rate; but, as the air flow rate is further increased, little change in response occurs.

Few people have studied the effect of carrier gas flow rate on response, possibly because most of the studies reported use a flame ionization detector by itself with a constant flow of sample into the detector. For these reasons, no carrier gas is necessary, and frequently none is used. DESTY *et al.*[4], MCWILLIAM[10] and STERNBERG *et al.*[13] report that adding carrier gas in increasing amounts causes response (amperes) to increase to a maximum, and then fall off. HALÁSZ AND SCHNEIDER[8a] also report an increase in response (amperes) with an increase in carrier flow rate, but FOWLIS *et al.*[20] report that response (amperes) is relatively insensitive to carrier gas flow rate. DAL NOGARE AND JUVET[21] state that the flame ionization detector is insensitive to carrier gas flow. ETTRE AND KABOT[22,23] report this same conclusion, although it must be noted that WISEMAN[24] disagrees.

The situation is not made clearer by the conflicting statements of STERNBERG[14] and FETT[25]. STERNBERG states that "a rate of introduction sensing detector will be essentially unaffected" by additional carrier gas added between the detector and the column. FETT reports that adding carrier gas between a capillary column and the detector increases the response (coulombs). Perhaps it has been assumed that since the baseline from a flame ionization detector is not affected by changes in carrier gas flow rate[7,26], such flow changes also do not affect the sensitivity of the detector to the sample.

The effect of sample quantity on the response of the flame ionization detector has been studied, with a number of different ways of measuring the sample. Those workers[3,4,8,8a,10,13] who use a continuous flow of sample usually measure this sample in terms of the rate at which it enters the detector, although occasionally, concentration of sample in the carrier gas is used[1,3,8]. Workers[15–19,26–29] who inject slug samples find it more convenient to measure the sample in terms of the weight (or volume) of sample injected.

It is widely accepted that, basically, the response (amperes) of a flame ionization detector is proportional to the rate of introduction of the sample into the detector[3,4,8a,11,13,21] rather than to the concentration of the sample in the carrier gas.

Generally, the important thing is not the absolute amount of sample entering the detector; but, rather, the ratio of the largest sample to the smallest sample for which detector response is a linear function of the sample size. This is what is usually referred to as "linear range". Several people, such as LOVELOCK[30], DAL NOGARE AND JUVET[21], MCNAIR *et al.*[31], RITTER[28] and GILL[29], report a linear range of 10^6 to 1; while others[3,13,33] report a range of 10^7 to 1. In our study of a number of papers[1–4,8,8a,10,13,18,19,26–30,33], most papers[1,3,4,8,8a,10,18,26,27,27a] show data for only a very limited linear range, *i.e.* less than 1000 to 1. STERNBERG *et al.*[13] and BRUDERRECK *et al.*[2] show data for a linear range of 10^4 to 1. Thus, it appears that while an extended linear range is possible, in actual practice a much smaller range is usually attained. Also, it has been shown[32] that use of a detector whose response deviates from a linear response by 2% can lead to errors of 13% in a sample range of 1000 if linear response is assumed. BRUDERRECK's work[2] indicates that a large linear range is only available under certain operating conditions, such as a certain range of polarizing voltage.

A parameter which has been little investigated is that of retention time. BREDEL[34] reports that the response (coulombs) is proportional to retention time. MIYAKE AND MITOOKA[35], on the other hand, report that retention time has no effect on response (coulombs). None of the other papers consulted refers to this parameter; those few in which samples are injected by syringe into a column say nothing of the effect of retention time. In most of the work reported in which sample flows constantly into the detector, there is no such thing as retention time; consequently, no measure of the effect of such a parameter could be made.

In addition to reporting the effects of individual parameters on response, a number of authors have reported the combined effects of two parameters on response. These combined effects, or interactions, describe a situation where the effect on response of simultaneous changes in two parameters is different from the sum of the changes in response due to changing each parameter separately.

BRUDERRECK *et al.*[2] and MCTAGGART AND MORTIMER[9] report the effect of polarizing voltage–sample interaction on response (amperes). The effect of the interaction of hydrogen flow rate and carrier flow rate has been described by several workers[6,10,12,16,17], most of whom[10,12,16,17] find that there is an optimum ratio of hydrogen flow rate to carrier flow rate. ANDREATCH AND FEINLAND[1] find an interaction between hydrogen flow rate and sample flow rate. Interaction between hydrogen flow rate and sample type has also been found[2,9,10]; normalization factors for different compounds change with changing hydrogen flow. BRUDERRECK *et al.*[2], and MCTAGGART AND MORTIMER[9] also find an interaction between hydrogen flow rate and the geometry of the detector.

Even such a cursory literature survey leads to several conclusions. The most careful and detailed studies have been made under highly specialized conditions, intended solely for the study of the detector. Results obtained from more nearly normal conditions (from the viewpoint of practical analyses) seem to be generally less favorable than those obtained in the more controlled studies. Significant numbers of conflicting reports are present. Finally, interactions among variables are obviously present but have not been systematically studied. This leads to the hypothesis that data gathered from a study of isolated system components, or combinations of components, may describe the behavior of the complete system only vaguely or not at all.

Since much chromatography is conducted under conditions which are far from ideal (*e.g.* adjacent electronic noise sources, electrical noise from the power line, column bleed, dirty detector, poor injection practices, splitter non-linearity, etc.), it would seem logical to study the whole "system" simultaneously. Such a study would use commercially available instruments placed in a normally busy laboratory, and operated by personnel who would normally use the instruments, with operating techniques as near the usual as possible. This is what has been attempted.

DESIGN OF EXPERIMENTS

It was evident that a large number of variables at several levels required investigation to determine sufficiently the nature of the response (coulombs) of the flame ionization detector–chromatograph system. In the general case, the number of recognizable variables is so large as to require prohibitive expenditures of time and effort for a comprehensive treatment. Consequently, the number of parameters was limited to those whose values might normally be adjusted in day-to-day operation to insure acceptable results. As shown later, this number was further decreased in the light of early results.

The customary fashion of varying one parameter and holding the rest constant was rejected for several reasons. This technique does not necessarily outline the true characteristics of the response surface, it is inefficient, and requires a maximum of experimental effort.

In a complex situation, such as this, expenditure of a reasonable amount of effort using this technique only elucidates the effect of each parameter under "set" conditions and does not give any indication of interactions among the different parameters. If a great deal of effort is expended so that the variation of each parameter is studied at each of many values for each of the other parameters, then a great mass of data results, which is very difficult to condense to a coherent overall picture.

Use of the statistical technique, multiple regression analysis, makes it possible to determine the effect of each parameter, individually, and in combination (interactions), from a comparatively few experimental data points. This technique requires that these data points have a particular relationship to each other, *i.e.*, the data points cannot be chosen capriciously, but must be chosen according to a preset plan. These plans vary, depending, among other things, on the number of parameters chosen for study and the number of values (levels) for each parameter. While it is possible to work out such a plan from a knowledge of statistics, and then to interpret the results, it is much easier to choose an appropriate plan from a text on statistical designs, such as COCHRAN AND COX[36] and then to use a computer to perform the multiple regression analysis.

Accordingly, a factorial design of the experiment was chosen as being the most efficient, requiring a minimum of experimental effort, and making the utmost use of previous knowledge of operating characteristics.

The first experimental design must be able to accommodate four factors each investigated at three levels and two factors each considered at two levels. Following Plan 6A.18 of COCHRAN AND COX[36], it was possible to use a 3^4 factorial design in a 1/3 replicate where the 3 represents the levels and 4 the factors. This experimental design requires 27 experimental data points. The two factors at two levels were investigated at a full 2^2 design. The combination of these two designs into one, a $2^2(1/3\ 3^4)$, requires a total of 108 experimental points. The completion of this experiment and subsequent analysis of the data, reduced the number of factors to five. Based on the knowledge obtained from the previous experimental design, it was possible to determine the range of the maximum importance for each factor. Plan 8A.2 of COCHRAN AND COX, which requires 27 experimental data points for the completion of the study, could then be used. Each of the data points was duplicated as an indicator of precision.

EXPERIMENTAL

The first experimental design was done with a Micro-Tek model 2500R instrument using a Kiethley model 415 micro-microammeter as an electrometer amplifier, and a battery for polarizing voltage. A 1-mV Bristol recorder equipped with a Perkin-Elmer model 194 printing integrator was used to record and measure peak areas. Samples of 1 μl volume were injected by Micro-Tek dipper and universal inlet system. The temperature of the column was 150°, the inlet 300°, and the detector

TABLE I

FACTORS AND THE LEVELS OF THESE FACTORS STUDIED IN THE FIRST DESIGN WITH THE MICRO-TEK 2500R

Variable	*Designation* X_1	*Levels*		
		0	*1*	*2*
Column length (ft)	A	2	4	—
Hydrogen flow rate (ml/min)	B	30	60	90
Air flow rate (ml/min)	C	500	900	—
Polarizing voltage (V)	D	100	200	300
Carrier gas flow rate (ml/min)	E	20	40	80
Sample size (g-atoms of carbon)				
n-C_7	F	$5.7 \cdot 10^{-8}$	$5.29 \cdot 10^{-7}$	$4.28 \cdot 10^{-5}$
n-C_{10}	F	$5.12 \cdot 10^{-5}$	$5.05 \cdot 10^{-5}$	$4.44 \cdot 10^{-6}$

base 220°; the carrier gas was nitrogen. Table I lists the variables studied and the different levels of each variable.

Phillips pure-grade *n*-heptane and *n*-decane were used without further purifica-

TABLE II

FACTORS AND THE LEVELS OF THESE FACTORS STUDIED IN THE SECOND DESIGN WITH THE MICRO-TEK 2500R

Variable	*Designation* X_i	*Levels*				
		−2	*−1*	*0*	*+1*	*+2*
Sample size (g-atoms of carbon)	Z_1	$2.55 \cdot 10^{-9}$	$14.1 \cdot 10^{-9}$	$25.6 \cdot 10^{-9}$	$37.0 \cdot 10^{-9}$	$48.0 \cdot 10^{-9}$
Polarizing voltage (V)	Z_2	100	150	200	250	300
Carrier gas flow rate (ml/min)	Z_3	20	30	40	50	60
Hydrogen flow rate (ml/min)	Z_4	30	45	60	75	90
Air flow rate (ml/min)	Z_5	500	600	700	800	900

TABLE III

FACTORS AND THE LEVELS OF THESE FACTORS STUDIED IN THE SECOND DESIGN WITH THE AEROGRAPH 660

Variable	*Designation* X_i	*Levels*				
		−2	*−1*	*0*	*+1*	*+2*
Sample size (g-atoms of carbon)	Z_1	$2.55 \cdot 10^{-9}$	$14.1 \cdot 10^{-9}$	$25.6 \cdot 10^{-9}$	$37.0 \cdot 10^{-9}$	$48.0 \cdot 10^{-9}$
Polarizing voltage (V)	Z_2	100	150	200	250	300
Carrier gas flow rate (ml/min)	Z_3	10	20	30	40	50
Hydrogen flow rate (ml/min)	Z_4	20	25	30	35	40
Air flow rate (ml/min)	Z_5	380	430	480	530	580

TABLE IV

FACTORS AND THE LEVELS OF THESE FACTORS STUDIED IN THE SECOND DESIGN WITH THE PERKIN-ELMER 800

Variable	*Designation* X_i	*Level*				
		−2	*−1*	*0*	*+1*	*+2*
Sample Size (g-atoms of carbon)	Z_1	$2.55 \cdot 10^{-9}$	$14.1 \cdot 10^{-9}$	$25.6 \cdot 10^{-9}$	$37.0 \cdot 10^{-9}$	$48.0 \cdot 10^{-9}$
Polarizing voltage (V)	Z_2	100	150	200	250	300
Carrier gas flow rate (ml/min)	Z_3	10	20	30	40	50
Hydrogen flow rate (ml/min)	Z_4	15	25	35	45	55
Air flow rate (ml/min)	Z_5	500	600	700	800	900

tion in the first experiment design. For the other experiment designs, the *n*-decane was purified by using a large-scale preparative chromatograph.

Some further work was done with the Micro-Tek instrument; with certain exceptions the same apparatus and conditions were used as in the first experimental design. One of the exceptions was the samples; these were made from an equal-weight mixture of *n*-heptane, *n*-octane, *n*-nonane and *n*-decane dissolved in *n*-dodecane. The *n*-dodecane was Phillips pure-grade, purified by large-scale preparative chromatography. The other paraffins were Phillips pure-grade used without further purification.

For some work, a "T" joint was installed between the column and the detector. A source of carrier gas separate from the column flow controls was connected to the third opening of the "T". This allowed the flow of carrier gas through the column to be adjusted independently of the total flow through the detector. A 2-foot, 0.25-in column of 20% SE-30 on 70–80 mesh Anakrom ABS was used for most of the work reported here. In addition, a few runs were made on a 21-foot, 0.040-in stainless steel column packed with 80–100 mesh glass beads which were coated *in situ* with SE-30.

The second experimental design was also run on the Micro-Tek model 2500R instrument under the same conditions except for those listed as variables in Table II.

The second experimental design was repeated with the Aerograph model 660. Again the same conditions and other apparatus as before were used, except for the sampling device and the variables listed in Table III. The samples of 1 μl volume were injected through a septum with a Hamilton model 7005, 5-μl syringe.

The second experimental design was repeated again with a Perkin-Elmer model 800 instrument. The conditions and other apparatus were those used before, except for the items in Table IV, and the electrometer, which was the one built into the instrument.

RESULTS AND DISCUSSION

The response of the chromatograph–flame ionization detector system is affected by many factors and by interactions among these factors. This almost certainly gives rise to a very complex situation and one in which a very great amount of tedious work would be required to perform all the research necessary to determine the effects of these variables over a meaningful range of values. The technique of of varying one factor at a time would eventually map out the total response surface, but would almost certainly leave one in a maze of data from which an orderly analysis would be impossible. The approach taken here readily lends itself to mathematical manipulation. This approach is to investigate certain factors systematically over a specified range and to eliminate those parameters which do not affect the response surface to an extent greater than the experimental error. The remaining parameters are then the basis for a new, simpler design. Furthermore, the use of these experimental designs allows the estimation of interaction effects and reduces the total number of data points required.

The first experiment was concerned with six variables, five of which are commonly adjusted in routine laboratory operations: column length (peak shape), hydrogen flow rate, polarizing voltage, carrier gas flow rate, air flow rate, and sample size. Polarizing voltage, normally not considered a variable, was included for several reasons. The voltage across the detector can decrease, owing to the voltage drop produced across the electrometer input resistor when current flows in the detector circuit. The polarizing voltage can change because of voltage fluctuations in the power lines, or because of ageing of batteries. This experiment required 108 duplicate sample runs. The 108 averaged experimental data points were used as a basis for a least-squares multiple regression computer program which fits the data to a polynomial. The analysis of variance indicated a good fit of the data and, furthermore, illustrated three important points. First, in further experiments the column length could be removed as a factor. Second, there are no interactions higher than second order, and third, the sample sizes investigated were at the extreme upper limits of concentrations sought. This preliminary investigation clearly showed that a nonlinear region had been chosen.

Information from the first experiment made it possible to use a subsequent design which required only 27 duplicate runs. Since column length was no longer to be considered, the number of variables was reduced to five. This shorter experiment was performed on all three instruments; in general, the widest practicable range of each variable was studied. In some cases, this range was restricted by the limitations of the particular instrument. For example, the maximum carrier gas flow rate used with the Aerograph and Perkin-Elmer instruments was the greatest flow that would not extinguish the flame.

After each experiment was run, the data were correlated by the computer using a multiple regression program. These correlations made it possible to choose those factors with an effect on response significantly different from zero. Those coefficients with $F_{\mathrm{calc}} > F_{\alpha}$, where α represents the probability of error and F the ratio of two variances S_1^2 and S_2^2 of 1, and ν_2, degrees of freedom, were chosen as significant and remain in the equations. Consequently, those that failed this test were rejected and the computation repeated. The F_{calc} values were computed and the F_{α} table values were used to aid in the determination of the significance of the various terms. Once a term was considered not significant, it was omitted from the equation and the coefficients for the remaining terms recalculated.

The data for each experiment and instrument were fitted to a polynomial containing the linear effects and all possible second-order effects for the five factors

TABLE V

EQUATIONS OF RESPONSE
(Micro-Tek 2500R (modified))

$$Y = 1036 + 486X_1 - X_2 + 288X_3 - 57X_4 - 20X_5 + 126X_1X_3 - 37X_1X_4 - 78X_3X_4 + 26X_3X_3 \qquad (1)$$

Aerograph 660 (modified)

$$Y = 5573 + 2364X_1 - 152X_2 + 1244X_3 - 219X_4 + 76X_5 + 577X_1X_3 - 173X_3X_4 \qquad (2)$$

Perkin-Elmer 800

$$Y = 98{,}342 + 32{,}480X_1 + 30{,}476X_3 + 13{,}247X_4 + 15{,}517X_1X_3 + 7961X_1X_4 + 6580X_3X_4 + 34{,}359X_3X_5 - 7265X_1X_1 - 6415X_3X_3 - 11{,}665X_4X_4 \qquad (3)$$

Y = Detector response (coulombs).
X_1 = Sample size.
X_2 = Polarizing voltage.
X_3 = Carrier gas flow rate.
X_4 = Hydrogen flow rate.
X_5 = Air flow rate.

investigated. This fit was compared with a logarithmic equation and in each case the log equation could be rejected without equivocation. Finally, a second-order polynomial equation which best fitted the data and which showed the combined effect on response of all significant variables was achieved. These equations, one for each instrument, are given in Table V. The values of response given by the equations are approximate. The accuracy is greater near the midrange of the data where data points are more plentiful, and becomes less accurate toward the extremes where data points are fewer. Greater accuracy can be obtained by providing more data, but the amount of data obtained is sufficient for the purposes of this work, *i.e.* to determine the significant variables and the region of linear response with sample size.

Equation of response

The response equations presented in Table V are valid for the specific instruments indicated and within the ranges as indicated in Tables II–IV. The extent of the effect of each variable and of each interaction can be ascertained with the equations in Table V. The use of these equations in such a method of interpretation must be carried out carefully, so that the true effect is elucidated. The detector response, Y, is a number directly proportional to the area of the response level. The sample size, X_1, polarizing voltage, X_2, carrier gas flow rate, X_5, are unitless quantities representing the incremental change in level from -2 to 2. The X_i values are obtained by the following equations in the case of the Perkin-Elmer model 800 instrument:

$$X_1 = \frac{Z_1 - 25.6 \cdot 10^{-9}}{11.5 \cdot 10^{-9}} \tag{1}$$

$$X_2 = \frac{Z_2 - 200}{50} \tag{2}$$

$$X_3 = \frac{Z_3 - 30}{10} \tag{3}$$

$$X_4 = \frac{Z_4 - 35}{10} \tag{4}$$

$$X_5 = \frac{Z_5 - 700}{100} \tag{5}$$

Therefore, the constant, coefficients, and Y, in eqn. (3), Table V, have the same units. Similarly, the transformation equations for the X_i values in eqns. (2) and (3), Table V, can be obtained from the data in Tables II and III. The change in Y with a specified change in any one of the five variables can be determined by the use of eqns. (1), (2), and (3), Table V, in levels rather than specific changes in the variables. It is readily seen for the Perkin-Elmer model 800 that the sample size and carrier gas flow rate affect the response in almost equivalent amounts for the experimental levels chosen in this experiment. Corresponding interpretations can be made with the other variables. The change in response as a function of a change in the individual variables can be obtained by transforming the equations in Table V with eqns. (1)–(5) and changing the units of sample size to ng-atoms of carbon for the simplification, by letting

$$Z_1 = W \cdot 10^{-9} \tag{6}$$

Then eqn. (3), Table V, becomes

$$Y = 608{,}294 - 837W - 22{,}930Z_3 + 5749Z_4 - 1032Z_5 + 135WZ_3 + 69WZ_4 + 66Z_3Z_4 + 34Z_3Z_5 + 55W^2 - 64Z_3^2 - 117Z_4^2 \tag{7}$$

The results of this work are graphed for each variable *vs.* response and are shown in Figs. 1–5.

In each case all variables except the one being plotted are taken at the "0" level (see Tables II, III and IV). These graphs show the nature and magnitude of the effect each variable has on response. Note that the abscissa is in arbitrary units. This was done so that the three curves could be graphed together without regard for absolute values of response. The intention is to compare the shapes of these curves over the range of the independent variable studied, not the absolute values of response.

The effect of each single variable is best discussed individually including later work in addition to the statistical studies. Interactions will be discussed separately.

Sample size

Over the range studied (20 to 1), response was a linear function of sample size (Fig. 1) except for the Perkin-Elmer model 800 instrument. At this point it should be made quite clear that these three instruments were selected because they

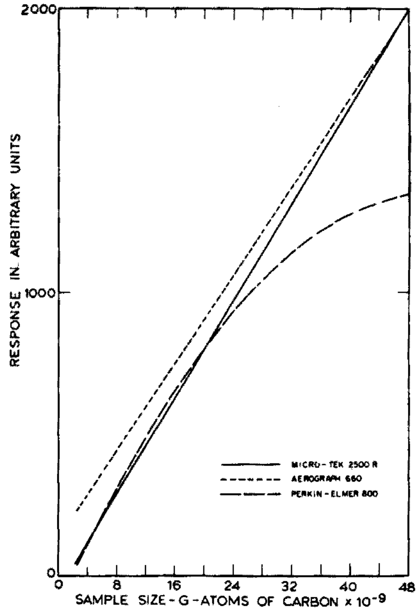


Fig. 1. Graph of response *vs.* sample size for the three instruments.

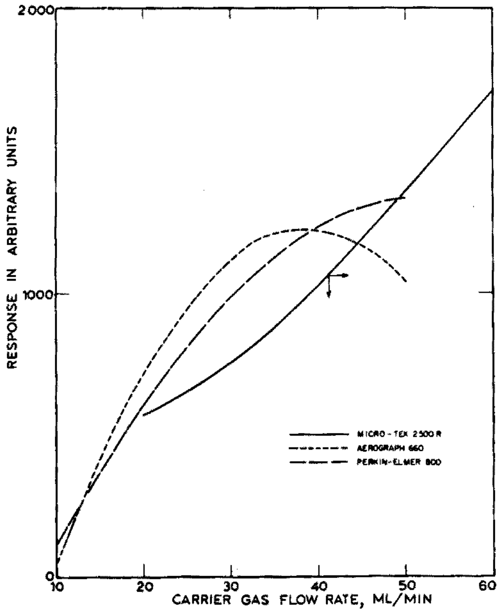


Fig. 2. Graph of response *vs.* carrier gas flow rate for the three instruments studied.

were available; the instruments must be considered as individuals, so that general conclusions concerning any particular brand or model of instrument cannot be made without data from other individuals of that class. What can be concluded is that an instrument must be considered as an individual when part of a chromatographic system, and prior claims made for that instrument, as for any isolated component of the system, must be rechecked for their applicability to the system as a whole.

Further work with the Micro-Tek instrument indicated that the maximum sample size for linear response was *ca.* 10^{-7} g-atoms of carbon which gave a peak height, or instantaneous signal current, of about $1 \cdot 10^{-9}$ A. This indicates a linear range of about 100 to 1.

The results agree with most of the literature references cited, in which plots of sample quantity *vs.* response show linear ranges from 10 to 1 to as much as 1000 to 1. The limiting factor for linear range in the present work appeared to be noise level which was 10–100 times greater than that in the work of BRUDERRECK *et al.*[2], who reported a linear range of 10^4 to 1. An extremely low noise level, which permits a greater linear range, can be achieved where the detector is isolated and studied by itself. In a study of integral chromatographic systems in which the detector is not isolated but is considered only as a component part of the system, a higher noise level is a necessary evil. Such a noise level arises from many sources, the column, the injection port, the samples themselves, electrical and vibrational interference from the laboratory surroundings which includes the instrument itself, etc. These are a normal part of laboratory conditions encountered in making routine analyses and it is impossible, or at least not feasible, to eliminate all such sources of noise. Since this study was planned to be done under conditions used in actual analyses, no attempt was made to eliminate such noise sources.

Carrier gas flow rate

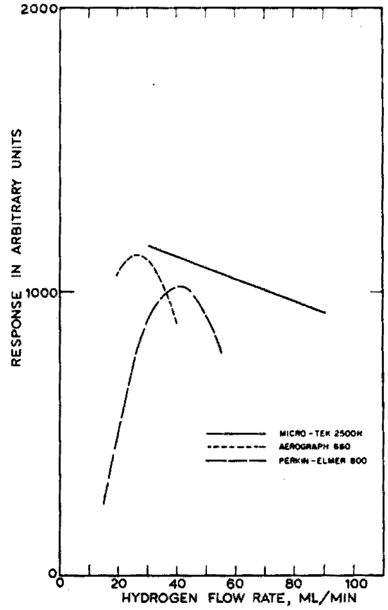
Over most of the range studied, carrier gas flow rate (Fig. 2) had at least as great an effect on response (coulombs) as any other variable including sample size. This appears to conflict with the bulk of the literature which says that the flame ionization detector is not sensitive to carrier gas flow rate. This work is not intended to conflict with previously published works which, properly, were confined to the study of the detector alone. This work is an extension of published work, in that it concerns the chromatograph as a whole system. Thus, the effect of carrier gas flow rate arises from the whole system and not necessarily just from the flame ionization detector.

Response (coulombs) is a non-linear function of carrier gas flow rate; the curve shows a maximum at a rate just below that which extinguishes the flame for two of the instruments studied. Additional work with the Micro-Tek instrument, extending the range of flow rate studied, showed that this instrument also gave rise to a response (coulombs)–carrier gas flow rate curve with a maximum which was similar to that obtained from the other two instruments. If the flow rate could be maintained at the optimum, then small changes would have little effect on response. Practically, this can be done. Addition of extra carrier gas between the column and the detector allows the flow of carrier gas through the detector to be maintained at the optimum value while the flow through the column can be set for any value between zero and the optimum[13]. Later work showed that with this arrangement little change in response occurred with a large change in carrier gas flow rate (Fig. 6).

The anomalous behavior of the small sample at a very low flow rate (Fig. 6) may be related to impurities in the diluent or to the inability to distinguish the peak properly from background noise. It is interesting to note that changing to a 21-foot 0.040-in column, which provided sharper peaks, eliminated this anomalous behavior.

Hydrogen flow rate

The effect of the hydrogen flow rate (Fig. 3) is the same as that reported in the literature for the detector alone. There is an optimum value which gives maximum response; away from this value the effect on response (coulombs) is quite large.



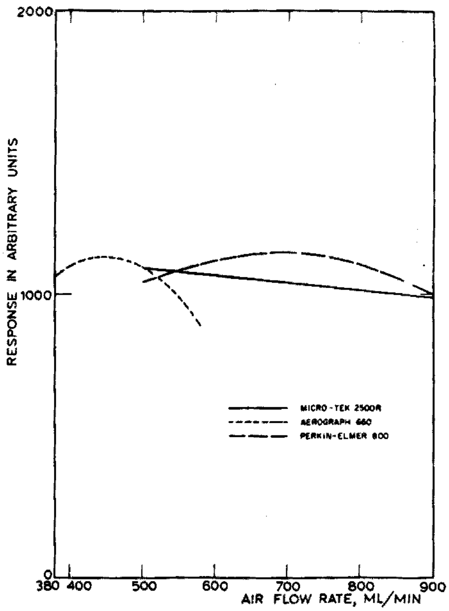


Fig. 3. Graph of response *vs.* hydrogen flow rate for the three instruments studied.

Fig. 4. Graph of response *vs.* air flow rate for the three instruments studied.

Air flow rate

Air flow rate (Fig. 4) has little effect on response (coulombs) if the rate is kept above a minimum value. This is in agreement with literature reports of the behavior of the detector alone.

Polarizing voltage

In the range studied, polarizing voltage (Fig. 5) has little effect on response (coulombs). Later work showed that for very small sample sizes no polarizing voltage at all is necessary, but response tends to fall off for larger samples under these conditions.

Column length

Column length was varied in order to obtain different peak shapes. The longer column gave rise to lower broader peaks than the shorter column. The first

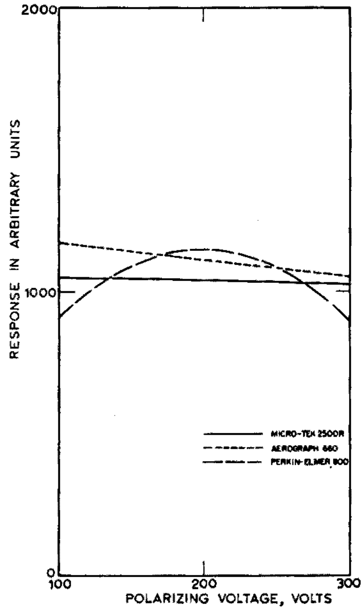


Fig. 5. Graph of response *vs.* polarizing voltage for the three instruments studied.

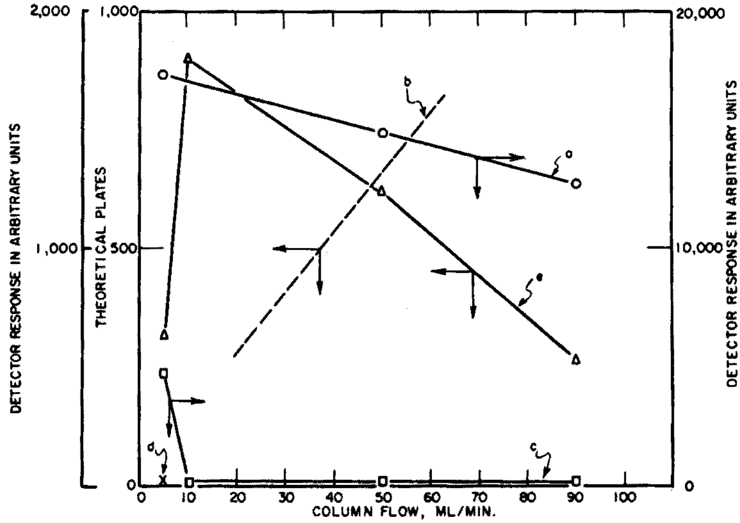


Fig. 6. Graph of response *vs.* carrier gas flow showing effect of constant and varying flow through detector. Instrument: Mikro-Tek 2500 R. (a) Constant flow through detector. (b) Varying flow: detector flow is the same as column flow (from Fig. 2). (c) Constant flow through detector: small sample size ($2.4 \cdot 10^{-9}$ g-atoms carbon). (d) Same conditions as (c) using 0.040 in i. diam. column. (e) Graph of the number of theoretical plates *vs.* column flow; obtained from the runs of which the data are plotted in curve (c).

statistical experiment showed that column length and, therefore, peak shape had no effect on response.

Apparently the lower, broader peak is compensated by its increased width, so that the total signal is the same as for the higher, narrower peak.

Interactions

If the sample size and carrier gas flow rate are varied simultaneously, the effect can be greater than the sum of the effects of each variation alone. This interaction effect of sample size and carrier gas flow rate is the most important of the interaction effects discovered in this work.

Sample size–hydrogen flow rate and carrier gas flow rate–hydrogen flow rate interactions show some importance. These effects are less important than the first mentioned and show considerable variations from one instrument to another. Both of these interactions are reported in the literature in studies of the detector alone[1,6,10,12,16,17]; and some authors[10,12,16,17] state that the ratio of hydrogen flow rate to carrier flow rate is an important parameter.

The statistical experiments reported here do not indicate the importance of the ratio of hydrogen flow rate to carrier flow rate. It may be that the importance of such a ratio is dependent on the detector geometry; it may be significant in one detector and not in another.

The three instruments used in this work have detectors with a similar geometry, *i.e.*, the burner jet does not form one of the two electrodes. This immediately suggests possible differences in behavior from a detector in which the jet is one of the electrodes. Therefore, one should be extremely cautious in applying the results of this work to instruments having detectors with a different geometry.

The double terms in the equations such as the X_5X_5 term in the equation for the Aerograph 660 indicate non-linearity in the relation of response and the factor, X_i, in this case air flow rate, X_5. Such interactions are of minor importance and actually appeared only in one case, the Perkin-Elmer model 800 instrument.

The use of statistical designs for the experimental work, whose results are statistically interpreted with the aid of a computer, suggests another method of quantitative analysis, in which important variables need not be held constant. Empirical equations, such as those in Table V, can be used to obtain quantitative detector response values. With the current use of digital computers, this type of equation is easily obtained and stored within the computer. On running a sample the values of the various parameters are presented as data along with the experimental area response and the correct equation is applied to the data to yield quantitative results.

The authors wish to express their appreciation for the assistance of Mr. A. B. CAREL in the purification of materials, for the advice of Dr. DALE COOPER in the proper use of the multiple regression analysis computer program, and for the valuable suggestions offered by Dr. GERALD PERKINS, JR.

SUMMARY

A statistically designed and interpreted series of experiments were performed with three commercially available chromatographs equipped with flame ionization detectors and operated with columns and under the conditions normally encountered in routine operation. The results in many cases agree with those previously published in studies of the detector system alone. In both cases the effect of air flow rate, polarizing voltage, and hydrogen flow rate are approximately the same. The linear range of sample size found was somewhat less than several published ranges, probably because of greater background noise. Carrier gas flow rate affected response, in contrast to the behavior of an isolated flame ionization detector. An important interaction of carrier gas flow rate and sample size was found; hydrogen flow rate–sample size, and hydrogen flow rate–carrier gas flow rate interactions were confirmed. It is suggested that additional carrier gas be added between column and detector to allow maintenance of optimum carrier flow rate. This study shows that system performance is generally less adequate than isolated component performance, being subject to various interactions which can most readily be examined by statistically designed experiments.

RÉSUMÉ

Une étude statistique est effectuée avec interprétation des expériences faites avec trois chromatographes équipés avec détecteurs d'ionisation à flamme et en opérant avec des colonnes dans des conditions généralement observées pour les déterminations de routine. Les résultats correspondant à ceux publiés, utilisant le système de détecteur seul. Dans les deux cas l'influence du débit d'air, du voltage polarisant, du débit d'hydrogène est approximativement la même.

ZUSAMMENFASSUNG

Es wurde mit 3 kommerziell verfügbaren Gaschromatographen mit Flammenionisationsdetektoren unter normalen Bedingungen eine Reihe von Experimenten durchgeführt, die zum Zwecke einer statistischen Auswertung geplant waren. Die Ergebnisse stimmen in vielen Fällen mit früher veröffentlichten Untersuchungen über das Detektorsystem allein überein. In beiden Fällen ist der Einfluss der Strömungsgeschwindigkeit für Luft und Wasserstoff und der Polarisationsspannung nahezu der gleiche. Die Probengrösse, für die Linearität gilt, ist etwas kleiner, da das Grundsignal grösser ist. Im Gegensatz zum Verhalten eines isolierten Flammenionisationsdetektors macht sich ein Einfluss durch die Strömungsgeschwindigkeit des Trägergases bemerkbar. Ein Zusammenhang zwischen der Strömungsgeschwindigkeit des Wasserstoffs und der Probengrösse und der Strömungsgeschwindigkeit des Wasserstoffs und der des Trägergases wurde festgestellt. Die Untersuchung zeigt, dass eine zusammengefasste Anordnung im allgemeinen weniger zweckentsprechend ist als eine Anordnung aus einzelnen Komponenten, welche zahlreichen Einflüssen unterworfen ist, die schnell durch statistisch geplante Experimente geprüft werden können.

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EVALUATION OF ELECTRON SPIN RESONANCE FOR QUANTITATIVE DETERMINATIONS OF GADOLINIUM, CHROMIUM, IRON, COPPER AND MANGANESE

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Electron spin resonance (e.s.r.) as a routine spectroscopic technique in structure elucidation has become widely accepted in recent years. The wide availability of relatively inexpensive e.s.r. spectrometers suggests that extension of the techniques of e.s.r. to quantitative analysis of inorganic radicals may be of considerable value. In particular, many oxidation states of the transition metals are paramagnetic; the relative analytical importance of e.s.r. in the determination of various metal ions in solution has not been evaluated. A preliminary investigation of the quantitative aspects of e.s.r. in the determination of aqueous solutions of manganese(II) has been recently reported by GUILBAULT AND LUBRANO[1], who found a linear relationship between the amplitude of the first derivative signal, adjusted for modulation amplitude and receiver gain, and the concentration of the manganese(II) in aqueous solution. The range of analytical utility for manganese(II) determinations was reported[1] to be 10^{-3}–10^{-6} M; above 10^{-3} M there was negative deviation of the analytical curve. The relative precision of measurement was found to be about 0.4%; an accuracy of about 2% was routinely obtained[1].

The full evaluation of e.s.r. as a quantitative analytical tool requires a thorough study of numerous instrumental, environmental and procedural variables. Included among these variables are modulation amplitude and receiver gain, which were studied by GUILBAULT AND LUBRANO[1]. There are, however, a number of other significant experimental variables which affect the measured signal in quantitative e.s.r.: the microwave power supplied to the sample cavity; the power saturation characteristics of a particular sample; the temperature of the sample; the effect of cell geometry; and the solvent system. It is important, moreover, in the description of a new analytical tool also to determine the selectivity of the method. For these reasons the present investigation was undertaken. The application of quantitative e.s.r. to aqueous and ethanolic solutions of numerous transition metals and rare earths is also reported.

EXPERIMENTAL

A Varian E-3 spectrometer was used for all e.s.r. measurements. The E-3 is equipped with an aqueous sample cell and holder and may be operated with a variable temperature accessory. Normal operating procedures for the e.s.r. were followed with the changes noted by GUILBAULT AND LUBRANO[1]. Stock solutions (0.1 g/ml) of several

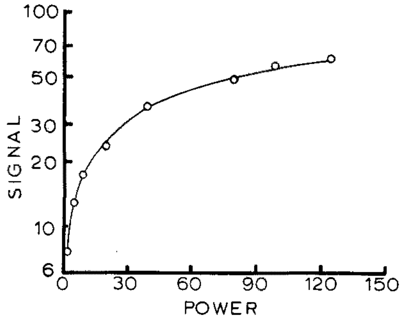


Fig. 1. Microwave power saturation curve for $GdCl_3\cdot 6\ H_2O$ ($1.02\cdot 10^{-1}M$). Signal axis is the signal height/gain/modulation amplitude$\cdot 10^4$.

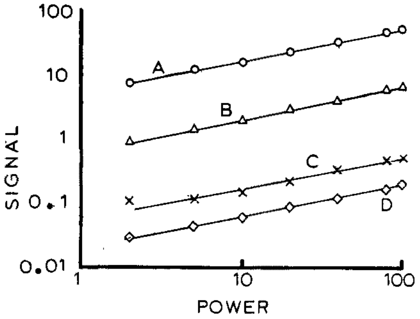


Fig. 2. Microwave power saturation curve for $GdCl_3\cdot 6\ H_2O$ in ethanolic solution at various concentrations. Signal axis is the signal height/gain/modulation amplitude$\cdot 10^4$. (A) $1.02\cdot 10^{-1}\ M$; (B) $1.02\cdot 10^{-2}M$; (C) $1.02\cdot 10^{-3}\ M$; (D) $5.1\cdot 10^{-4}\ M$.

TABLE I

REMOVAL OF SIGNAL-POWER VARIATION

Concentration[a] *(g/ml)*	*Power (P) (mW)*	*Height (H)*	*Gain (G)*	*Modulation (M) (Gauss)*	*H/GM*	*H/GM log P*
$1.02\cdot 10^{-1}$	2	19	$2.5\cdot 10^4$	1	$7.60\cdot 10^{-4}$	$2.45\cdot 10^{-3}$
	5	31.7	$2.5\cdot 10^4$	1	$1.27\cdot 10^{-3}$	$1.82\cdot 10^{-3}$
	10	43.6	$2.5\cdot 10^4$	1	$1.74\cdot 10^{-3}$	$1.74\cdot 10^{-3}$
	20	60.9	$2.5\cdot 10^4$	1	$2.43\cdot 10^{-3}$	$1.85\cdot 10^{-3}$
	40	91	$2.5\cdot 10^4$	1	$3.64\cdot 10^{-3}$	$2.25\cdot 10^{-3}$
	80	24.5	$5.0\cdot 10^3$	1	$4.90\cdot 10^{-3}$	$2.58\cdot 10^{-3}$
	100	28.3	$5.0\cdot 10^3$	1	$5.66\cdot 10^{-3}$	$2.83\cdot 10^{-3}$
	125	30.7	$5.0\cdot 10^3$	1	$6.14\cdot 10^{-3}$	$2.92\cdot 10^{-3}$
	160	35.0	$5.0\cdot 10^3$	1	$7.00\cdot 10^{-3}$	$3.18\cdot 10^{-3}$
	200	38.8	$5.0\cdot 10^3$	1	$7.76\cdot 10^{-3}$	$3.36\cdot 10^{-3}$
$1.02\cdot 10^{-2}$	2	28.6	$2.0\cdot 10^4$	16	$8.94\cdot 10^{-5}$	$2.89\cdot 10^{-4}$
	5	48	$2.0\cdot 10^4$	16	$1.50\cdot 10^{-4}$	$2.15\cdot 10^{-4}$
	10	65.2	$2.0\cdot 10^4$	16	$2.04\cdot 10^{-4}$	$2.04\cdot 10^{-4}$
	20	97.3	$2.0\cdot 10^4$	16	$3.04\cdot 10^{-4}$	$2.32\cdot 10^{-4}$
	40	27.2	$4.0\cdot 10^3$	16	$4.25\cdot 10^{-4}$	$2.62\cdot 10^{-4}$
	80	37.5	$4.0\cdot 10^3$	16	$5.87\cdot 10^{-4}$	$3.08\cdot 10^{-4}$
	100	42.5	$4.0\cdot 10^3$	16	$6.64\cdot 10^{-4}$	$3.32\cdot 10^{-4}$
	125	47.7	$4.0\cdot 10^3$	16	$7.45\cdot 10^{-4}$	$3.70\cdot 10^{-4}$
$1.02\cdot 10^{-3}$	2	34	$2.0\cdot 10^5$	16	$1.06\cdot 10^{-5}$	$3.42\cdot 10^{-5}$
	5	38.2	$2.0\cdot 10^5$	16	$1.19\cdot 10^{-5}$	$1.71\cdot 10^{-5}$
	10	51.0	$2.0\cdot 10^5$	16	$1.59\cdot 10^{-5}$	$1.59\cdot 10^{-5}$
	20	76.0	$2.0\cdot 10^5$	16	$2.38\cdot 10^{-5}$	$1.81\cdot 10^{-5}$
	40	109.5	$2.0\cdot 10^5$	16	$3.42\cdot 10^{-5}$	$2.11\cdot 10^{-5}$
	80	29.2	$4.0\cdot 10^4$	16	$4.57\cdot 10^{-5}$	$2.40\cdot 10^{-5}$
	100	33.7	$4.0\cdot 10^4$	16	$5.27\cdot 10^{-5}$	$2.64\cdot 10^{-5}$
	125	37.0	$4.0\cdot 10^4$	16	$5.78\cdot 10^{-5}$	$2.76\cdot 10^{-5}$
$1.27\cdot 10^{-4}$	2	30	$1.0\cdot 10^6$	40	$7.50\cdot 10^{-7}$	$2.42\cdot 10^{-6}$
	5	53.7	$1.0\cdot 10^6$	40	$1.34\cdot 10^{-6}$	$1.92\cdot 10^{-6}$
	10	55.0	$1.0\cdot 10^6$	40	$1.37\cdot 10^{-6}$	$1.37\cdot 10^{-6}$
	20	73.8	$1.0\cdot 10^6$	40	$1.84\cdot 10^{-6}$	$1.41\cdot 10^{-6}$
	40	51.5	$5.0\cdot 10^5$	40	$2.57\cdot 10^{-6}$	$1.59\cdot 10^{-6}$
	80	71.7	$5.0\cdot 10^5$	40	$3.59\cdot 10^{-6}$	$1.89\cdot 10^{-6}$
	100	76.2	$5.0\cdot 10^5$	40	$3.81\cdot 10^{-6}$	$1.90\cdot 10^{-6}$

[a] Gadolinium(III) chloride · 6 H_2O was the sample material for these data.

reagent-grade transition metal and rare earth salts were prepared; both aqueous and ethanolic solutions were used. Successive dilution of the stock solution was employed to obtain lower concentrations. Rare earth chlorides were prepared from the commercially obtained oxides (American Potash and Chemical Corp., West Chicago, Ill.).

RESULTS AND DISCUSSION

There are several variables which must be controlled and accurately known if one is to be successful in making quantitative e.s.r. measurements. Normal operating procedures for the instrument must be modified slightly in order to obtain reproducible and precise analytical results. For these reasons, it was deemed necessary to examine the effect of several experimental variables upon the measured signal. Before the effect of any variable can be considered, however, it is necessary to obtain a meaningful signal expression in terms of adjustable experimental variables. GUILBAULT AND LUBRANO[1] suggest that a meaningful expression for the quantitative signal is the value of the peak-to-peak derivative signal per unit gain and per unit modulation amplitude (in Gauss). This type of signal is useful only when all measurements are obtained at a constant value of microwave power. It is important to have the flexibility of varying microwave power incident upon the sample at various concentration levels. It will be shown below that facility in changing microwave power extends the range of analytical utility for the paramagnetic species under investigation.

It is necessary, therefore, to establish the effect upon measured signal of varying incident microwave power. A phenomenon well known in e.s.r. is the saturation effect of power on the derivative signal[2]; the signal does not increase linearly with power applied. There may in fact be, at high powers, a decrease in signal as the power is further increased. The exact variation with incident power depends upon the nature of the paramagnetic species being investigated. An empirical approach to removing the effect of incident power on the signal is developed below.

Removal of signal power variation

For all of the metal solutions investigated here, a very general phenomenon was observed. Shown in Fig. 1 are plots of signal (peak-to-peak height/gain/modulation amplitude) *vs.* incident microwave power for various concentrations of gadolinium(III). Exactly analogous variation was observed with all other metal ions studied; differences in signal magnitude were of course obtained from system to system. The nearly logarithmic functional relationship between signal and power at all concentrations led to the following attempts at removing the power variation on the signal. A plot of signal *vs.* the incident power for various sample concentrations is shown in Fig. 2. The linear relationship is at once obvious for the highest concentrations. Deviation from linearity at lower concentrations is attributable to precision errors. These results shown in Figs. 1 and 2 were quite general and were repeated for every metal ion studied; no decrease in signal was observed with further increase in applied power. These results suggest that the variation of signal with incident power may be removed by dividing the signal by the logarithm of the incident power. In order to test the validity of this approach to removing the power variation of the signal, signal levels for all metals were calculated for various power settings and various sample concentrations. The signal was calculated as follows:

$$\text{Signal} = \frac{\text{Peak-to-peak Height (divisions)}}{\text{Gain(arbitrary) Modulation(Gauss) log Power(mW)}}$$

If division by log power removes the signal variation with power then the signal at various power levels will be constant for a particular solution. These calculations were performed for all metal ions investigated; the results of a typical study are presented in Table I. Data such as that presented in Table I were determined for 5–8 concentration levels for each of the ions studied. The results were identical in all respects with regard to the following statements. Several important conclusions can be reached by observing the data presented in Table I. Correction of the power variation of the signal is possible over a relatively large range of incident power. For all concentrations, the region between about 5 mW and 160 mW is exceptionally well behaved. In all cases the datum at 2 mW is at distinct variance with the remainder of the data. This point suggests that small inaccuracies in power determination at very low power levels may be present to such an extent as to invalidate the power reading from the instrument dial.

If the correction of the signal for power variation were very precise, then only random experimental error should appear as the variation in the last column of Table I. This is not entirely the case, however, since some small regular variation of H/GM log P is apparent. This regular variation is probably due to under-correction for the power term; that is, the power saturation effect proceeds with greater rapidity than a simple log variation.

It is, however, important to note that the residual variation with power after division of the signal by log P is so small as to be practically negligible when compared to the routine precision and accuracy obtainable with this analytical method. An example of the significance of the above statement may be seen in Figs. 3a and b. Analytical curves for gadolinium(III) before (Fig. 3a) and after (Fig. 3b) correction of the signal for log P demonstrate that correction for power variation is possible and profitable.

Analytical curves and limits of detection

The limits of detection for five distinct metal ions and the range of linearity of the analytical curves are presented in Table II. The limit of detection in quantitative e.s.r. is not a straightforward quantity to define. Previous workers[3] have examined the statistical basis for an operating limit of detection based on the value of the "Student-t" test. It is difficult to apply such considerations to quantitative e.s.r. The signal level, on which there is superimposed the background noise, is taken as the peak-to-peak difference between the successive peaks of the derivative e.s.r. signal. As concentration levels of the analyte are decreased, the signal-to-noise ratio also decreases. The limit of detection, then, is necessarily that point at which the presence of analyte is just detectable above the peak-to-peak noise level. From an operational standpoint, at high gains, there is a great deal of non-linearity in the recorded baseline (*i.e.*, a plot of signal *vs.* Gauss obtained experimentally is not flat but may have a large positive or negative slope). The non-linearity in the base line requires interpolation of the derivative peak-to-peak heights, and at very low con-

TABLE II

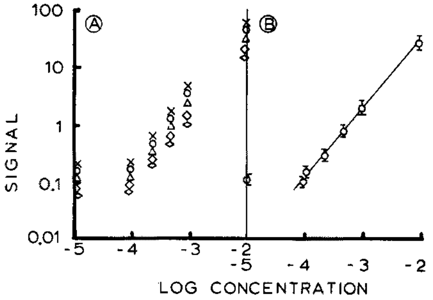
LIMITS OF DETECTION AND RANGES OF ANALYTICAL UTILITY FOR QUANTITATIVE E.S.R.

Species	*Limit of detection*[a] *(g/ml)*		*Range of analytical*[b] *utility (decades)*
	Aqueous	*Ethanolic*	
$GdCl_3 \cdot 6\ H_2O$	$4 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	3
$CrCl_3 \cdot 6\ H_2O$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-4}$	3
$FeCl_3 \cdot 6\ H_2O$	—[c]	$7 \cdot 10^{-5}$	3.5
$MnCl_2 \cdot 4\ H_2O$	$5 \cdot 10^{-8}$	$1 \cdot 10^{-6}$	5
$Cu(NO_3)_2 \cdot 3\ H_2O$	$3 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	4.5

[a] The limit of detection is defined as the point of intersection of the linear portion of the analytical curve with the background peak-to-peak noise level. These limits are for aqueous or ethanolic solutions measured with the aqueous sample cell arrangement.

[b] The range of analytical utility for the analytical curve is the number of decades of concentration over which the analytical curve is nearly linear.

[c] Not determined owing to trace interference from manganese(II).



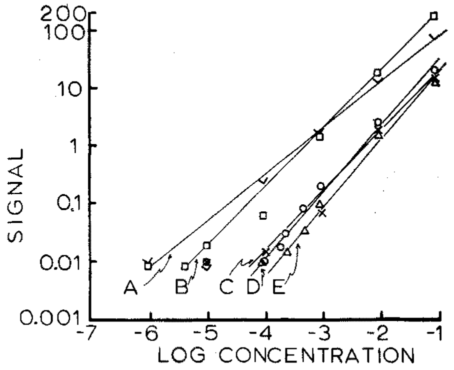


Fig. 3. Demonstration of the correction for power application to the sample for $GdCl_3 \cdot 6\ H_2O$ in ethanolic solution. (A) Signal axis is the signal height/gain/modulation amplitude$\cdot 10^5$. Power levels at each concentration are (from top to bottom) 80, 40, 20, 10 and 5 mW. (B) Signal axis is the signal height/gain/modulation amplitude/log power$\cdot 10^5$. Vertical bars indicate range of variation.

Fig. 4. Analytical curves for quantitative e.s.r. Concentrations are in g/ml in ethanolic solution. (A) $MnCl_2 \cdot 4\ H_2O$; (B) $Cu(NO_3)_2 \cdot 3\ H_2O$; (C) $FeCl_3 \cdot 6\ H_2O$; (D) $GdCl_3 \cdot 6\ H_2O$; (E) $CrCl_3 \cdot 6\ H_2O$.

centration levels the detection of the sample requires previous knowledge of optimum values for instrumental variables.

The excellent linearity of the analytical curves over very wide ranges of sample concentration is demonstrated in Fig. 4. It should be noted that all analytical curves are plotted with the signal being taken as the peak-to-peak height per unit gain, per unit modulation amplitude and per unit log microwave power.

Selectivity of the method

The selectivity of quantitative e.s.r. is best demonstrated by considering two examples of selectivity demonstrated in this work. All of the species found to display suitable e.s.r. signals have *g* values which are very similar[4]; in addition the line widths are so broad that spectral resolution is nearly impossible except for manganese(II). The e.s.r. signals for all species reported here are broad structureless single derivative peaks with the exception of manganese(II) which has the expected six-line spectrum.

Numerous metal salts were investigated for analytically useful e.s.r. signals. The following materials were found to display no useful e.s.r. signal in aqueous or ethanolic solutions: lanthanum, cerium, praseodymium, neodymium, samarium, europium, terbium, dysprosium, holmium, erbium ytterbium, cobalt and nickel. The excellent sensitivities obtained for gadolinium(III) and the absence of strong e.s.r. signals for other rare earths suggest useful selectivity characteristics. Further selectivity for quantitative e.s.r. may be realized through adjustment of line widths and *g* values by complexation[5]. It should be noted that considerably narrower line-widths for all species were obtained in aqueous solution compared to the widths in ethanolic solution.

In an attempt to improve the sensitivity and selectivity of quantitative e.s.r., the variable temperature accessory was installed on the instrument. Because it is impossible to use the aqueous cell for low temperature studies, the solutions were prepared in ethanol in order to prevent large dielectric loss in the cavity with the normal 4-mm sample tube. No significant improvements in signal intensity or reduction in line-widths were observed for temperatures down to about 90°K. In addition, there was a significant observable reduction in the "Q" of the cavity with the variable temperature acessory in place. It would seem that lower temperatures and better physical arrangements in the e.s.r. cavity could lead to narrower e.s.r. lines and therefore, greater selectivity.

Quantitative e.s.r. as an analytical tool does not compete either in sensitivity or selectivity with other current methods of atomic analysis. It has the distinct advantage, however, of good limits of detection and non-destructive sample handling. For routine low level determination, quantitative e.s.r. may have some analytical utility. The flexibility introduced by power variation adds considerably to the attractiveness of e.s.r. as a quantitative analytical technique.

SUMMARY

The use of e.s.r. as a routine quantitative analytical tool for non-destructive analysis of several metal ions in solution is examined. This application required the evaluation of numerous experimental parameters which affect the signal production. Limits of detection and analytical curves are presented for gadolinium, copper, iron, manganese, and chromium in ethanolic solution. Analytical selectivity and convenience of analysis are examined.

RÉSUMÉ

On examine l'utilisation de l'e.s.r. comme moyen d'analyse quantitative pour le dosage de plusieurs ions métalliques en solution. Cette application exige l'évaluation de nombreux paramètres affectant la production du signal. On présente les limites de détection et les courbes analytiques pour le gadolinium, le cuivre, le fer, le manganèse et le chrome en solution éthanolique. On examine également la sélectivité de cette méthode.

ZUSSAMMENFASSUNG

Es wird die Elektronenspinresonanz auf ihre Eignung als routinemässige quantitative analytische Methode zur zerstörungsfreien Analyse verschiedener Metallionen in Lösung geprüft. Die Anwendung erfordert die Bestimmung zahlreicher experimenteller Parameter, welche das Signal beeinflussen. Nachweisgrenzen und analytische Kurven folgender Elemente in äthanolischer Lösung werden angegeben: Gadolinium, Kupfer, Eisen, Mangan und Chrom. Die analytische Selektivität und die Bequemlichkeit der Analyse werden geprüft.

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THE DETERMINATION OF MIXTURES OF HYDRAZINE, MONOMETHYLHYDRAZINE AND 1,1-DIMETHYLHYDRAZINE

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Mixtures containing hydrazine and monomethylhydrazine (MMH) can be analysed by a differential oxidation method[1]. Non-aqueous methods for analysing admixtures of hydrazine with 1,1-dimethylhydrazine[2] (UDMH) or with secondary amines[3,4] have also been described; the UDMH or secondary amines were titrated with perchloric acid after the hydrazine had been removed by reaction with salicylaldehyde[2]. If the salicylaldehyde is replaced by either acetic anhydride[5] or phenylisocyanate[6], both hydrazine and MMH can be removed from activity in the solution, and therefore the analysis of other combinations of hydrazines becomes possible. SERENCHA *et al.*[7] extended MALONE's method[2] by using salicylaldehyde in the presence of excess of perchloric acid to determine admixtures of hydrazine and MMH. Such mixtures can also be analysed by gas chromatography[8,9].

Nevertheless, simple rapid chemical methods are still useful, *e.g.* in the analysis of mixtures of hydrazines blended for use as rocket fuels. This paper describes simple procedures for analysing admixtures of hydrazine with MMH and of hydrazine with UDMH. The total hydrazine content is found by titration with iodate[10]; addition of salicylaldehyde converts the hydrazine to salicylaldazine (disalicylhydrazine) which is removed by filtration, and subsequent titration with standard potassium iodate gives the MMH or UDMH content. This procedure can be combined with the non-aqueous titration method described previously[5] to give a method for the analysis of mixtures of hydrazine, MMH and UDMH; effective removal of the hydrazine and MMH as the corresponding hydrazides by adding acetic anhydride allows the UDMH present to be determined in dioxane as solvent with perchloric acid in acetic acid as titrant.

EXPERIMENTAL

Analyses of mixtures of hydrazine and monomethylhydrazine (Method A)

Preparation of samples. By pipette, add 1.5 ml of the mixture of hydrazines to a tared 50-ml standard flask containing 20 ml of distilled water and 10 ml of acetic acid. Cool to room temperature and weigh to 0.1 mg, by difference. Dilute to the mark with distilled water and mix carefully.

Determination of hydrazine + monomethylhydrazine. By pipette, add an aliquot (5 ml) of the hydrazine mixture to a 500-ml iodine flask containing 50 ml of 6 *N* hydrochloric acid. Add 25 ml of 12 *N* hydrochloric acid and 20 ml of chloroform. Titrate

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rapidly with 0.1 M potassium iodate[10], with shaking, until the dark brown colour becomes pale. Then add the iodate dropwise until the purple colour of the chloroform layer becomes colourless and the aqueous solution is yellow. This gives titre "A_1".

Determination of monomethylhydrazine. By pipette, add an aliquot (5 ml) of the mixture of hydrazines to a 400-ml beaker containing 50 ml of 6 N hydrochloric acid. Add 10 ml of a solution of salicylaldehyde in acetic acid (10%, v/v). The hydrazine gives a yellow precipitate of salicylaldazine. After 15 min, filter through Whatman No. 540 paper on a Büchner funnel, wash the precipitate several times with distilled water, and then transfer the filtrate to a 500-ml iodine flask, rinsing with several small portions of distilled water. Add 25 ml of 12 N hydrochloric acid and 20 ml of chloroform. Titrate rapidly with 0.1 M potassium iodate as described above for hydrazine + monomethylhydrazine. This gives titre "A_2". For calculation, see below.

Analyses of mixtures of hydrazine and 1,1-dimethylhydrazine (Method B)

Preparation of sample. Use the procedure outlined in Method A above.

Determination of hydrazine + 1,1-dimethylhydrazine. Use the procedure detailed in Method A for hydrazine + monomethylhydrazine, but ensure that the temperature lies within the range −10° to +10° by cooling in a carbon dioxide–acetone mixture. The titration can also be carried out potentiometrically with a platinum–calomel electrode system. This gives titre "B_1".

Determination of 1,1-dimethylhydrazine. Use the procedure detailed in Method A above for monomethylhydrazine, but maintain the temperature within the range −10° to +10°. The potentiometric end-point lies between 0.67 and 0.70 V. To minimise side-reactions, complete the titration[11] within 3–5 min. This gives titre "B_2".

Calculations

$N_2H_4 + KIO_3 + 2HCl = KCl + ICl + N_2 + 3H_2O$

$CH_3{\cdot}NH{\cdot}NH_2 + KIO_3 + 2HCl = KCl + ICl + CH_3OH + N_2 + 2H_2O$

$2[(CH_3)_2N{\cdot}NH_2] + KIO_3 + 2HCl = (CH_3)_2N{\cdot}N{=}N{\cdot}N(CH_3)_2 + KCl + ICl + 3H_2O$

Let the KIO_3 molarity = M. Then:

$$\%\ \text{hydrazine} = \frac{3{\cdot}20M\,[(A_1-A_2)\text{ or }(B_1-B_2)]}{\text{sample wt. (g)} \times 10}$$

$$\%\ \text{MMH} = \frac{4{\cdot}60MA_2}{\text{sample wt. (g)} \times 10}$$

$$\%\ \text{UDMH} = \frac{12{\cdot}02M\,B_2}{\text{sample wt. (g)} \times 10}$$

Analyses of mixtures of hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine (Method C)

Preparation of sample. By pipette, place 0.8 ml of the mixture of hydrazines into a tared 50-ml standard flask containing 20 ml of acetic acid. Weigh to 0.1 mg, by difference. Dilute to the mark with distilled water, and mix carefully.

Determination of hydrazine + monomethylhydrazine + 1,1-dimethylhydrazine. By pipette, add an aliquot (10 ml) of the hydrazine mixture to a 500-ml iodine flask containing 50 ml of 6 N hydrochloric acid. Proceed exactly as described in Method A above for the determination of hydrazine + monomethylhydrazine with potassium iodate. This gives titre "C_1".

Determination of monomethylhydrazine + 1,1-dimethylhydrazine. By pipette, add an aliquot (10 ml) of the mixture of hydrazines to a 400-ml beaker containing 50 ml of 6 *N* hydrochloric acid. Add 10 ml of a solution of salicylaldehyde in acetic acid (10%, v/v) and complete the determination of MMH+UDMH as described in Method A above for the determination of MMH alone. This gives titre "C_2".

Determination of 1,1-dimethylhydrazine. By pipette, add an aliquot (2 ml) of the mixture of hydrazines to a 100-ml beaker containing 20 ml of dioxane. Add 2 ml of acetic anhydride; both the hydrazine and monomethylhydrazine react to give hydrazides. Leave the reaction mixture for 30 min, and then titrate with 0.1 *N* perchloric acid in acetic acid; conduct a blank determination using the reagents only. The difference gives titre "C_3".

Calculations. Let the KIO_3 molarity $= M$, and the $HClO_4$ normality $= N$. Then:

$$\frac{\%\ \text{hydrazine}}{3.201} = \frac{M(C_1 - C_2)}{\text{sample wt. (g)} \times 5} = X$$

$$\frac{\%\ \text{UDMH}}{6.01} = \frac{NC_3}{\text{sample wt. (g)} \times 25} = Y$$

$$\%\ \text{MMH} = 100 - 4.60\left[\frac{MC_1}{\text{sample wt. (g)} \times 5} - \left(X + \frac{Y}{2}\right)\right]$$

RESULTS

Experiments with a large number of aldehydes showed that salicylaldehyde was the most suitable for the selective precipitation of hydrazine; it was also established

TABLE I

ANALYSES OF HYDRAZINE–MONOMETHYLHYDRAZINE MIXTURES

Found (%)		*Theoretical (%)*		*Difference (%)*	
N_2H_4	*MMH*	*N_2H_4*	*MMH*	*N_2H_4*	*MMH*
82.5	15.9	82.5	15.9	0.0	0.0
57.1	41.2	57.6	41.3	−0.5	−0.1
51.9	46.9	52.2	46.8	−0.3	+0.1
30.7	68.3	30.5	68.9	+0.2	−0.6
23.2	76.6	22.8	77.3	+0.4	−0.7
17.6	81.4	18.0	81.7	−0.4	−0.3

TABLE II

ANALYSES OF HYDRAZINE–DIMETHYLHYDRAZINE MIXTURES

Found (%)		*Theoretical (%)*		*Difference (%)*	
N_2H_4	*UDMH*	*N_2H_4*	*UDMH*	*N_2H_4*	*UDMH*
71.0	27.8	71.2	27.6	−0.2	+0.2
50.9	47.7	50.5	48.1	+0.4	−0.4
45.2	54.4	45.3	54.1	−0.1	+0.3
31.3	66.6	31.8	67.1	−0.5	−0.5

that only 1 ml of salicylaldehyde was required for the conditions described in Methods A and B.

Series of test mixtures of (*a*) hydrazine with MMH and (*b*) hydrazine with UDMH were prepared and analysed by Methods A and B. The results obtained are shown in Tables I and II respectively.

Table III shows the results obtained for all three components in test mixtures by Method C.

TABLE III

ANALYSES OF HYDRAZINE–MMH–UDMH MIXTURES

Found (%)			*Theoretical (%)*			*Difference (%)*		
N_2H_4	*MMH*	*UDMH*	N_2H_4	*MMH*	*UDMH*	N_2H_4	*MMH*	*UDMH*
35.9	32.5	29.8	36.9	31.9	29.1	−1.0	+0.6	+0.7
36.8	30.8	28.9	37.6	30.9	29.3	−0.8	−0.1	−0.4

DISCUSSION

Alternative analytical procedures for the reactions described here are possible. For example, in the determinations depending on the selective precipitation of one or more components, the precipitate could be filtered directly into the vessel used for the determination of MMH. The % hydrazine could also be determined gravimetrically as the azine; since this is soluble in chloroform, the titration could alternatively be conducted directly, without a filtration stage, by adding excess (50 ml) of chloroform. Unfortunately, the azine gives a yellow chloroform layer; the authors prefer to remove the azine precipitate by filtration. After this is done, the determination of MMH and UDMH (in the ternary mixture case) can be conducted potentiometrically, provided that the platinum–calomel electrode system is not coated by the azine nor by excess salicylaldehyde; rapid titration ($\ngtr$ 10 min) within the temperature range $-5°$ to $+5°$ is necessary to prevent side-reactions from occurring between potassium iodate and UDMH[11].

The well-known disadvantages of methods in which one component is found by difference apply here to the determination of the monomethylhydrazine present. Ammonia and aniline are common impurities in commercial hydrazine; nitrosodimethylamine, dimethylamine and other compounds are found[5] in MMH and UDMH.

We thank the Olin Corporation, New Haven, Conn., and the F.M.C. Corporation, Princeton, N.J. for providing quantities of hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine. We acknowledge the award of an American Air Force Systems Command Study Fellowship (to H.E.M.) which allowed these studies to be carried out in the University of Edinburgh.

SUMMARY

Admixtures of hydrazine and monomethylhydrazine (MMH) and of hydrazine with 1,1-dimethylhydrazine (UDMH) can be analysed by a titrimetric method in which two aliquots are titrated with potassium iodate: (*a*) directly to determine the sum of the hydrazines present, and (*b*) to determine the MMH or UDMH after selective reaction of the hydrazine with salicylaldehyde. For ternary mixtures, three aliquots are required: the sum of the hydrazines is determined with potassium iodate; the sum of MMH and UDMH is found after selective reaction of the hydrazine present with salicylaldehyde; and the UDMH content is obtained by non-aqueous solvent titrimetry after reaction of both hydrazine and MMH with acetic anhydride in dioxane.

RÉSUMÉ

Des mélanges d'hydrazine et de monométhylhydrazine (MMH), d'hydrazine et de 1,1-diméthylhydrazine (UDMH) peuvent être analysés par dosage titrimétrique. Cette méthode consiste à titrer deux parties aliquotes à l'aide d'iodate de potassium: (*a*) directement pour déterminer le total des hydrazines présentes et (*b*) pour déterminer MMH ou DDMH après réaction sélective de l'hydrazine avec la salicylaldéhyde. Pour des mélanges ternaires trois parties aliquotes sont nécessaires: le total des hydrazines est déterminé par iodate de potassium; la somme MMH+UDMH est obtenue après réaction sélective de l'hydrazine avec salicylaldéhyde; enfin la teneur en UDMH est mesurée par titrage en milieu non aqueux après réaction de l'hydrazine et de MMH avec anhydride acétique dans le dioxane.

ZUSAMMENFASSUNG

Mischungen von Hydrazin und Monomethylhydrazin (MMH) und von Hydrazin mit 1,1-Dimethylhydrazin(UDMH) können massanalytisch bestimmt werden. Dabei werden zwei aliquote Teile mit Kaliumjodat titriert und zwar wird zunächst die Summe der vorhandenen Hydrazine bestimmt und dann das MMH oder UDMH nach selektiver Reaktion des Hydrazins mit Salizylaldehyd. Bei ternären Mischungen wird zunächst die Summer der Hydrazine mit Kaliumjodat bestimmt, dann MMH und UDMH nach Reaktion des Hydrazins mit Salizyaldehyd und schliesslich der UDMH-Gehalt durch Titration in nichtwässrigem Lösungsmittel nach Reaktion sowohl von Hydrazin als auch MMH mit Essigsäureanhydrid in Dioxan.

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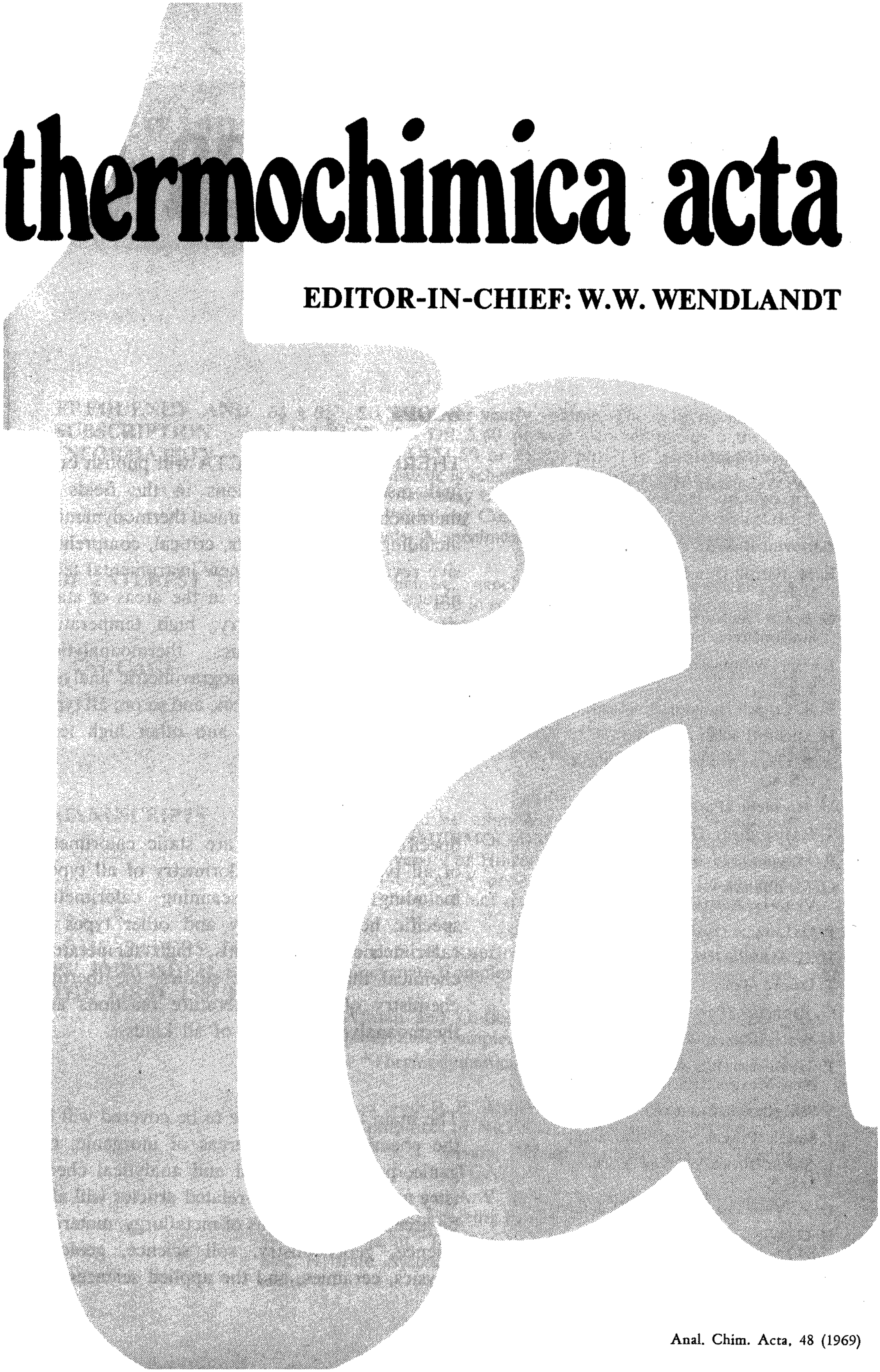

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SOME PAPERS TO BE PUBLISHED IN THE FIRST ISSUE

G. Beech and G. B. Kauffman, "Thermal Decomposition of Solid Isothiocyanate Complexes. Part I. Thermochemical Properties".

G. B. Kauffman and G. Beech, "Thermal Decomposition of Solid Isothiocyanate Complexes. Part II. Kinetic Parameters".

Jing Chao. "Thermodynamics of Vaporization of Alkali Fluorides".

K. Moedritzer and R. E. Miller. "Thermal Decomposition of Phosphine Complexes of Nickel (II) Dihalides".

L. Reich and S. S. Stivala, "Heat Transfer Effects During Teflon Degradation by TGA".

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THE GRAVIMETRIC DETERMINATION OF IRON WITH N-THIOBENZOYL-N-PHENYLHYDROXYLAMINE

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It was suggested in a previous paper[1] that N-thiobenzoyl-N-phenylhydroxylamine (TBPHA) shows the potential as a copper and iron reagent that was initially expected for cupferron[2]. Cupferron, the ammonium salt of nitrosophenylhydroxylamine, forms insoluble precipitates with a number of metal ions in acid solution. Although the iron and copper salts are insoluble in 3 *F* hydrochloric acid, neither copper nor iron can be singly precipitated in the presence of the other and separations of copper and iron with cupferron are based on treatment of the cupferronates with ammonia; the copper dissolves as the tetrammine complex and the iron remains undissolved as the hydrous oxide. Copper can be reprecipitated with cupferron after acidity adjustment but the copper complex, like all cupferronates, must be ignited to the oxide for weighing, and the tendency for the formation of mixed copper oxides makes the method unreliable.

Cupferron itself is not particularly stable and cupferron–metal complexes are not precipitated in a stoichiometric ratio that permits direct weighing. N-Benzoyl-N-phenylhydroxylamine (BPHA), in which the unstable cupferron nitroso group is replaced by a benzoyl group, was re-introduced by SHOME[3] in 1950; BPHA is stable indefinitely and produces precipitates which can be used as weighing forms for a number of metals. However, most precipitations are limited to dilute acid solutions and separation of copper and iron is not possible.

Replacement of the carbonyl oxygen of BPHA by a sulfur atom considerably increases the acidity of the reagent and thiobenzoylphenylhydroxylamine gives metal precipitates in more strongly acid solutions[4]. TBPHA has been used to separate and determine copper in the presence of iron and a large number of other common accompanying elements[1]; the precipitate is weighed as $Cu(C_{13}H_{10}NSO)_2$. The present work describes the determination of iron with TBPHA and its application to the separation and determination of copper and iron.

EXPERIMENTAL

Reagents

Iron(III) standard solutions were prepared from electrolytic iron ignited in moist hydrogen and analyzed to be 100.0% pure (G. F. Smith Chemical Co., Columbus, Ohio). The metal was dissolved in hydrochloric acid, and oxidized with a few drops of nitric acid, and the solutions were diluted to contain *ca.* 1 mg of iron per ml.

TBPHA was prepared as previously described[1,4] and was used as a 1% solution in ethanol or 1 *F* ammonia.

Procedure

Make the iron(III) solution containing 5–50 mg of iron such that it will be 1 *M* in hydrochloric acid after the addition of reagent. Precipitate the iron at room temperature with a 1% TBPHA solution in 1 *F* ammonia until a 5:1 molar excess of reagent has been added; if the approximate iron concentration is unknown, add reagent until the supernatant liquid exhibits a cloudy white coloration. Digest for 1 h in a water bath at 50° and cool to room temperature before filtering. Filter through a loose open-textured quantitative filter paper (S & S 589 black ribbon) and wash with a maximum of 50 ml of a saturated aqueous solution (0.01%) of reagent. Ignite the precipitate to the oxide, charring first under an infrared lamp, and weigh as Fe_2O_3.

RESULTS AND DISCUSSION

Typical results are shown in Table I. The results show that a number of metals commonly associated with iron do not interfere. EDTA and anions such as fluoride, phosphate, and tartrate are also without interference. The slightly high

TABLE I

DETERMINATION OF IRON WITH TBPHA

	Fe_2O_3 taken (mg)	*Fe_2O_3 found (mg)*	*Conditions*
1	21.60	21.63 ± 0.02	100-ml volume; average of 6 determinations
2	30.00	30.50 ± 0.03	200-ml volume; average of 9 determinations
3	21.60	21.58	Solution 0.5 *F* in hydrochloric acid
4	21.60	21.38	Solution 2 *F* in hydrochloric acid
5	21.60	21.57	Solution 0.5 *F* in sulfuric acid
6	21.60	21.62	Solution 3 *F* in sulfuric acid
7	29.63	29.33	Solution 5% in ethanol
8	21.60	21.61	As 1 but 20 mg manganese present
9	21.60	21.63	As 1 but 20 mg mercury(II) present
10	30.00	30.03	As 2 but 30 mg zinc present
11	30.00	30.03	As 2 but 30 mg lead present
12	30.00	30.03	As 2 but 15 mg nickel present
13	30.00	31.97	As 2 but 30 mg nickel present
14	30.00	30.04	As 2 but 30 mg iron-free cobalt present
15	21.60	21.72	As 2 but 20 mg reagent-grade cobalt present
16	21.60	21.80	As 1 but 20 mg reagent-grade aluminium present
17	21.60	21.75	As 1 but 20 mg reagent-grade chromium present
18	21.60	21.85	As 1 but 20 mg reagent-grade uranium(VI) present
19	21.60	21.77	As 1 but 20 mg reagent-grade thorium present
20	30.00	30.06	As 2 but 30 mg zirconium and 90 mg fluoride present
21	21.60	21.62	As 1 but 375 mg EDTA present
22	21.60	21.64	As 1 but 100 mg phosphate present
23	21.60	21.55	As 1 but 150 mg tartrate present
24	30.00	30.06	As 2 but 200 mg fluoride present

results (15–19, Table I) obtained in the presence of a number of reagent-grade metal salts are due to traces of iron found to be present in stock solutions on spot-testing; result 14, Table I, obtained when an iron-free cobalt(II) sulfate solution was used for salting, lends further support to this conclusion. Results are satisfactory when moderate amounts of nickel are present (12, Table I) but high results, caused by some precipitation of the nickel complex, are obtained at higher concentrations (13, Table I).

Bismuth, copper, tin, tungsten, vanadium and zirconium can be quantitatively precipitated in 1 *F* hydrochloric acid by TBPHA[1] and interfere in the determination of iron. Zirconium can be masked with fluoride (20, Table I) and fluoride should be equally effective in preventing possible titanium interference.

Quantitative precipitation is obtained in 1 *F* hydrochloric acid and 3 *F* sulfuric acid but is incomplete at higher concentrations of these acids when a 5:1 molar excess of reagent to metal is used. Iron can be quantitatively precipitated at higher acidities when a much larger excess of reagent is added[1], but, because of reagent insolubility, such a procedure is not very practicable. Interference from other metals is similar in both hydrochloric and sulfuric acid solutions and there is no advantage in precipitating iron from sulfuric acid solutions.

The procedure recommends digestion for 1 h at 50°. Quantitative precipitation is obtained at room temperature only if the precipitate is allowed to stand for 5 h; low results are obtained if a shorter digestion period is used because the precipitate is partially colloidal and passes through the filter paper. At temperatures higher than 50°, the precipitate adheres to the walls of the beaker and quantitative transfer to the filter paper is extremely difficult.

The iron complex is sufficiently insoluble to obviate the need for careful control of the solution volume used for precipitation; results are the same for iron (21.60 mg Fe_2O_3) precipitated from 100- and 400-ml volumes. The procedure for the determination of copper with TBPHA requires precipitation in 35–75% ethanolic solution to prevent co-precipitation of reagent; a similar procedure cannot be used for iron because of the high solubility of the iron complex in alcohol (7, Table I) and the precipitate must be ignited to the oxide for weighing purposes.

Nature of the precipitate

The iron complex is prepared in a pure form by recrystallization from ethanol of the precipitate obtained on adding a 2.9-*M* excess of ammoniacal reagent solution to an acidic iron(III) solution. The initial precipitate is allowed to stand for 1 h before filtering and is washed first with acid to remove any excess iron and then with ammonia to remove possible unreacted reagent; the complex is dried under vacuum at 60° for 5 h. The melting point of the pure complex is $156 \pm 0.5°$.

Thermogravimetric analysis (Fig. 1) shows a small amount of sublimation at 150° continuing into a decomposition over the range 200 – 850°. The decomposition shows two definite steps, the first (200–450°) corresponding to the loss of two moles of TBPHA and the second (500–850°) corresponding to one mole of TBPHA. A sublimation product forms on the cooler parts of the ignition tube of the thermogravimetric apparatus and is found to be the iron complex with melting point 156°. Complete sublimation may be effected if the sample is heated slowly and maintained at 154° over 10–12 h.

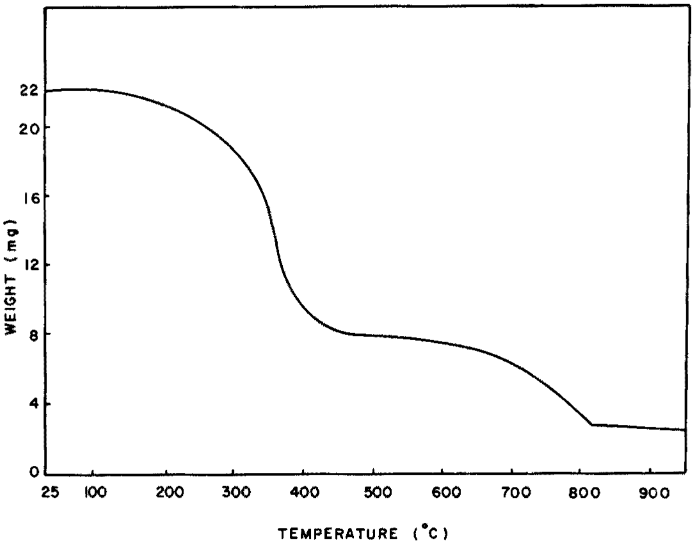

Fig. 1. Thermogravimetric curve for iron–TBPHA complex; heating rate 0.5° per min.

Ignition of complex and weighing the iron oxide obtained confirms that the pure compound is $Fe(C_{13}H_{10}NSO)_3$. For example, from 251.44 mg of compound, 27.18 mg of Fe_2O_3 are obtained which gives a calculated mole ratio of reagent to iron of 2.997; similar results were found on analysis of three additional samples. Although the pure compound has a definite composition, it cannot be used as a weighing form because the complex is highly contaminated by reagent under the usual precipitation conditions; attempts to remove reagent by taking advantage of reagent solubility in ammonia were unsuccessful.

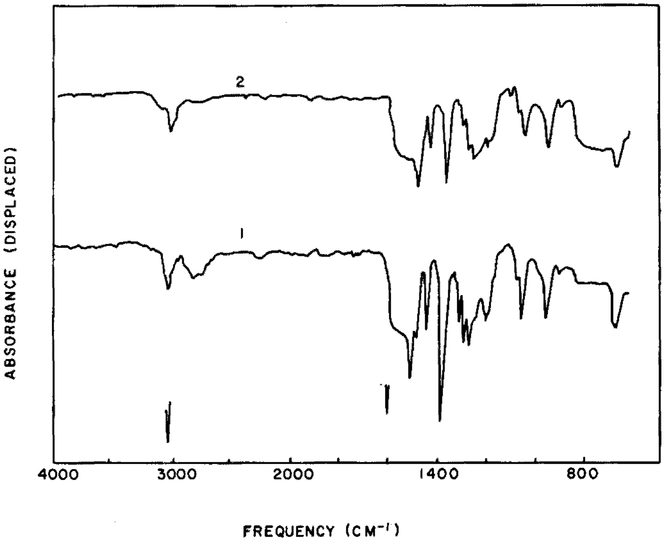

Fig. 2. Infrared spectra for reagent (1) and complex (2).

Figure 2 shows the infrared spectra of reagent and complex. The broad band near 2700 cm^{-1} in the infrared spectrum of the reagent can be assigned to the –SH group present in TBPHA. The disappearance of this band in the complex shows that the proton is removed, on reaction with iron, even in 1 F hydrochloric acid.

Simultaneous determination of copper and iron

Copper can be quantitatively determined in the presence of iron and other metals by precipitation with TBPHA at pH 2 with EDTA as a masking agent[1]. EDTA does not interfere, however, in the precipitation of iron from 1 F hydrochloric acid and it is therefore possible to determine iron directly in the filtrate from copper precipitation after acidity adjustment. The copper is precipitated as previously described[1] and weighed as $Cu(C_{13}H_{10}NSO)_2$; the filtrate is evaporated to a minimum volume to remove alcohol, the solution is made 1 F in hydrochloric acid and the iron is precipitated with TBPHA. If a copper determination is not required, copper can be separated from iron by precipitation at pH 2 in the presence of EDTA without the necessity for alcohol to be present; in such cases it is not necessary to evaporate the filtrate before determining iron. Typical results are shown in Table II.

TABLE II

ANALYSIS OF COPPER–IRON SAMPLES

Cu taken (mg)	*Cu found (mg)*	*Fe_2O_3 taken (mg)*	*Fe_2O_3 found (mg)*	*Conditions*
17.30	17.31	21.59	21.61	Copper precipitated from ethanolic solution, filtrate evaporated almost to dryness and iron determined in filtrate after acidity adjustment.
17.30	17.33	21.59	21.66	
17.30	—	21.59	21.54	Copper removed by precipitation from non-alcoholic solution and iron determined directly in filtrate after acidity adjustment.
17.30	—	21.59	21.58	

Steel and iron ore analyses

As a further check on the value of TBPHA for the gravimetric determination of iron, a standard steel (C, Mn, P, S, Si, Cr, Ni and Mo present) and an iron ore were analyzed. The samples were dissolved in hydrochloric acid, a few drops of concentrated nitric acid were added to ensure that the iron was present as iron(III), and the solutions were filtered. The iron was precipitated with TBPHA after dilution and adjustment to *ca.* 1 F in acid. For the steel containing 97.23% Fe, 97.23 ± 0.01% Fe (four results) was obtained; the iron ore containing 22.59% Fe gave 22.59 ± 0.02% Fe (four results).

Conclusions

TBPHA is an excellent reagent for the gravimetric determination of iron. TBPHA shows the potential as a copper–iron reagent that was initially expected for cupferron; copper can be precipitated in the presence of iron and weighed as the copper–TBPHA complex and iron can then be determined directly in the filtrate by precipitation with TBPHA.

This work was supported by grants from the National Research Council and Defence Research Board.

SUMMARY

Thiobenzoylphenylhydroxylamine (TBPHA) quantitatively precipitates iron(III) in 1 *F* acid solution as $Fe(C_{13}H_{10}NSO)_3$; the complex is ignited to Fe_2O_3. Aluminium, chromium, manganese and a number of common accompanying elements do not interfere. TBPHA can be used to separate copper from iron and to determine iron directly in the filtrate from the copper precipitation. Results obtained for iron standards, copper–iron mixtures, and steel and ore analyses are tabulated.

RÉSUMÉ

La thiobenzoylphénylhydroxylamine (TBPHA) précipite quantitativement le fer(III) en solution acide sous forme de $Fe(C_{13}H_{10}NSO)_3$; le complexe formé est calciné en Fe_2O_3. L'aluminium, le chrome, le manganèse et un certain nombre d'éléments accompagnant généralement le fer ne gênent pas. TBPHA permet de séparer le cuivre d'avec le fer et de doser le fer directement dans le filtrat. On indique les résultats obtenus pour des étalons de fer, des mélanges cuivre–fer, des aciers et des minerais.

ZUSAMMENFASSUNG

Thiobenzoylphenylhydroxylamin (TBPHA) fällt Eisen(III) aus saurer Lösung als $Fe(C_{13}H_{10}NSO)_3$. Der Komplex wird zu Fe_2O_3 verglüht. Aluminium, Chrom, Mangan und eine Anzahl anderer Begleitelemente stören nicht. TBPHA kann zur Abtrennung des Kupfers vom Eisen verwendet werden. Das Eisen wird direkt im Filtrat der Kupferfällung bestimmt. Ergebnisse, die mit Eisenstandards, Kupfer–Eisen-Mischungen, Stählen und Erzen erhalten wurden, werden angegeben.

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L'EXTRACTION DES LANTHANIDES ET DES ACTINIDES PAR LES OXYDES D'ALKYLPHOSPHINE

TOME V. L'EXTRACTION DES ACTINIDES TRIVALENTS PAR QUELQUES DIOXYDES DE DIPHOSPHINE[*]

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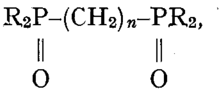
Les dioxydes de diphosphine, de formule générale



$$\underset{\underset{O}{\|}}{R_2P}-(CH_2)_n-\underset{\underset{O}{\|}}{PR_2},$$

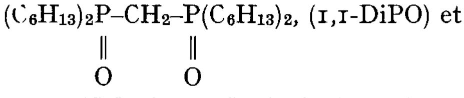
présentent un intérêt tout particulier pour l'extraction liquide–liquide: ce sont, en effet, des composés organo-phosphorés qui contiennent, d'une part, des groupements PO très basiques[1] et qui permettent, d'autre part, la formation de complexes de chélation avec les métaux.

BANKS *et al.*[2–4] ont étudié l'influence du nombre de $-CH_2-$ entre les deux groupements PO des dioxydes de diphosphine dans l'extraction du nitrate d'uranyle. Ils ont montré[4] que le coefficient de partage augmente, toutes conditions égales, suivant la séquence

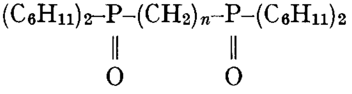
$$\text{TOPO} < 1{,}1\text{-DiPO} < 1{,}4\text{-DiPO} < 1{,}3\text{-DiPO} < 1{,}2\text{-DiPO}$$

dans laquelle 1,n-DiPO représente le dioxyde de diphosphine avec n ($-CH_2-$) entre les deux groupements PO.

Il nous est apparu intéressant, dans le cadre de nos recherches, d'étudier l'extraction de quelques actinides trivalents par les trois dioxydes de diphosphine que nous avons synthétisés à savoir:



$$(C_6H_{13})_2\underset{\underset{O}{\|}}{P}-CH_2-\underset{\underset{O}{\|}}{P}(C_6H_{13})_2,\ (1{,}1\text{-DiPO})\ \text{et}$$



$$(C_6H_{11})_2-\underset{\underset{O}{\|}}{P}-(CH_2)_n-\underset{\underset{O}{\|}}{P}-(C_6H_{11})_2$$

avec $n = 4$ (1,4-DiPO) et $n = 5$ (1,5-DiPO).

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PARTIE EXPÉRIMENTALE

Toutes les manipulations sont effectuées en boîte à gants. L'actinide à extraire est mis en solution dans la phase aqueuse contenant $NaNO_3$ 2 *M* et HNO_3 10^{-2} *N* ou 10^{-3} *N*. Cette solution est alors équilibrée à 25° avec un volume égal d'une solution benzénique de dioxyde de diphosphine. Après centrifugation, trois prélèvements sont effectués dans chacune des phases. L'activité de ces aliquotes est mesurée soit par comptage de l'émission-γ dans le cas de ^{241}Am, soit par scintillation liquide-α pour le ^{244}Cm et le $^{250-252}$Cf.

Les résultats expérimentaux obtenus avec ces trois actinides et le 1,5-DiPO figurent dans les Tableaux I et II. La distribution de ^{241}Am a été étudiée avec le 1,4-DiPO (Tableau III) et le 1,1-DiPO (Tableaux IV et V).

TABLEAU I

DISTRIBUTION DE ^{241}Am ENTRE LE 1,5-DiPO DANS LE BENZÈNE ET UNE PHASE AQUEUSE 2 *M* EN $NaNO_3$ + 10^{-2} *N* EN HNO_3

C_o^i(*1,5-DiPO*) (*M*)	[*1,5-DiPO*]$_o$ (*M*)	D_{Am}	K_{Am}'' (M^{-2})
$5.44 \cdot 10^{-2}$	$4.69 \cdot 10^{-2}$	500	—
$1.69 \cdot 10^{-2}$	$1.27 \cdot 10^{-2}$	130	—
$1.16 \cdot 10^{-2}$	$8.49 \cdot 10^{-3}$	55	$7.6 \cdot 10^5$
$8.80 \cdot 10^{-3}$	$6.25 \cdot 10^{-3}$	32	$8.2 \cdot 10^5$
$6.45 \cdot 10^{-3}$	$4.48 \cdot 10^{-3}$	16	$8.0 \cdot 10^5$
$6.13 \cdot 10^{-3}$	$4.25 \cdot 10^{-3}$	15	$8.3 \cdot 10^5$
$4.38 \cdot 10^{-3}$	$2.98 \cdot 10^{-3}$	7.4	$8.3 \cdot 10^5$
$4.11 \cdot 10^{-3}$	$2.79 \cdot 10^{-3}$	7.0	$9.0 \cdot 10^5$
$2.47 \cdot 10^{-3}$	$1.65 \cdot 10^{-3}$	2.30	$8.4 \cdot 10^5$
$2.30 \cdot 10^{-3}$	$1.53 \cdot 10^{-3}$	2.14	$9.1 \cdot 10^5$
$1.80 \cdot 10^{-3}$	$1.17 \cdot 10^{-3}$	1.25	$9.1 \cdot 10^5$
$1.23 \cdot 10^{-3}$	$8.0 \cdot 10^{-4}$	0.50	$7.8 \cdot 10^5$
$1.23 \cdot 10^{-3}$	$8.0 \cdot 10^{-4}$	0.59	$8.5 \cdot 10^5$
$6.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	0.14	$8.7 \cdot 10^5$
$3.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	0.05	—
$1.0 \cdot 10^{-4}$	$6.5 \cdot 10^{-5}$	$8.0 \cdot 10^{-3}$	—
$7.4 \cdot 10^{-5}$	$4.8 \cdot 10^{-5}$	$4.3 \cdot 10^{-3}$	—
$5.5 \cdot 10^{-5}$	$3.6 \cdot 10^{-5}$	$3.0 \cdot 10^{-3}$	—
$3.5 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$	$1.7 \cdot 10^{-3}$	—
$2.2 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$0.7 \cdot 10^{-3}$	—
$1.0 \cdot 10^{-5}$	$0.7 \cdot 10^{-5}$	$0.3 \cdot 10^{-3}$	—

TABLEAU II

DISTRIBUTION DU ^{244}Cm ET DU $^{250-252}$Cf ENTRE LE 1,5-DiPO DANS LE BENZÈNE ET UNE PHASE AQUEUSE 2 *M* EN $NaNO_3$+10^{-2} *N* EN HNO_3

C_o^i(*1,5-DiPO*) (*M*)	[*1,5-DiPO*]$_o$ (*M*)	D_{Cm}	K_{Cm}'' (M^{-2})	D_{Cf}	K_{Cf}'' (M^{-2})
$5.44 \cdot 10^{-2}$	$4.69 \cdot 10^{-2}$	420		620	
$1.16 \cdot 10^{-2}$	$8.49 \cdot 10^{-3}$	39.0	$5.4 \cdot 10^5$	57	$7.9 \cdot 10^5$
$6.45 \cdot 10^{-3}$	$4.48 \cdot 10^{-3}$	10.8	$5.4 \cdot 10^5$	15.7	$7.8 \cdot 10^5$
$4.38 \cdot 10^{-3}$	$2.98 \cdot 10^{-3}$	5.8	$6.5 \cdot 10^5$	8.1	$9.1 \cdot 10^5$
$2.30 \cdot 10^{-3}$	$1.53 \cdot 10^{-3}$	1.39	$5.9 \cdot 10^5$	2.1	$9.0 \cdot 10^5$
$1.23 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	0.34	$5.3 \cdot 10^5$	0.60	$9.4 \cdot 10^5$
$6.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-3}$	0.087	$5.4 \cdot 10^5$	0.14	$8.8 \cdot 10^5$

INTERPRÉTATION DES RÉSULTATS

Les mesures de distribution ont été menées à concentration variable en dioxyde de diphosphine et à phase aqueuse pratiquement constante, étant donné la forte concentration en nitrate, vis-à-vis du cation à extraire. Elles vont nous permettre de tirer des renseignements sur la stoechiométrie des complexes formés en phase organique. Nous pouvons, en effet, appliquer à l'équation de distribution

$$\mathrm{Act}^{3+}{}_{\mathrm{a}} + 3\ \mathrm{NO_3}^{-}{}_{\mathrm{a}} + x(1,n\text{-}\mathrm{DiPO})_{\mathrm{o}} \rightleftharpoons \mathrm{Act(NO_3)_3}\cdot x\,(1,n\text{-}\mathrm{DiPO})_{\mathrm{o}} \qquad (1)$$

la loi d'action des masses.

$$\frac{[\mathrm{Act(NO_3)_3}\cdot x\,(1,n\text{-}\mathrm{DiPO})]_{\mathrm{o}}\gamma_2}{[\mathrm{Act}^{3+}]_{\mathrm{a}}\,[1,n\text{-}\mathrm{DiPO}]_{\mathrm{o}}{}^{x}\,\gamma_1} = K'_{(\mathrm{Act})} \qquad (2)$$

Si nous introduisons dans cette équation le coefficient de partage de l'actinide D_{Act} et si nous faisons entrer les coefficients d'activité supposés constants dans la constante d'équilibre, nous pouvons écrire la relation suivante:

$$\log D_{\mathrm{Act}} = \log K''_{(\mathrm{Act})} + x \log\,[1,n\text{-}\mathrm{DiPO}]_{\mathrm{o}} \qquad (3)$$

Il est important de souligner que $[1,n\text{-}\mathrm{DiPO}]_{\mathrm{o}}$ représente la concentration en réactif libre dans la phase organique: connaissant les concentrations en réactif, $C_{\mathrm{o}}{}^{1}\,(1,n\text{-}\mathrm{DiPO})$ et en acide nitrique, $C_{\mathrm{a}}{}^{1}\,(\mathrm{HNO_3})$, il nous est possible de calculer la concentration en réactif libre sur la base des constantes établies précédemment[1] pour la neutralisation du réactif par l'acide nitrique. Dans ces conditions,

$$[1,n\text{-}\mathrm{DiPO}]_{\mathrm{o}} = \frac{C_{\mathrm{o}}{}^{1}(1,n\text{-}\mathrm{DiPO}) - \{C_{\mathrm{a}}{}^{1}(\mathrm{HNO_3}) - C_{\mathrm{a}}(\mathrm{HNO_3})\}}{1 + K_{\mathrm{I}}''\,C_{\mathrm{a}}(\mathrm{HNO_3}) + K_{\mathrm{I}}''\,K_{\mathrm{II}}''\,C_{\mathrm{a}}{}^{2}(\mathrm{HNO_3})} \qquad (4)$$

La Fig. 1 indique que pour les trois actinides trivalents, la pente vaut deux pour le 1,5-DiPO dans un domaine de concentrations allant de 10^{-4} à 10^{-2} M. Le complexe extrait peut donc s'écrire

$\mathrm{Act(NO_3)_3}\cdot 2\ (1,5\text{-}\mathrm{DiPO})$

La constante d'équilibre K'' vaut à 25°:

$K''_{(\mathrm{Am})} = (8.4 \pm 0.5)\ 10^{5}\ M^{-2}$

$K''_{(\mathrm{Cf})} = (8.7 \pm 0.6)\ 10^{5}\ M^{-2}$

$K''_{(\mathrm{Cm})} = (5.6 \pm 0.4)\ 10^{5}\ M^{-2}$

Le 1,4-DiPO ne présente aucune particularité par rapport au 1,5-DiPO ainsi que l'indique la Fig. 2. Le calcul de la constante apparente de stabilité du complexe $\mathrm{Am(NO_3)_3}\cdot 2(1,4\text{-}\mathrm{DiPO})$ nous fournit une valeur de $(3.7 \pm 0.3)\ 10^{6}\ M^{-2}$ à 25°.

Pour les concentrations en 1,4-DiPO et en 1,5-DiPO inférieures à 10^{-4} M, la Fig. 2 semble indiquer un léger écart entre la droite de pente 2.0 et la courbe expérimentale. Cet écart ne peut être dû à une impureté-γ de ^{241}Am qui s'extrairait mieux que celui-ci: en effet, le spectre-γ des phases organiques enregistré au spectromètre RIDL modèle 34-12 ne révèle aucune impuréte décelable et les équilibrations

TABLEAU III

DISTRIBUTION DE ^{241}Am ENTRE LE 1,4-DiPO DANS LE BENZÈNE ET LE $NaNO_3$ 2 *M*

C_0^t(*1,4-DiPO*) (*M*)	C_0(HNO_3) (*M*)	[*1,4-DiPO*]$_0$ (*M*)	D_{Am}	K_{Am}'' (M^{-2})
0.0237	0.0048	0.0189		
0.0198	0.0042	0.0156		
0.0158	0.0033	0.0125		
0.0119	0.0029	0.0090		
0.00795	0.00195	0.0060		
0.0050	0.0014	0.0036	45.2	$3.5\cdot10^{6}$
0.0040	0.0011	0.0029		
0.0025	0.0007	0.0018	11.4	$3.5\cdot10^{6}$
0.00195	0.0005	0.00145		
		Valeurs calculées		
$7.5\cdot10^{-4}$		$5.7\cdot10^{-4}$	1.35	$4.2\cdot10^{6}$
$5.0\cdot10^{-4}$		$3.8\cdot10^{-4}$	0.52	$3.6\cdot10^{6}$
$2.5\cdot10^{-4}$		$1.9\cdot10^{-4}$	0.12	$3.3\cdot10^{6}$
$1.0\cdot10^{-4}$		$0.75\cdot10^{-4}$	0.020	$3.6\cdot10^{6}$
$0.5\cdot10^{-4}$		$0.38\cdot10^{-4}$	0.006	$4.2\cdot10^{6}$

TABLEAU IV

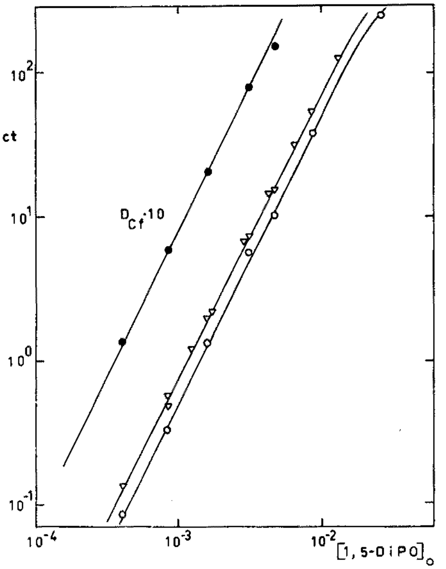
DISTRIBUTION DE ^{241}Am ENTRE LE 1,1-DiPO DANS LE BENZÈNE ET LE $NaNO_3$ 2 *M*

C_0^t(*1,1-DiPO*) (*M*)	C_0(HNO_3) (*M*)	[*1,1-DiPO*]$_0$ (*M*)	D_{Am}
$10.0\cdot10^{-2}$	0.0053	$9.47\cdot10^{-2}$	410
$5.30\cdot10^{-2}$	0.0032	$4.98\cdot10^{-2}$	210
$5.00\cdot10^{-2}$	0.0031	$4.69\cdot10^{-2}$	190
$4.16\cdot10^{-2}$	0.0026	$3.90\cdot10^{-2}$	150
$3.33\cdot10^{-2}$	0.0022	$3.11\cdot10^{-2}$	93
$2.50\cdot10^{-2}$	0.0017	$2.33\cdot10^{-2}$	40
$1.67\cdot10^{-2}$	0.0012	$1.55\cdot10^{-2}$	13
$1.00\cdot10^{-2}$	0.00076	$9.2\cdot10^{-3}$	3.6
$0.84\cdot10^{-2}$	0.00060	$7.8\cdot10^{-3}$	2.4
		Valeurs calculées	
$5.00\cdot10^{-3}$		$4.6\cdot10^{-3}$	0.46
$2.53\cdot10^{-3}$		$2.3\cdot10^{-3}$	0.11
$1.26\cdot10^{-3}$		$1.2\cdot10^{-3}$	0.037
$1.00\cdot10^{-3}$		$9.1\cdot10^{-4}$	0.027
$7.00\cdot10^{-4}$		$6.3\cdot10^{-4}$	0.013
$5.1\cdot10^{-4}$		$4.6\cdot10^{-4}$	0.010
$2.7\cdot10^{-4}$		$2.4\cdot10^{-4}$	0.006
$1.0\cdot10^{-4}$		$9.1\cdot10^{-5}$	0.002

TABLEAU V

DISTRIBUTION DE ^{241}Am ENTRE LE 1,1-DiPO DANS LE BENZÈNE ET UNE SOLUTION AQUEUSE $NaNO_3$ 2 *M* + HNO_3 10^{-3} *N*

C_0^t(*1,1-DiPO*) (*M*)	[*1,1-DiPO*]$_0$ (*M*) *Valeurs calculées*	D_{Am}
$1.23\cdot10^{-3}$	$1.22\cdot10^{-3}$	$5.2\cdot10^{-2}$
$9.8\cdot10^{-4}$	$9.7\cdot10^{-4}$	$3.1\cdot10^{-2}$
$7.0\cdot10^{-4}$	$6.9\cdot10^{-4}$	$2.2\cdot10^{-2}$
$5.1\cdot10^{-4}$	$5.1\cdot10^{-4}$	$1.3\cdot10^{-2}$
$1.0\cdot10^{-4}$	$1\cdot10^{-4}$	$3\cdot10^{-3}$



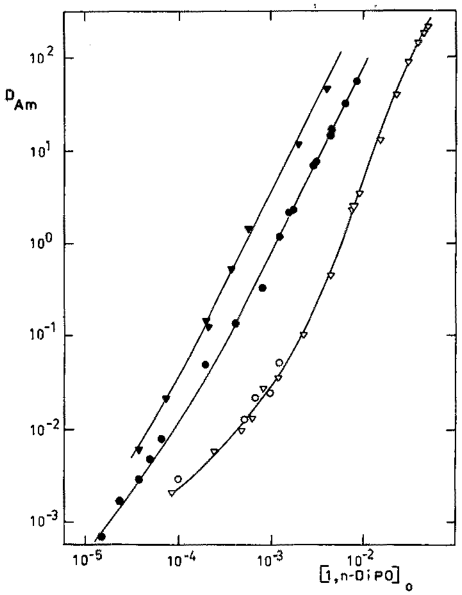


Fig. 1. Distribution de quelques actinides trivalents entre le 1,5-DiPO dans le benzène et une phase aqueuse de force ionique constante. (○) ^{244}Cm, (▽) ^{241}Am, (●) $^{250-252}$Cf.

Fig. 2. Distribution de ^{241}Am entre quelques dioxydes de diphosphine dans le benzène et une phase aqueuse de force ionique constante. HNO_3 10^{-2}: (▽) 1,1-DiPO, (●) 1,5-DiPO, (▼) 1,4-DiPO; HNO_3 10^{-3}: (○) 1,1-DiPO.

successives d'une même phase aqueuse avec plusieurs phases organiques fraîches fournissent des coefficients de partage identiques aux erreurs expérimentales près. On peut avancer deux hypothèses pour rendre compte de ce phénomène:

1. il pourrait y avoir une dissociation du complexe $DiPO \cdot HNO_3$ en phase organique pour les faibles concentrations en réactif basique. Ceci conduirait à une augmentation de la concentration en ligand libre, disponible alors pour complexer le métal.

2. les dioxydes de diphosphine, 1,4-DiPO et 1,5-DiPO, auraient tendance à former, aux faibles concentrations, des complexes moins riches en DiPO que Act-$(NO_3)_3 \cdot 2(1,n\text{-DiPO})$. Cette hypothèse n'excluant pas la première, d'ailleurs, semble recevoir une confirmation lorsqu'on examine les résultats obtenus avec le 1,1-DiPO (Fig. 2).

L'isotherme de distribution de ^{241}Am entre la phase aqueuse et le 1,1-DiPO en solution dans le benzène peut se décomposer en plusieurs parties.

1. La première est comprise entre 10^{-4} et 10^{-3} M en 1,1-DiPO. Nous pouvons constater, sur la Fig. 2, que la courbe d'extraction peut être assimilée approximativement à une droite de pente 1. L'allure de cet isotherme est indépendante de la concentration en acide nitrique: les mesures effectuées en milieu 10^{-2} ou 10^{-3} N en acide nitrique sont pratiquement identiques si l'on tient compte du partage de l'acide entre les deux phases. Ceci permet de conclure à l'absence de molécule de HNO_3 dans le

complexe qui doit avoir la formule $\mathrm{Act(NO_3)_3 \cdot (1{,}1\text{-}DiPO)}$. La réaction de formation est

$$\mathrm{Act^{3+}{}_a + 3\ NO_3{}^-{}_a + (1{,}1\text{-}DiPO)_o \rightleftharpoons Act(NO_3)_3 \cdot (1{,}1\text{-}DiPO)_o} \tag{5}$$

avec

$$K''_{\mathrm{Act}} = \frac{D_{\mathrm{Act}}}{[\mathrm{1{,}1\text{-}DiPO}]_o} = \frac{D_{\mathrm{Act}}\{1 + K_{\mathrm{I}}''\, C_a(\mathrm{HNO_3}) + K_{\mathrm{I}}''\, K_{\mathrm{II}}''\, C_a^2(\mathrm{HNO_3})\}}{C_o^i(\mathrm{1{,}1\text{-}DiPO}) - \{C_a^i(\mathrm{HNO_3}) - C_a(\mathrm{HNO_3})\}} \tag{6}$$

où K_{I}'' et K_{II}'' sont les constantes de stabilité des complexes $\mathrm{1{,}1\text{-}DiPO \cdot HNO_3}$ et $\mathrm{1{,}1\text{-}DiPO \cdot 2\ HNO_3}$[1].

En exploitant les résultats expérimentaux des Tableaux IV et V, on peut calculer $K''_{\mathrm{Am}} = 27 \pm 4\ M^{-1}$.

2. Après une zone de transition caractérisée par une courbure dans l'isotherme de distribution, on peut observer, sur la Fig. 2, une nouvelle position de droite pour des concentrations en 1,1-DiPO allant de $5 \cdot 10^{-3}$ à $5 \cdot 10^{-2}\ M$. La pente calculée est de 2.8 et l'on peut supposer l'existence d'un complexe de stoechiométrie 1:3, stoechiométrie que nous avons déjà mise en évidence avec d'autres oxydes d'alkylphosphine[5].

DISCUSSION

Si nous comparons, toutes conditions égales, l'extraction des actinides trivalents pour les composés organo-phosphorés neutres que nous avons étudiés, nous pouvons remarquer que le coefficient de partage d'un même cation augmente selon la séquence:

$$\mathrm{TBP < TOPO < 1{,}1\text{-}DiPO < 1{,}5\text{-}DiPO < 1{,}4\text{-}DiPO}$$

Cette suite n'est pas strictement la même que celle mise en évidence pour la stabilité des complexes acide nitrique–composés organo-phosphorés. Nous avons, en effet, établi pour ces derniers la séquence:

$$\mathrm{TBP < 1{,}1\text{-}DiPO < TOPO < 1{,}4\text{-}DiPO < 1{,}5\text{-}DiPO}$$

On peut en déduire que la basicité des groupements PO du complexant n'est pas le seul facteur déterminant l'extraction des cations. La structure du complexant joue probablement un rôle très important. C'est dans ce sens qu'il faut rechercher la cause de la haute efficacité du 1,4-DiPO et 1,5-DiPO comparée à celle du 1,1-DiPO dont la conformation permet cependant la formation de cycles à six pièces.

Des études de spectrométries infrarouge et Raman[6-8] ont montré récemment que, dans les complexes extraits en milieu nitrique, d'une part, les ions $\mathrm{NO_3^-}$ peuvent soit se situer dans la sphère de coordination interne du cation central, soit se trouver dans la sphère externe et former une véritable paire d'ions et, d'autre part, les ions $\mathrm{NO_3^-}$ peuvent être liés au cation par un ou deux oxygènes[7].

Il existe donc à priori une gamme importante de structures possibles dont nous nous proposons d'étudier l'influence sur l'extraction.

Nous tenons à remercier Euratom et l'Institut Interuniversitaire des Sciences Nucléaires pour les subsides accordés à notre laboratoire. Que Monsieur F. GILNAY soit aussi remercié pour son aide technique.

RÉSUMÉ

La distribution des actinides trivalents entre une phase aqueuse de force ionique constante ($NaNO_3$ 2 M) et une solution organique de dioxyde de diphosphine peut s'expliquer par la réaction

$$Act^{3+}{}_a + 3\ NO_3{}^-{}_a + x(1,n\text{-DiPO})_o \rightleftharpoons Act(NO_3)_3 \cdot x(1,n\text{-DiPO})_o$$

Les constantes apparentes de stabilité ont été établies à 25°: elles valent respectivement

$(3.7 \pm 0.3)\ 10^6\ M^{-2}$ pour $Am(NO_3)_3 \cdot 2$ (1,4-DiPO)

$(8.4 \pm 0.5)\ 10^5\ M^{-2}$ pour $Am(NO_3)_3 \cdot 2$(1,5-DiPO)

$(5.6 \pm 0.4)\ 10^5\ M^{-2}$ pour $Cm(NO_3)_3 \cdot 2$(1,5-DiPO)

$(8.7 \pm 0.5)\ 10^5\ M^{-2}$ pour $Cf(NO_3)_3 \cdot 2$(1,5-DiPO)

$27 \pm 4\ M^{-1}$ pour $Am(NO_3)_3 \cdot$(1,1-DiPO)

SUMMARY

The distribution of trivalent actinides between an aqueous phase of constant ionic strength (2 M $NaNO_3$) and an organic solution of a diphosphine dioxide can be explained by the reaction:

$$Act^{3+}{}_a + 3\ NO_3{}^-{}_a + x(1,n\text{-DiPO})_o \rightleftharpoons Act(NO_3)_3 \cdot x(1,n\text{-DiPO})_o$$

The apparent stability constants were determined at 25° for some complexes:

$Am(NO_3)_3 \cdot 2$(1,4-DiPO): $(3.7 \pm 0.3)\ 10^6\ M^{-2}$

$Am(NO_3)_3 \cdot 2$(1,5-DiPO): $(8.4 \pm 0.5)\ 10^5\ M^{-2}$

$Cm(NO_3)_3 \cdot 2$(1,5-DiPO): $(5.6 \pm 0.4)\ 10^5\ M^{-2}$

$Cf(NO_3)_3 \cdot 2$(1,5-DiPO): $(8.7 \pm 0.5)\ 10^5\ M^{-2}$

$Am(NO_3)_3 \cdot$(1,1-DiPO): $27 \pm 4\ M^{-1}$

ZUSAMMENFASSUNG

Die Verteilung der dreiwertigen Aktiniden zwischen einer wässrigen Phase konstanter Ionenstärke und einer organischen Lösung von Diphosphindioxiden kann durch folgende Reaktion interpretiert werden:

$$Akt^{3+}{}_w + 3\ NO_3{}^-{}_w + x(1,n\text{-DiPO})_o \rightleftharpoons Akt\ (NO_3)_3 \cdot x(1,n\text{-DiPO})_o$$

Die Werte der Konstanten betragen bei 25°:

$(3.7 \pm 0.3)\ 10^6\ M^{-2}$ für $Am(NO_3)_3 \cdot 2$(1,4-DiPO)

$(8.4 \pm 0.5)\ 10^5\ M^{-2}$ für $Am(NO_3)_3 \cdot 2$(1,5-DiPO)

$(5.6 \pm 0.4)\ 10^5\ M^{-2}$ für $Cm(NO_3)_3 \cdot 2$(1,5-DiPO)

$(8.7 \pm 0.5)\ 10^5\ M^{-2}$ für $Cf(NO_3)_3 \cdot 2$(1,5-DiPO)

$27 \pm 4\ M^{-1}$ für $Am(NO_3)_3 \cdot$(1,1-DiPO)

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METALLEXTRAKTION MIT ALIPHATISCHEN KETONEN

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(Eingegangen den 27. Juli, 1969)

Eingehende Untersuchungen führten schon 1957 zu dem Ergebnis, dass organische Lösungsmittel mit den Gruppen C=O oder P=O zur Extraktion von Metallen besonders gut geeignet sind[1,2]. In der Folge findet man verschiedentlich Arbeiten, die sich mit den theoretischen Grundlagen von Extraktionsvorgängen beschäftigen[3-5], vor allem bei Verwendung von organischen Solvenzien, die eine C=O Gruppe, oder ganz allgemein ein Sauerstoffatom mit Elektronendonatoreigenschaften enthalten. Daraus ist zu entnehmen, dass besonders einwertig geladene Komplexanionen in guter Ausbeute in die organische Phase überführt werden. So berichtet IRVING[6], dass Palladium(II) und Platin(IV) aus 6 *M* Salzsäure mittels Diäthyläther kaum extrahiert werden, obwohl beide starke Chlorokomplexe der Form $[PdCl_4]^{2-}$ und $[PtCl_6]^{2-}$ bilden. Dagegen lassen sich bekanntlich $[FeCl_4]^-$ und $[AuCl_4]^-$ sehr gut extrahieren. Ausserdem stehen diese Ergebnisse im Einklang mit Resultaten dünnschichtchromatographischer und Ionenaustauscher-Untersuchungen, da es sich ja auch bei diesen Trennverfahren um Verteilungs- bzw. Adsorptionsverfahren handelt. KRAUS *et al.*[7] nehmen an, dass z.B. Indium in salzsaurem Medium den Komplex $[InCl_6]^{3-}$ bildet, der sich im Gleichgewicht mit $[InCl_4]^-$ befindet. Das gleiche Ergebnis leitet sich aus den R_F-Werten der Dünnschichtchromatographie auf Cellulose ab, denn die Doppelflecken, die man in Propanol-1 und Butanol-1 als Laufmittel bei 3 bzw. 5 *N* Salzsäure erhält, beweisen das Vorliegen dieser beiden Komplexe[8].

Vorliegende Untersuchungen sollen nun die Extrahierbarkeit der Metalle aus salzsauren Lösungen mit aliphatischen Ketonen beschreiben. Ausserdem wird aufgrund der Extraktionsergebnisse der einzelnen Metalle gezeigt, dass auch hier der oben beschriebene Extraktionsmechanismus vorliegt.

Für unsere Untersuchungen verwendeten wir: Äthylmethylketon (Butanon-2), Methylpropylketon (Pentanon-2), Äthylbutylketon (Heptanon-3).

Diese drei Ketone wurden ausgewählt, da sie einen guten Querschnitt des Extraktionsverhaltens von *n*-aliphatischen Ketonen C_4–C_7 ergaben und auch preismässig günstig liegen. Wegen der grösseren Löslichkeit der Ketone bei höherer Säurekonzentration verwendeten wir jeweils eine Mischung von 30 ml Keton + 20 ml Tetrachlorkohlenstoff für die Extraktion. Daraus ergibt sich auch arbeitstechnisch ein Vorteil, da sich die organische Phase dadurch im unteren Teil des Schüttelgefässes befindet.

EXPERIMENTELLER TEIL

Reagenzien

Äthylmethylketon reinst (E. Merck), Methylpropylketon purum (Fluka), Äthylbutylketon pract. (Fluka), Tetrachlorkohlenstoff purum.

Allgemeine Arbeitsvorschrift

Die zu untersuchende Metallsalzlösung wird in einem 50- oder 100-ml Masskolben auf die gewünschte Salzsäurekonzentration gebracht. Davon werden 20 ml in einen 250-ml Schütteltrichter übergeführt. Man kann aber auch so verfahren, dass man einen aliquoten Teil einer Metallsalzlösung in den Schütteltrichter einpipettiert und danach mit Salzsäure die gewünschte Normalität (20 ml Volumen) einstellt. Dazu gibt man das Gemisch von 30 ml Keton + 20 ml Tetrachlorkohlenstoff; nun wird *ca.* 30 sec geschüttelt. Zwischendurch wird einmal kurz entlüftet. Sollte die Phasentrennung nach dem Schüttelvorgang nicht rasch erfolgen, so kann man diese durch Hinzugeben einiger Tropfen Tetrachlorkohlenstoff beschleunigen. Nach der Trennung wird die im unteren Ende des Schütteltrichters befindliche organische Phase in ein zweites Schüttelgefäss abgelassen. Die wässrige Phase wird nochmals mit dem Gemisch Keton–Tetrachlorkohlenstoff geschüttelt. Beide organischen Phasen werden vereinigt. In der wässrigen Phase kann nun bei nicht vollständiger Extraktion das verbleibende Metall bestimmt werden. Die vereinigten organischen Phasen werden 2 mal mit je 40 ml Wasser geschüttelt und dadurch das extrahierte Metall zurückgewonnen. Soll in einer der beiden erhaltenen wässrigen Phasen das Metall durch eine spektralphotometrische Methode bestimmt werden, so empfiehlt sich in den meisten Fällen das in geringem Masse gelöste Keton zu entfernen, was durch Verkochen, bzw. Eindampfen bis zur Trockene leicht zu bewerkstelligen ist. In manchen Fällen erweist es sich als günstig mit conz. Schwefelsäure einzudampfen. Sollte dabei eine Braunfärbung auftreten, so genügt der Zusatz einiger Tropfen Salpetersäure, um diese zu entfernen.

EXTRAKTIONSERGEBNISSE

Zur Feststellung der Extrahierbarkeit von Metallen aus salzsauren Lösungen verwendeten wir pro Extraktion jeweils zwischen 30 und 60 mg Metall. In besonderen Fällen, etwa bei den Elementen Mo(VI), Tl(III) und Te(VI), wurde die Metallkonzentration bis zu 150 mg erhöht um eine eventuelle Konzentrationsabhängigkeit der Extraktion in diesem Bereich festzustellen. Fallweise bestimmten wir auch die Extrahierbarkeit im μg-Bereich, um die Metalle direkt spektralphotometrisch bestimmen zu können.

Fig. 1 vermittelt einen Querschnitt über das Extraktionsverhalten der einzelnen Metalle, bezogen auf 6 N salzsaure Lösungen. Ausserdem lassen sich daraus einzelne Trennungsmöglichkeiten entnehmen.

Metalle, die bei unseren Untersuchungen keine Berücksichtigung fanden wurden in Fig. 1 mit keinem Symbol versehen. Im folgenden soll das Extraktionsverhalten von einzelnen Metallen eingehender besprochen werden.

Vanadin(V)

Wie aus Fig. 2 hervorgeht, konnte die Extrahierbarkeit von Vanadin(V) mit 2-

Butanon nicht geklärt werden, da beim Extraktionsvorgang teilweise Reduktion zu Vanadin(IV) eintrat. Dagegen trifft diese Erscheinung für höhere Ketone nicht zu. Die Bestimmung des Vanadins erfolgte komplexometrisch[9] und mittels Kupferronatfällung als V_2O_5[10].

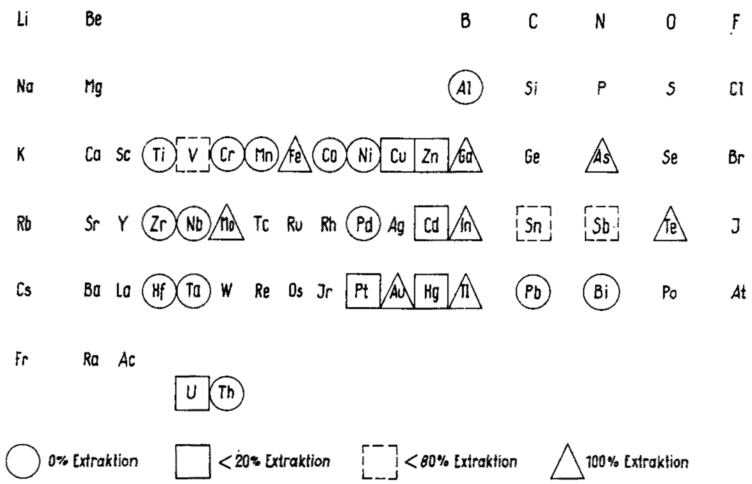
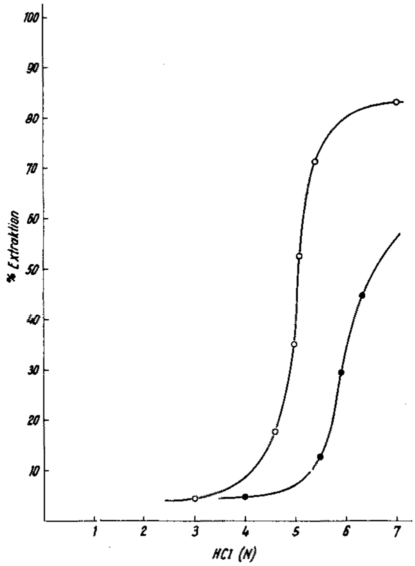


Fig. 1. Extrahierbarkeit der untersuchten Elemente aus 6 *N* HCl-Lösung.

Molybdän(VI)

Das Extraktionsverhalten dieses Metalles ist in Fig. 3 dargestellt.



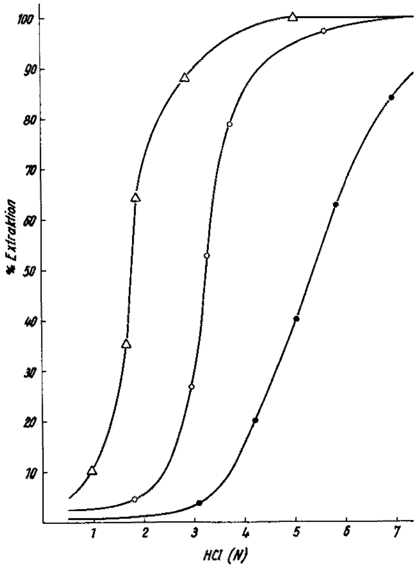


Fig. 2. Extrahierbarkeit von Vanadin(V) mittels 2-Pentanon (○) bzw. 3-Heptanon (●) in Abhängigkeit von der Salzsäurenormalität.

Fig. 3. Extrahierbarkeit von Molybdän(VI) mittels 2-Butanon (△), 2-Pentanon (○) bzw. 3-Heptanon (●) in Abhängigkeit von der Salzsäurenormalität.

Die Bestimmung erfolgte durch Oxinatfällung[10]. Die Rückextraktion aus der organischen Phase muss in diesem Fall mit Natronlösung erfolgen, da mit Wasser allein kein quantitatives Ergebnis erzielt wird. Wie aus den Fign. 1 und 3 ersichtlich ist, ergibt sich eine Möglichkeit, Eisen und Molybdän gemeinsam von anderen Metallen abzutrennen. Um diese beiden Elemente aus der organischen Phase zu extrahieren, erwies es sich als vorteilhaft diese Phase zunächst zweimal mit Wasser und danach mit NaOH-lösung zu schütteln. Die alkalischen Rückextrakte werden neutralisiert und mit den wässrigen Extrakten vereinigt. Hierauf wird eingeengt und das Extrakt in 10%ige NaOH-lösung gebracht. Das nun ausfallende Eisenhydroxid wird abfiltriert; im Filtrat kann Molybdän bestimmt werden.

Die vereinigten Rückextrakte lassen sich zur Bestimmung der beiden Metalle nach der Methode von SUCHA[11] weiterverarbeiten.

Mit 3-Heptanon ist diese Trennung nicht durchzuführen, da Molybdän aus 6 N salzsaurer Lösung nur zu etwa 70% extrahiert wird.

Wir ermittelten Eisen und Molybdän aus zwei Analysen-Kontrollproben der Bundesanstalt für Materialprüfung (BAM) Berlin-Dahlem mit diesem Trennverfahren, wobei wir Äthylmethylketon als Extraktant verwendeten.

Probe 1: C, Si, Mn, P, S, Cr, Ni, Nb, Ta, N. Fe: 68.95%; Mo: 0.213%.

Der gefundene Eisenwert betrug 68.92%; Molybdän 0.28%.

Probe 2: C, Si, Mn, P, Cr, V, Ni. Fe: 96.034%; Mo: 1.146%.

Gefunden: Eisen = 96.10%; Molybdän = 1.11%.

Eisen(III)

Das Extraktionsverhalten von Eisen(III) mit 2-Butanon als Solvens wurde bereits untersucht[12]. Eine Übersicht der Extrahierbarkeit von Eisen mit Ketonen bringen BANKMANN UND SPECKER[13].

Gold(III)

JORDANOV *et al.*[14] beschreiben die gute Extrahierbarkeit dieses Metalls aus salzsauren Lösungen mit 2-Butanon als Solvens. Ihre Ergebnisse finden auch bei diesen Untersuchungen ihre Bestätigung, denn das Metall wird auch von 2-Pentanon und 3-Heptanon als Lösungsmittel aus salzsauren Medien quantitativ extrahiert.

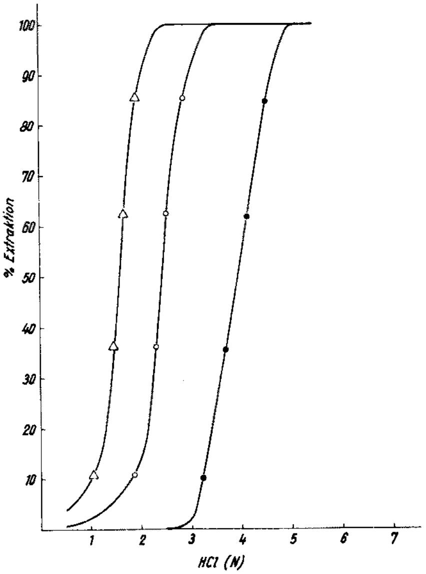
Die Bestimmung des Metalls kann komplexirnetrisch mit SAS-SN als Indikator[15] oder spektralphotometrisch mit Rhodamin B[16] erfolgen, wobei in beiden Fällen die organische Phase abdestilliert und der Rückstand mit Königswasser in Lösung gebracht wird.

Gallium(III), Indium(III)

Für die Bestimmung dieser Elemente wurde nach der Extraktion die kompleximetrische Rücktitration mit Zinksulfat verwendet. Gallium wurde ausserdem noch gravimetrisch nach der Oxinatmethode ermittelt[10]. Das Extraktionsverhalten geben Fign. 4 und 5 wieder.

Thallium(III)

Thallium(III) wird wie Gold aus salzsauren Lösungen quantitativ extrahiert. JORDANOV UND HAVESOV[5] schreiben die gute Extrahierbarkeit von Gold(III) der hohen Stabilität von $[AuCl_4]^-$ zu (pK = 21.3), und gibt die Anzahl der koordinativ gebundenen Solvensmolekel mit 2 an, was die Ausbildung eines Oktaeders bedeutet. Für Thallium(III) treffen dieselben Stabilitätsverhältnisse zu (pK=18.4). Mittels Anwendung der Methode von McKay[17] bestimmten wir die Anzahl der gebundenen Solvensmolekel ebenfalls mit 2.



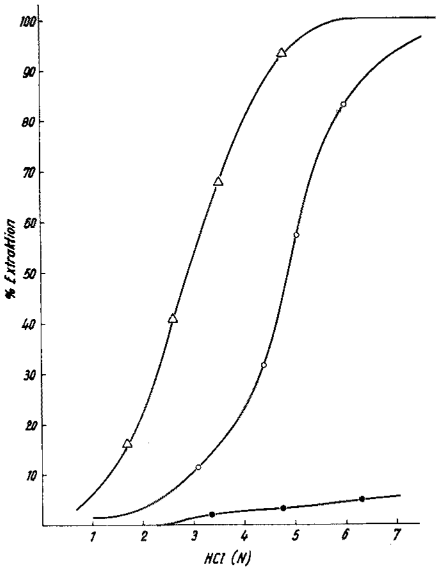


Fig. 4. Extrahierbarkeit von Gallium(III) mittels 2-Butanon (△), 2-Pentanon (○) bzw. 3-Heptanon (●) in Abhängigkeit von der Salzsäurenormalität.

Fig. 5. Extrahierbarkeit von Indium(III) mittels 2-Butanon (△), 2-Pentanon (○) bzw. 3-Heptanon (●) in Abhängigkeit von der Salzsäurenormalität.

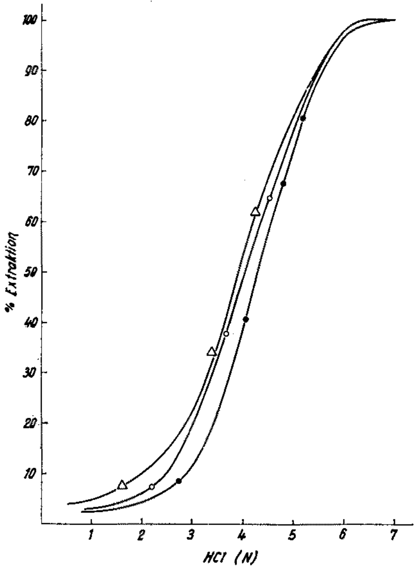


Fig. 6. Extrahierbarkeit von Arsen(III) mittels 2-Butanon (△), 2-Pentanon (○) bzw. 3-Heptanon (●) in Abhängigkeit von der Säurenormalität.

Arsen(III)

Dieses Element wird von den 3 Ketonen in annähernd gleicher Weise extrahiert (Fig. 6), was wohl auf die Existenz von $AsCl_3$ in der organischen Phase zurückzuführen ist.

Die Bestimmung des Elementes erfolgte durch jodometrische Titration.

Das Extraktionsverhalten der übrigen von uns untersuchten Metalle, die verhältnismässig geringe Extrahierbarkeit aufweisen, soll in Tabelle I für 6 *N* salzsaure Lösung wiedergegeben werden.

Aus Tabelle I und den Figuren ist zu entnehmen, dass die Extrahierbarkeit mit steigender Kohlenstoffanzahl des verwendeten Ketons abnimmt.

Aufgrund der Untersuchungen von JORDANOV UND HAVESOV[5], die für die Extraktion von Gold(III) einen Hydrat–Solvat-Mechanismus beschreiben, ist anzunehmen, dass dieser mit Zunahme der Kettenlänge des Solvens beeinflusst wird.

TABELLE I

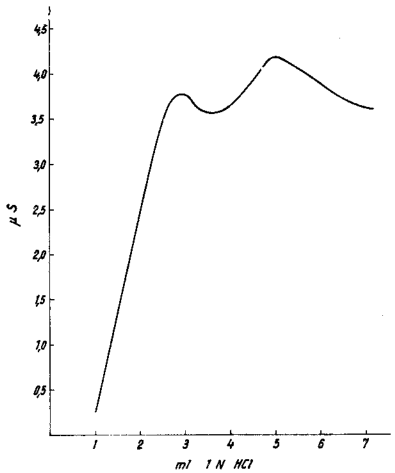
EXTRAHIERBARKEIT AUS 6 *N* SALZSAUREN LÖSUNGEN

Metall	*% Extraktion*			*Bestimmungs-methode*
	2-Butanon	*2-Pentanon*	*3-Heptanon*	
Pt(IV)	19.8	11.0	7.3	Photometr.[16]
Cu(II)	6.2	5.2	4.2	Komplexim.[9]
Zn(II)	4.4	3.5	2.0	Komplexim.[9]
Cd(II)	6.8	2.4	6.4	Komplexim.[9]
Hg(II)	4.7	4.8	3.1	Komplexim.[15]
Sn(IV)	61.0	75.0	8.3	Komplexim.[9]
Sb(III)	67.9	66.0	27.9	Jodometr.[10]

KONDUKTOMETRISCHE EXTRAKTIONSTITRATION

Im Bestreben festzustellen, ob auch bei den vorliegenden Untersuchungen die Extraktion von einwertig negativ geladenen Komplexen bevorzugt wird, brachten wir für zwei Metalle, Gallium(III) und Molybdän(VI) die konduktometrische Extraktionstitration[3] in Anwendung.

Die Durchführung ist relativ einfach: Im Schütteltrichter, der die organische Phase (30 ml Keton + 20 ml Tetrachlorkohlenstoff) sowie die wässrige Phase (10 ml) mit einer genau bekannten Menge des zu extrahierenden Kations (1 mMol) enthält, wird ein bestimmtes Volumen eingestellter HCl-Titerlösung (1 *N* HCl) hinzupipettiert. Danach wird etwa 30 sec geschüttelt. Nach Trennung der beiden Phasen wird der organische Anteil in ein 100-ml Becherglas abgelassen und die Leitfähigkeit mittels einer Tauchzelle gemessen. Diese Operation wird mit steigender Anzahl des zugefügten Volumens HCl-Lösung wiederholt. Die Leitfähigkeitsmessung wurde mit dem Konduktoskop E 365 B (Metrohm), durchgeführt. Messzellenkonstante $= 0.93\ cm^{-1}$. Die Messwerte werden gegen den Halogenidzusatz aufgetragen. Im Äquivalenzpunkt, der den einfach negativ geladenen Komplex voll ausgebildet enthält und daher gut extrahiert wird, weist die Kurve einen Sprung auf. Damit konnte nachgewiesen werden, dass



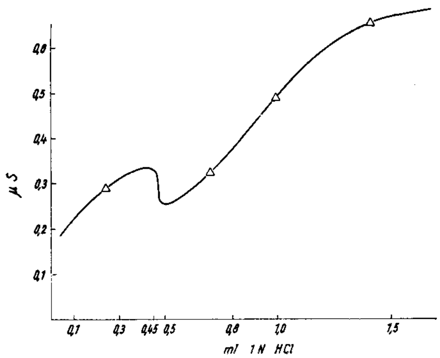


Fig. 7. Konduktometrische Extraktionstitration von Molybdän(VI).

Fig. 8. Konduktometrische Extraktionstitration von Gallium(III). Metallkonz.=0.45 mMol.

Gallium als $[GaCl_4]^-$, Molybdän als $[MoO_2Cl_3]^-$ und $[MoOCl_5]^-$ extrahiert werden (Fign. 7,8).

ZUSAMMENFASSUNG

Eine Reihe von Elementen wird hinsichtlich der Extrahierbarkeit aus salzsauren Lösungen mit Äthylmethylketon, Methylpropylketon und Äthylbutylketon als Solvenzien untersucht. Für Metalle die sich gut extrahieren lassen, ist eine genaue Arbeitsvorschrift angegeben. Auf einige Trennungsmöglichkeiten wird verwiesen. Bei zwei Metallen erfolgt die Bestimmung der Zusammensetzung der extrahierten Verbindung mittels konduktometrischer Extraktionstitration.

SUMMARY

The extractability of a series of elements from hydrochloric acid solutions with ethyl methyl ketone, methyl propyl ketone and ethyl butyl ketone was investigated. Quantitative extraction of molybdenum(VI), iron(III), gold(III), gallium(III), indium(III), thallium(III) and arsenic(III) was obtained. Some separations are outlined. Conductometric extraction titrations established that gallium was extracted as $[GaCl_4]^-$ and molybdenum as $[MoO_2Cl_3]^-$ and $[MoOCl_5]^-$.

RÉSUMÉ

On examine les possibilités d'extraction d'une série d'éléments en solutions acide chlorhydrique–éthylméthylcétone, méthylpropylcétone, et éthylbutylcétone. On peut obtenir une extraction quantitative du molybdène(VI), fer(III), or(III), gallium(III), indium(III), thallium(III) et arsenic(III). Quelques séparations sont décrites. Les titrages conductimétriques après extraction montrent que le gallium est extrait sous forme de $[GaCl_4]^-$ et le molybdène, comme $[MoO_2Cl_3)^-$ et $[MoOCl_5]^-$.

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CHELATE VON β-DICARBONYLVERBINDUNGEN UND IHREN DERIVATEN[1]

XVI. THIODIBENZOYLMETHAN ALS EXTRAKTIONSPHOTOMETRISCHES UND GRAVIMETRISCHES REAGENS FÜR KOBALT

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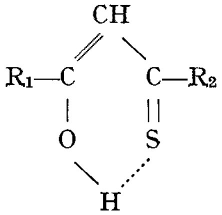
(Eingegangen den 23. Juni, 1969)

β-Thioxoketone der allgemeinen Formel



bilden mit zahlreichen thiophilen Metallen intensivfarbige und recht stabile Metallchelate (vgl. Lit.[2–4]). Mit Kobalt entstehen zumeist diamagnetische Tris-Chelate des dreiwertigen Metalles. Bis-Chelate mit Kobalt(II) sind präparativ schwierig zugänglich, da das Kobalt bei Luftzutritt, bei höherer Temperatur oder bei ungenügender Abführung der Reaktionswärme rasch in den dreiwertigen Zustand übergeht. Versuche zur Darstellung von Kobalt(II)-Chelaten fluorierter β-Thioxoketone schlugen fehl[5], dagegen gelang die Isolierung von Bis(thiodibenzoylmethanato)–kobalt(II) durch Umsetzung des Liganden mit Kobaltacetat bei Temperaturen unterhalb 20° und in Gegenwart von Piperidin[4]. Eine andere günstige Methode zur Herstellung von Kobalt(II)-Chelaten, die ursprünglich für Acetylacetonate beschrieben wurde[6], beruht auf der Reaktion der Komplexbildner mit Metallnaphthenaten oder -oktoaten in unpolaren Lösungsmitteln. Auf diese Weise wurden die Kobalt(II)-Komplexe von Thiothenoyltrifluoraceton und Thioisobutyrylaceton durch anaerobe Arbeitsweise bei tiefen Temperaturen erhalten.

Die über Phosphorpentoxid getrockneten Chelate zeigten magnetische Momente von 4.02–4.1 B.M. und liegen damit an der unteren Grenze des für tetraedrische Kobalt(II)-Komplexe gefundenen Bereiches von 4.1–4.7 B.M. Während die Nickel(II)-, Mangan(III)- und Eisen(III)-Komplexe von β-Thioxoketonen[7–9] die Niederspin-Anordnung einnehmen oder leicht in diese übergehen, liegen die Kobalt(II)-Komplexe in der tetraedrischen Hochspinform vor.

Die Beständigkeit der Kobalt(II)-Bis-Chelate in Lösung ist ausserordentlich gering, so erwiesen Untersuchungen zur Zusammensetzung des Kobaltchelates von

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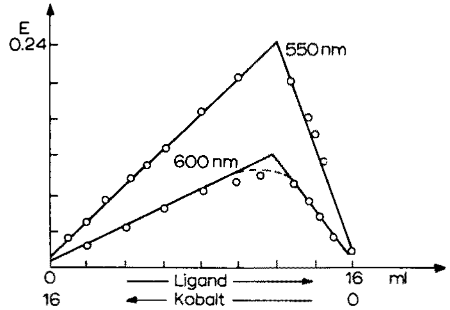
Thiodibenzoylmethan mit der Methode der kontinuierlichen Variation nach Job[10] selbst in Gegenwart geringer Mengen Ascorbinsäure stets das Vorliegen des Tris-Komplexes (s. Fig. 1). Allerdings wird erst nach 15 Min Farbkonstanz erzielt. Die Bildung eines Bisligand-Komplexes konnte aber auch bei sehr schnellem Arbeiten (Messung innerhalb von 30 sec) unter Schutzgas nicht nachgewiesen werden.

EXPERIMENTELLES

Reagenzien und Apparate

Die verwendeten organischen Lösungsmittel waren von p.a.-Qualität oder wurden durch Destillation gereinigt. Alle sonstigen Chemikalien waren von analytischer Reinheit. Zur Herstellung der Lösungen kam demineralisiertes Wasser zum Einsatz. Die Metallkonzentration der Kobaltstammlösung wurde durch eine gravimetrische Standardmethode mit α-Nitroso-β-naphthol ermittelt. Thiodibenzoylmethan wurde nach den Angaben der Literatur[11] dargestellt und zeigte nach zweimaligem Umkristallisieren einen Schmelzpunkt von 83–84°. Die Bestimmung der magnetischen Momente erfolgte mit einer Magnetwaage nach Gouy.

Für die spektralphotometrischen Untersuchungen diente das Spektralkolorimeter "Spekol" des VEB Carl Zeiss, Jena, mit Zusatzverstärker ZV.



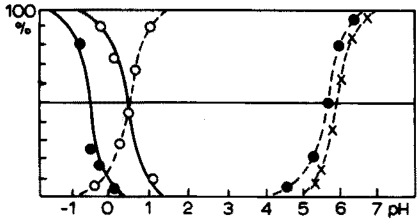


Fig. 1. Jobsche Kurve des Kobaltchelates von Thiodibenzoylmethan für $5 \cdot 10^{-4}$ *M* Lösungen in Äthanol.

Fig. 2. Extraktionskurven (-----) und Reextraktionskurven (———) von Thiodibenzoylmethan-Chelaten in Abhängigkeit vom pH-Wert. (●) Ni, (○) Cu, (×) Co.

Aufnahme der Jobschen Kurve

x ml einer $5 \cdot 10^{-4}$ *M* Kobaltlösung in Äthanol, die pro 100 ml 0.5 g Natriumacetat-trihydrat enthielt, wurden mit *y* ml einer $5 \cdot 10^{-4}$ *M* Lösung von Thiodibenzoylmethan in Äthanol gemischt und gegen eine Vergleichslösung gleicher Konzentration an Komplexbildner, aber ohne Metallzusatz, gemessen ($d = 1$ cm).

Darstellung der Kobalt(II)-Chelate

Bis(thiothenoyltrifluoracetonato)-kobalt(II). 1 g Kobaltnaphthenat (Kobaltgehalt 6%) wird in wenig tiefsiedendem Petroläther gelöst und mit Trockeneis abgekühlt. Dazu gibt man in einer geschlossenen Apparatur unter Stickstoff eine ebenfalls gekühlte Lösung von 480 mg des Komplexbildners[7] in wenig Petroläther. Das sofort ausfallende rotbraune amorphe Pulver wird unter Stickstoff abgesaugt und über Phosphorpentoxid getrocknet.

Analyse: Ber. C 36.03%, H 1.52%, S 24.04%. Gef. C 36.60%, H 2.13%, S 23.65%. Magnetisches Moment: 4.05 B.M.

In ähnlicher Weise wurde das orangerote Bis(thioisobutyrylacetonato)-kobalt(II) dargestellt. Diese Substanz ist äusserst luft- und feuchtigkeitsempfindlich und muss sofort nach dem Trocknen über Phosphorpentoxid magnetisch vermessen werden. Magnetisches Moment: 3.70 B.M.

Thioisobutyrylaceton ist durch Claisenkondensation von Aceton mit Thionisobuttersäureester leicht zugänglich[12].

EXTRAKTIONSPHOTOMETRISCHE KOBALTBESTIMMUNG

Die Verwendung von Thiodibenzoylmethan zur Extraktion thiophiler Metalle aus wässrigen Lösungen wurde bereits früher[13] untersucht. Dabei wird Kobalt stets als Kobalt(III)-Chelat extrahiert. Das Absorptionsspektrum dieser Verbindung ist durch eine starke Absorption im sichtbaren Bereich charakterisiert, die eine photometrische Bestimmung des Metalls ermöglicht. Dabei ist es erforderlich, den zur Extraktion des Kobalts benötigten Überschuss an Ligand vor der photometrischen Messung mit Alkali wieder vollständig aus der organischen Phase zu entfernen. Bei Verwendung von Cyclohexan als Lösungsmittel gelingt dies recht gut, auch die Löslichkeit des gebildeten Kobaltkomplexes in diesem Lösungsmittel ist hinreichend gross.

Störungen der Kobaltbestimmung mit Thiodibenzoylmethan sind vor allem durch Kupfer und Nickel zu erwarten, die ebenfalls alkalibeständige Chelate bilden[13], während viele andere Metallchelate des Reagenses durch Lauge zersetzt werden. Das Kobalt(III)-Chelat des Thiodibenzoylmethans zeichnet sich durch eine bedeutende kinetische Stabilität aus. Während die Kupfer- und Nickelkomplexe dieses Liganden durch Säure bzw. andere Komplexbildner leicht zersetzt werden, bleibt das einmal gebildete Kobalt(III)-Chelat resistent. Extraktions- und Reextraktionskurven der Kupfer-, Nickel-, und Kobaltchelate sind in den Fign. 2 und 3 wiedergegeben.

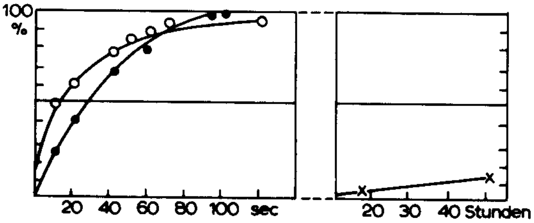


Fig. 3. Zersetzung von Thiodibenzoylmethan-Chelaten in Cyclohexan durch Extraktion mit 0.1 N NaOH (2%ig an KCN) in Abhängigkeit von der Zeit. (○) Cu, (●) Ni, (×) Co; Metallkonzentration 2 μg/ml.

Zur Aufnahme der Reextraktionskurven wurden die in n-Heptan (Kupfer, Nickel) bzw. Toluol (Kobalt) gelösten festen Chelate mit Salzsäure verschiedener Konzentration 2 Min extrahiert, die organische Phase kurzzeitig mit 0.01 N Natronlauge behandelt und die Extinktion der zentrifugierten organischen Phase gemessen. Aus der Abnahme der Extinktion wurde die prozentuale Reextraktion errechnet.

Die Reextraktionskurven zeigen die hohe kinetische Stabilität des Kobaltchelates. Selbst bei 15 stündigem Schütteln mit 2.5 *N* Salzsäure bleibt der Kobaltkomplex unverändert. Daher sollte es möglich sein, durch Behandeln mit halbkonzentrierter Salzsäure die mitextrahierten, störenden Metallchelate wieder zu zersetzen und das zurückbleibende Kobaltchelat spezifisch photometrisch zu bestimmen. Die hohe Salzsäurekonzentration erschwert jedoch die Phasentrennung, so dass keine gute Reproduzierbarkeit der Bestimmung erreicht werden konnte. Es wurde deshalb versucht, die störenden Metall–Thiodibenzoylmethan-Chelate mit anderen Komplexbildnern in wasserlösliche Komplexe zu überführen. Dabei erwiesen sich Ammoniak und EDTA als nicht wirksam genug, dagegen Kaliumcyanid als gut geeignet.

Zur Aufnahme der Reextraktionskurven mit Kaliumcyanid (Fig. 3) wurden organische Lösungen der Metallchelate (mit 2 μg Metall pro ml) mit 0.1 *N* Natronlauge, die 2%ig an Kaliumcyanid war, bei gleicher Schüttelfrequenz unterschiedliche Zeit geschüttelt und nach der Phasentrennung die Extinktion gemessen. Die Kurven zeigen, dass cyanidhaltige 0.1 *N* Natronlauge ein geeignetes Mittel zur Abtrennung störender Metallchelate bei der extraktionsphotometrischen Kobaltbestimmung mit Thiodibenzoylmethan darstellt. Störungen, die durch die Anwesenheit von Kupfer hervorgerufen werden, lassen sich auf diese Weise jedoch nicht beseitigen.

Arbeitsvorschrift zur extraktionsphotometrischen Kobaltbestimmung

Zu 20 ml neutraler oder schwach saurer Probelösung, die bis zu 30 μg Kobalt

TABELLE I

KENNGRÖSSEN FÜR DIE PHOTOMETRISCHE KOBALTBESTIMMUNG MIT THIODIBENZOYLMETHAN BEI 410 nm

Molarer Extinktionskoeffizient	12600
Empfindlichkeit nach SANDELL[14]	0.047 $\mu g/cm^2$
relative Standardabweichung	± 3.5%

TABELLE II

BELEGANALYSEN ZUR EXTRAKTIONSPHOTOMETRISCHEN KOBALTBESTIMMUNG MIT THIODIBENZOYLMETHAN

(vorgelegte Kobaltmenge 18 μg, Sollwert der Extinktion 0.476)

Fremdion		*Extinktion*	*Differenz*
Art	*Konzentration (μg)*		
Ni(II)	200	0.480	+0.004
	400	0.450	−0.036
	2000	0.245	−0.231
Zn(II)	200	0.478	+0.002
	2000	0.170	−0.306
Fe(III)	200	0.450	−0.020
Pb(II)	2000	0.480	+0.004
	10000	0.530	+0.054
In(III)	1000	0.475	−0.001
Ni(II), Zn(II)	je 200	0.460	−0.016
Fe(III), Pb(II)		0.485	+0.009
In(III)	1000	0.458	−0.018

enthalten kann, gibt man 5 ml Pufferlösung (0.1 *M* Ammoniumchloridlösung, die mit konzentriertem Ammoniak auf pH 9 eingestellt wurde) und 10 ml einer 10^{-3} *M* Lösung von Thiodibenzoylmethan in Cyclohexan. Man extrahiert 3 Min, trennt die Phasen und lässt die organische Phase eine halbe Stunde stehen. Danach wird kurzzeitig dreimal mit je 20 ml 0.1 *N* Natronlauge (2%ig Kaliumcyanid) durchgeschüttelt und die Extinktion der abgetrennten organischen Phase bei 410 nm ($d = 1$ cm) gegen Cyclohexan gemessen.

Einige Kenngrössen für die photometrische Kobaltbestimmung sind in Tabelle I zusammengestellt. Tabelle II zeigt die Beeinflussung der Bestimmung durch Fremdionen, wenn nach der angegebenen Arbeitsvorschrift verfahren wird.

GRAVIMETRISCHE BESTIMMUNG VON KOBALT MIT THIODIBENZOYLMETHAN

Die Schwerlöslichkeit des Kobalt(III)-Chelates, seine thermische Beständigkeit (s. Fig. 4), sowie die solvatfreie formelreine Zusammensetzung und das hohe Molekulargewicht ermöglichen die Verwendung von Thiodibenzoylmethan als Reagens zur gravimetrischen Kobaltbestimmung. Da Thiodibenzoylmethan in Wasser fast völlig unlöslich ist, muss in alkoholisch-wässrigen Lösungen gearbeitet werden. Die Löslichkeit des Tris(thiodibenzoylmethanato)-kobalt(III) beträgt unter diesen Bedingungen etwa $5 \cdot 10^{-6}$ Mol/l. Die Löslichkeit ist damit ausreichend gering, um genaue gravimetrische Bestimmungen ausführen zu können.

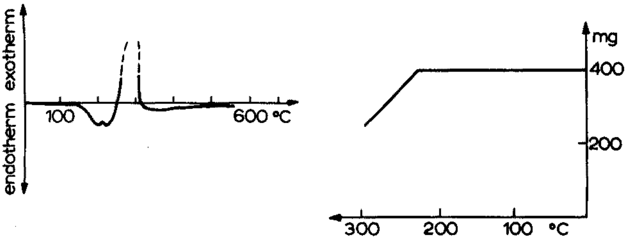


Fig. 4. Thermogravimetrie und Differentialthermoanalyse von Tris(thiodibenzoylmethanato)-kobalt(III).

Arbeitsvorschrift

Zu 50 ml der schwach sauren Probelösung, die zwischen 2 und 15 mg Kobalt enthalten soll, gibt man 100 ml Alkohol und erhitzt zum Sieden. Nun werden 50 ml Reagenslösung unter kräftigem Sieden zugegeben und das Rühren 2 bis 3 Min fortgesetzt. In dieser Zeit färbt sich die Lösung dunkel und der zuerst ausgefallene amorphe braune Niederschlag geht in Lösung. Die Probe soll jetzt dunkel und klar sein. Während des Abkühlens (2 bis 3 Stunden) scheidet sich ein kristalliner schwarzer Niederschlag ab. Man filtriert über eine G 4-Fritte und wäscht mit warmem Methanol, dann mit heissem Wasser und zum Schluss nochmals mit Methanol. Bei 110° wird eine Stunde getrocknet und dann zur Auswaage gebracht.

Die Reagenslösung enthält 2 g kristallisiertes Natriumacetat und 200 mg Thiodibenzoylmethan in 50 ml 90%igem Alkohol. Die Haltbarkeit dieser Lösung ist auf 36 Stunden beschränkt, ohne Zusatz von Natriumacetat und bei Aufbewahrung in braunen Flaschen ist die Lösung jedoch über Tage haltbar.

Beleganalysen für die gravimetrische Kobaltbestimmung sind in Tabelle III zusammengestellt.

Thiodibenzoylmethan gestattet die gravimetrische Bestimmung von Kobalt im Bereich von 2 bis 15 mg je Probe. Die Analysendurchführung ist einfach und ermöglicht auch dem analytischen Anfänger eine exakte Bestimmung. Durch Komplexbildner, die selbst mit Kobalt kinetisch stabile Metallkomplexe ergeben, wird die Metallbestimmung empfindlich gestört und liefert dann zu niedrige Ergebnisse. Tartrat kann bis zum fünffachen, Citrat bis zum zehnfachen Überschuss anwesend sein, auch in Gegenwart von Ammoniak wurde keine Störung der Bestimmung beobachtet. Für die Maskierung von anwesendem Kupfer wichtig ist der Befund, dass

TABELLE III

BELEGANALYSEN FÜR DIE GRAVIMETRISCHE EINZELBESTIMMUNG VON KOBALT MIT THIODIBENZOYLMETHAN

Kobalt vorgelegt (mg)	*Kobalt gefunden (mg)*	*relativer Fehler (%)*
2.02	2.02	0
2.02	2.02	0
2.02	1.99	−2.0
4.52	4.52	0
4.98	4.97	−0.2
6.06	6.13	+1.1
6.78	6.65	−1.9
9.04	8.95	−1.0
9.04	9.03	−0.1
10.37	10.36	−0.1
11.20	11.20	0
11.80	11.79	−0.1

Durchschnittlicher relativer Fehler ±0.6%.

TABELLE IV

EINFLUSS VON FREMDIONEN AUF DIE GRAVIMETRISCHE KOBALTBESTIMMUNG MIT THIODIBENZOYLMETHAN

Fremdionen		*Maskierungsmittel*	*Kobalt (mg)*		*relativer*
Art	*Konzentration (mg)*	*(mg)*	*vorgelegt*	*gefunden*	*Fehler (%)*
Mangan(II)	10	Thioharnstoff 50	11.20	11.20	0
	50	Thioharnstoff 250	14.25	14.20	−0.35
	100	Thioharnstoff 500	11.80	11.90	+0.85
	150	Thioharnstoff 750	11.20	11.20	0
	200	Thioharnstoff 1000	11.80	12.75	+8.05
Kupfer(II)	10	Thioharnstoff 50	11.20	11.81	+3.48
	10	Thioharnstoff 100	11.20	11.08	−1.07
	50	Thioharnstoff 500	11.20	11.32	+1.07
	100	Thioharnstoff 1000	11.80	11.87	+0.60
	200	Thioharnstoff 2000	11.20	11.08	−1.07
Zink(II)	10	Thioharnstoff 100	14.45	14.40	−0.35
	50	Thioharnstoff 500	11.80	11.50	−2.90
	50	Ammoniak/Thiocyanat	14.45	14.40	−0.35
	100	Ammoniak/Thiocyanat	11.80	11.70	−0.85
	200	Ammoniak/Thiocyanat	11.80	11.62	−1.53

Thioharnstoff auch in grösserer Menge anwesend sein darf. Bei Gegenwart von Thioharnstoff kann die Kobaltbestimmung auch neben Mangan durchgeführt werden, weil dann die durch Mangansalze katalysierte Oxydation von Thiodibenzoylmethan zu seinem Disulfid unterbleibt. Zink kann durch Zusatz von Ammoniak und Ammoniumthiocyanat in Lösung gehalten werden, während Eisen vor der Kobaltbestimmung durch Ausäthern entfernt sein muss. Die Kobaltbestimmung kann so auch neben einem jeweils zehnfachen Überschuss an Kupfer, Mangan und Zink durchgeführt werden (s. Tabelle IV).

Bestimmung von Kobalt neben Kupfer, Zink und Mangan

Die Probelösung, deren Volumen 100 ml betragen soll, wird zunächst zur Maskierung des Kupfers mit einer ausreichenden Menge Thioharnstoff (15 facher Überschuss bezogen auf Kupfer) versetzt und 30 ml halbkonzentrierter Ammoniak zugegeben. Man erhitzt und fällt dann mit Thiodibenzoylmethan. Die Lösung bleibt nun eine halbe Stunde stehen und wird dann mit 20 g Ammoniumthiocyanat versetzt. Nach abermaligem Aufkochen bleibt die Lösung 2 bis 3 Stunden stehen. Während dieser Zeit setzt sich ein schwarzer Niederschlag ab, der gut abgesaugt werden kann. Man wäscht nacheinander mit heissem Methanol, heisser 3 *N* Salzsäure, heissem Wasser und nochmals mit Methanol. Der Niederschlag wird bei 110° getrocknet.

Frl. H. SCHMIDT, Herrn R. STAROSKE und Herrn M. SCHÖNEKERL danken wir für die exakte Durchführung der gravimetrischen Bestimmungen.

ZUSAMMENFASSUNG

Kobalt(II)-Salze reagieren mit β-Thioxoketonen sehr schnell zu entsprechenden Kobalt(III)-Chelaten. Bei tiefen Temperaturen und unter anaeroben Bedingungen konnten Kobalt(II)-Chelate von Thiothenoyltrifluoraceton und Thioisobutyrylaceton erhalten werden. Ihr magnetisches Verhalten spricht für tetraedrische Struktur. Die Verwendung von Thiodibenzoylmethan zur extraktionsphotometrischen Bestimmung von Kobalt wird beschrieben. Die bedeutende kinetische Stabilität des gebildeten Kobalt(III)-Chelates ermöglicht die Abtrennung störender Metalle durch Reextraktion mit cyanidhaltiger Natronlauge. Anwesendes Kupfer stört die Kobaltbestimmung. Thiodibenzoylmethan ist auch für die gravimetrische Bestimmung von Kobalt im Bereich von 2–15 mg geeignet. Bei Gegenwart von Thioharnstoff stören Kupfer und Mangan in jeweils 10 fachem Überschuss nicht. Zink kann bis zum gleichen Überschuss durch Ammoniak und Ammoniumthiocyanat in Lösung gehalten werden, Eisen ist durch Ausäthern abzutrennen.

SUMMARY

Cobalt(II) salts react rapidly with monothio-β-diketones to form cobalt(III) chelates. At low temperatures and under anaerobic conditions, cobalt(II) chelates of thiothenoyltrifluoracetone and thioisobutyrylacetone can be isolated; their magnetic behaviour indicates a tetrahedral structure. The use of thiodibenzoylmethane for the extraction–photometric determination of cobalt is described. Owing to the considerable kinetic stability of the formed cobalt(III) chelate, interfering metals can be separated by reextraction with sodium hydroxide solution containing cyanide, except in the case of copper. Thiodibenzoylmethane is also suitable for the gravimetric determination of cobalt in the range 2–15 mg. In the presence of thiourea, copper and manganese do not interfere in up to 10-fold amounts; zinc can be kept in solution by means of ammonia and ammonium thiocyanate, but iron must be separated by ether extraction.

RÉSUMÉ

Les sels de cobalt(II) réagissent rapidement avec les β-monothiocétones pour former des chélates de cobalt(III). On a pu isoler les chélates obtenus avec la thiothénoyltrifluoracétone et la thioisobutyrylacétone. On décrit un dosage de cobalt au moyen de thiodibenzoylméthane par extraction et photométrie. Grâce à la grande stabilité du chélate de cobalt(III) formé, les métaux gènants peuvent être séparés par réextraction au moyen d'une solution d'hydroxyde de sodium contenant du cyanure, à l'exception du cuivre. Le thiodibenzoylméthane permet également un dosage gravimétrique du cobalt (2–15 mg). En présence de thiourée, le cuivre et le manganèse ne gènent pas, en concentrations 100 fois supérieures. Le zinc peut être maintenu en solution au moyen d'ammoniaque et de thiocyanate d'ammonium, le fer doit être séparé par extraction à l'éther.

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A RAPID AND HIGHLY SENSITIVE SINGLE-SWEEP POLAROGRAPHIC METHOD OF ANALYSIS FOR ARSENIC(III) IN DRINKING WATER

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The polarographic determination of arsenic has been extensively studied[1-5] but the technique has not found wide application in the analysis of drinking water. In acidic media[1,2] the polarographic waves have been reported as both poorly and well-defined, while in alkaline media some investigators were unable to obtain a reduction wave for the arsenite ion. Recently a well-defined reduction wave has been reported around -1.8 V in 0.1 M lithium chloride and 0.01 M lithium hydroxide solution[6]. Since the voltage range in which the arsenic peak occurs in acidic media seems best suited for analytical purposes with drinking water, these media were investigated.

The U.S. Federal Register has listed the maximum permissible level of arsenic in drinking water as 50 parts-per-billion (p.p.b.). The Gutzeit test for arsenic[7] is generally used to determine the level of arsenic in drinking water. However, this test is not very significant below 50 p.p.b. of arsenic, which is the concentration range of arsenic in most drinking water. The Gutzeit method for successful application requires considerable practice and a pretreatment of the sample including the liberation of arsenic as arsine. The entire procedure is time-consuming, and very susceptible to loss of arsine, and the results are questionable with water containing 40 p.p.b. arsenic or less.

It is the purpose of this work to present and describe a relatively simple, precise, and extremely sensitive polarographic analysis for arsenic in drinking water, and show its application to the analysis of arsenic in several well waters and spring waters found in the Mojave Desert region of California (Indian Wells Valley).

EXPERIMENTAL

Apparatus and materials

A linear sweep cathode-ray polarotrace (Southern Analytical Instruments, Ltd., England) was used throughout this work. The dropping mercury electrode had a drop time of 7 sec in distilled water and $m = 4.4$ mg/drop. All measurements were made at 25° ± 0.10°. All current peak potentials are referred to the mercury pool. A Moseley Model 2-D X-Y recorder (F. L. Moseley Co., Pasadena, Calif.) was used to record the polarograms.

The sulfuric acid used (General Chemical Division, Allied Chemical) was C. P. Reagent Grade. The arsenic content of the sulfuric acid was less than $5 \cdot 10^{-7}\%$.

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The well water was collected and stored in 25-ml polystyrene vials with a snap cap of polyethylene for analysis. The samples were analyzed within 24 h after collection.

Standard solutions of arsenic(III) were prepared from resublimed arsenious acid (National Bureau of Standards As_2O_3), which was dissolved in sodium hydroxide (arsenic-free) and neutralized with dilute sulfuric acid. A stock solution containing 1 mg/ml of arsenic was then prepared with conductivity water and diluted to a solution containing $1 \cdot 10^{-5}$ g/ml of arsenic. Fresh solutions were used throughout the study. Well water (2 ml) was placed in a polarographic cell and micro-aliquots of the $1 \cdot 10^{-5}$ g/ml of arsenic(III) standard solution were then added for analysis. The method of standard addition was used to eliminate any effect from a sample matrix change with different well waters.

Procedure

A 2-ml sample of well water was placed in a 5-ml polarographic cell containing a pool of mercury as the anode. The cell solution was flushed with nitrogen for 5 min after the addition of 3 drops of concentrated sulfuric acid. The voltage range from -0.70 to -1.20 V was then scanned with the 2-sec sweep of the polarograph. The current voltage curve was recorded after about 6–8 sweeps of the instrument. The peak for arsenic(III) occurred at about -0.97 V.

After the unknown polarogram had been recorded, a micro-aliquot of the $1 \cdot 10^{-5}$ g/ml of arsenic standard solution was added to the solution in the cell and the solution was flushed for 5 min. The voltage was again scanned from -0.70 to -1.20 V and after 6–8 sweeps, the wave height and peak for arsenic were again measured. The concentration of arsenic(III) in the sample was then obtained from a ratio of the two wave-heights. Additions of 0.01–0.05 ml of the arsenic(III) standard solution ($1 \cdot 10^{-5}$ g/ml) were added to minimize volume effects.

RESULTS AND DISCUSSION

The data in all Figures and Tables were obtained with raw drinking water. No filtration or other pretreatment was given the sample before analysis. The only contamination contribution in the analysis was from the storage vials. These were carefully cleaned with sulfuric acid, washed with conductivity water, and dried before collecting the sample. Samples of well water with known additions of arsenic(III) were allowed to stand in the storage vials used in this work for a period of 1 week. No loss of arsenic(III) to the container or other interference was observed.

As a supporting electrolyte several concentrations (0.01–0.5 *M*) of sulfuric, hydrochloric, acetic, phosphoric, and perchloric acid, respectively, were tried. The sulfuric acid solutions appeared to give the sharpest peaks and most reproducible polarograms for measurement. Since one wants to obtain the greatest sensitivity possible without pretreatment and possible contamination of the sample, the addition of a few drops of concentrated sulfuric acid to the raw water in the polarographic cell was used in this work.

Table I shows both polarographic and Gutzeit analyses for arsenic(III) in 16 samples of well water used for drinking water. The arsenic(III) content of these samples ranged from 8 to 30 p.p.b. as determined by the proposed single-sweep polaro-

TABLE I

DETERMINATION OF ARSENIC(III) IN DRINKING WATER

Well no.	*Arsenic(III) concentration (p.p.m.)*		*Well no.*	*Arsenic(III) concentration (p.p.m.)*	
	Gutzeit (colorimetric)	*Single-sweep polarography*		*Gutzeit (colorimetric)*	*Single-sweep polarography*
7	0.000	0.019	21	0.000	0.016
12	0.000	0.027	22	0.000	0.033
14	0.000	0.008	23	0.000	0.019
15	0.000	0.027	25	0.000	0.031
16	0.000	0.027	27	0.029	0.016
18	0.006	0.025	28	0.000	0.027
19	0.008	0.019	29	0.022	0.027
20	0.000	0.008	Composite[a]	0.000	0.020

[a] Sample taken at point where water from above 15 wells is mixed.

TABLE II

DETERMINATION OF ARSENIC(III) IN DRINKING WATER

Well no.	*Arsenic(III) concentration (p.p.m.)*	*Well no.*	*Arsenic(III) concentration (p.p.m.)*
A	0.030	G	0.024
B	0.007	H	0.043
C	0.040	I	0.019
D	0.039	J	0.008
E	0.019	K	0.043
F	0.020	L[a]	0.200

[a] Well L lay to the south of the area shown in Fig. 1 in the El Paso mountains.

graphic technique. These same samples, by the Gutzeit method, showed arsenic to be present in only four of the samples. From the results of the Gutzeit analysis one can only say that all samples analyzed contained less than the 50 p.p.b. maximum arsenic content established for safe drinking water. The polarographic analysis agrees with the Gutzeit analysis but also provides a quantitative figure for comparative analysis. It can also be seen from the results that arsenic(III) is measurable by the polarographic technique down to about 5 p.p.b. Thus, it would appear that the single-sweep polarographic technique presented here is approximately ten times more sensitive for arsenic than the colorimetric Gutzeit technique currently used by most laboratories for the analysis of arsenic in drinking water. The relative error of the polarographic method is 5–10% of the arsenic concentration in the water.

In Table II, the arsenic(III) content of several spring waters and private wells in the area are shown. These results were all obtained by the proposed polarographic method. It can be seen that concentrations as high as 200 p.p.b. can also be determined on the raw sample without dilution. Well number L is a natural spring where it can be noted that the arsenic concentration is much higher.

An index map of Indian Wells Valley (Fig. 1) shows the geographic location of the well water analyzed for arsenic in this paper. The open circles in the Fig. represent

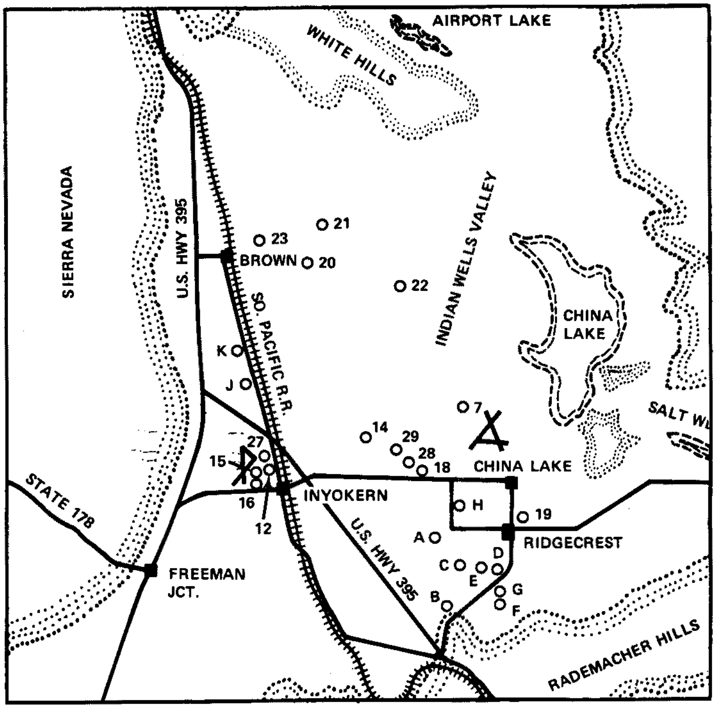

Fig. 1. Index map of Indian Wells Valley.

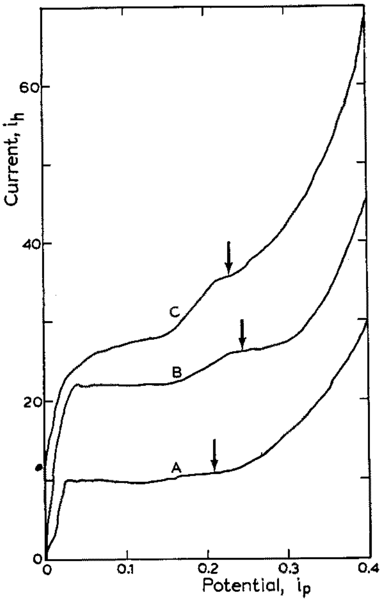

Fig. 2. Single-sweep polarograms of arsenic(III) in well water. 3 drops conc. H_2SO_4 in 2-ml sample. Start potential= −0.70 V. Shunt scale factor = XI-2.5; Amp. scale factor = X-1; Comp. = 1/4; Slope = 3.0.

the precise locations of the wells. The circles with numbers represent the wells reported in Table I, while the circles with letters represent other wells in the area (Table II).

Figure 2 shows three single-sweep polarograms for arsenic(III) recorded by the X-Y recorder from three different well water samples. Curve A represents an arsenic(III) concentration of 8 p.p.b., Curve B 30 p.p.b., and Curve C 65 p.p.b., by the standard addition technique with direct current of the single-sweep polarograph.

Arsenic(V) can be determined by treating the sample with hydrazine sulfate in sulfuric acid solution[3] to convert it to the arsenic(III) state and then measuring another polarogram according to the procedure.

SUMMARY

A simple, rapid, and extremely sensitive method of analysis for arsenic in drinking water is presented. The method is a single-sweep polarographic technique that will determine as little as 5 p.p.b. arsenic with a relative error of 5–10% of the actual concentration. No special treatment of the sample is needed before the analysis. The method is useful in the examination of well water, spring water, and other drinking waters that contain arsenic in very low quantities (50 p.p.b. or less). The method is shown to give more reliable results on drinking water than the Gutzeit method currently used by water chemists in the analysis of arsenic at low levels.

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REACTION THERMAL ANALYSIS OF ORGANOPOLYSILOXANES

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Thermal analysis is a comparatively recent analytical method, but has already been modified and extended in various different ways, *e.g.* thermogravimetry (TGA), differential thermal analysis (DTA), gas evolution analysis (GEA), thermogravimetry connected with mass spectrometry (TGA–MS), etc.

Thermal analysis has very many uses, as can be seen from several recent review articles[1–3]. Generally, only changes caused by increasing temperatures are investigated. In some cases, the changes caused by the reaction between the test substance and the ambient atmosphere[4] have been investigated; recently the reactions during which new compounds are formed, have also been studied[5], this method being used to identify certain substances.

Some papers have dealt with the identification of cleavage products created by thermal decomposition. The identification is carried out either by mass spectrometry[6–9] or by gas chromatography[10,11] by accumulating the gaseous cleavage products and feeding them regularly to the mass spectrograph or gas chromatograph.

The present authors have previously described a method[12] involving the use of a gas-chromatographic detector for identifying cleavage products. The use of the so-called "reaction chromatography" for identification or for structural analysis of organic substances has also been discussed[13]; the test substance is split in the presence of various reagents and the cleavage products are identified by chromatographic methods.

In the previous work, it was often found that the cleavage reactions occurred at increasing temperatures in different ways, depending on the structural arrangement of the molecule, although the substances in question were very similar. Accordingly, a study has been made of the possibility of utilizing this phenomenon for the structural analysis of organic substances together with the exploitation of the possibility of detecting cleavage products by gas chromatography. The first group to be analysed by the "reaction thermal analysis" method was a set of low-molecular-weight organopolysiloxanes. The cleavage products were again identified by gas chromatography.

Basically, it is a question of determining the moment, or rather the temperature at which the individual functional groups are separated in the molecule, when the molecule reacts with a suitable reagent. The thermogram obtained is characteristic of particular functional groups, as well as of their arrangement in the molecule. In the course of the reaction, the products formed are fed to the gas-chromatographic detector, where the time of maximum concentration is determined.

EXPERIMENTAL

Equipment

The reaction thermal analysis (RTA) apparatus is shown schematically in Fig. 1. It consists of am pressure vessel (1) which is the source of the carrier gas (nitrogen). The carrier gas passes through a manostat (2), a needle valve (3) and a manometer (4), into an oven (5) in which on a thermo-couple (6) (iron-constantan), a platinum vessel (7) is fixed with the sample and the reagent. The oven is designed so that the temperature can be programmed. The oven is followed by an absorption device (8) which is designed to capture any volatile portions of the reagent. This absorption device however, lets through the gaseous cleavage products, which are then fed into a combustion oven (9) to be burnt to carbon dioxide and hydrogen; after the carbon dioxide has been removed in an absorber (10) the amount of hydrogen is measured by a thermal conductivity sensor (11)[13]. The carrier gas then passes through a flow meter (12) to the atmosphere. The sensor and the thermo-couple are connected to a recorder (13) which alternately records the signals from the sensor and the thermocouple. The switching is carried out automatically by a switch (14). In some cases it is more convenient to record the temperature curve separately.

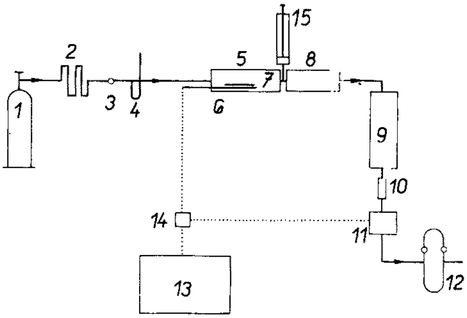


Fig 1. Schematic diagram of the RTA equipment.

In order to be able to determine which functional group splits out in the temperature interval investigated, a 20-ml injection syringe (15) is inserted between the oven and the absorption device. The syringe has an injection needle of very small diameter (0.4 mm) and is inserted into a rubber connection between the oven and the absorption device. A small portion of the carrier gas, together with the cleavage products, raises the piston of the injection syringe during the measurement. At suitable intervals, 5–10 ml of these products are fed to the gas chromatograph and the individual components are identified. Methane and benzene were identified by normal gas-chromatographic techniques.

Procedure

The sample is weighed into a small platinum vessel (Fig. 2). In order to guarantee that the sample is perfectly distributed and that it comes into the greatest possible contact with the reagent used, first about 20 mg of glass beads (diameter 0.1 mm) or asbestos are put into the vessel, followed by about 2.5 mg of the sample. This is covered by a layer of about 15 mg of liquid reagent. It is very important that the optimal ratio of sample to reagent be found, in order to prevent a large excess or insufficient amount of reagent. The vessel is placed on the thermo-couple and inserted into the oven. The carrier-gas input is opened so that the flow rate is 15 ml/min. The programmed oven heating is then switched on at a rate of 15°/min. Simultaneously, the recorder is switched on (0–1 mV range) and the thermogram is recorded.

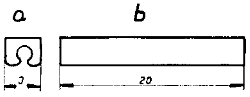


Fig. 2. Platinum vessel.

For cleavage of the organopolysiloxanes examined, concentrated sulphuric acid was used; this was pre-heated until white fumes evolved. Soda asbestos of grain size *ca.* 2 mm, was used as the absorbing agent in the absorption device.

After each measurement, it is necessary to clean not only the vessel in which the reaction takes place, but also the whole oven, in which the vessel is located. It is, therefore, best to design the equipment so that a quartz tube (diameter 4 mm, length 9 cm) can be inserted into the oven orifice; this is then easy to remove and clean.

The thermo-couple is located in a stainless steel pipe of diameter 2 mm, sealed at the end. The positioning of the thermo-couple and the feeding of the carrier gas have been described previously[12].

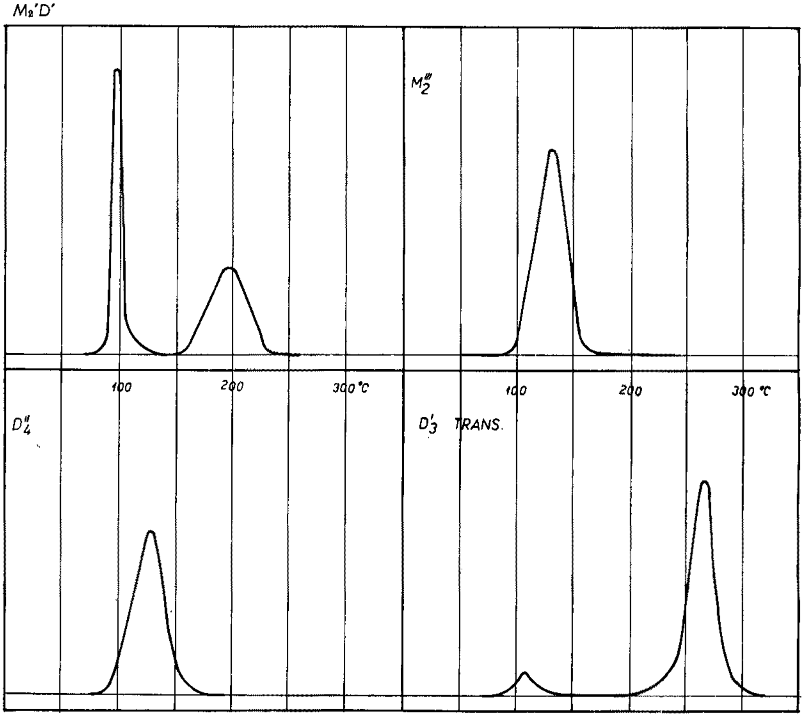
The cleavage reaction involves splitting out of methane and benzene, and the residue consists mainly of silicic acid with, possibly, some undecomposed residue. High-molecular-weight organopolysiloxanes may result from the reaction with sulphuric acid, which acts as a polymerisation catalyst; however, their cleavage reactions appeared to be the same as those of lower-molecular-weight organopolysiloxanes.

RESULTS AND DISCUSSION

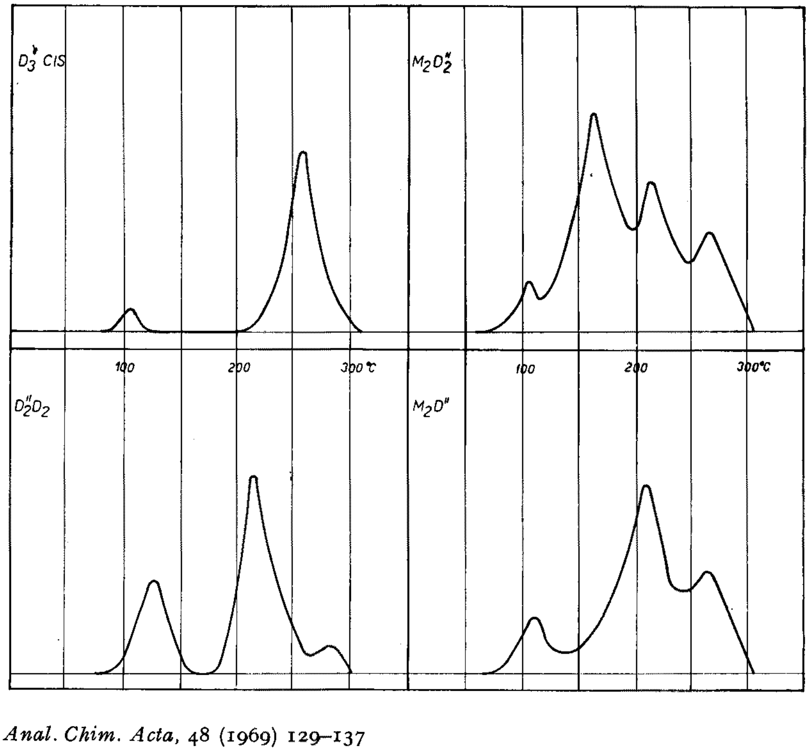
Figure 3 shows curves which were obtained by reaction thermal analysis during the splitting of organopolysiloxanes by concentrated sulphuric acid in the temperature range 20–300°.

These curves show that if the molecule has the same structure, the temperatures at which the splitting takes place, are identical within a small interval. An attempt was, therefore, made to attribute the individual maxima of the thermogram to certain functional groups and their arrangement in the molecule. This is reviewed in Table I. The Table was also assembled with the help of gas chromatography, which made it possible to determine to which functional group the maximum of the appropriate thermogram belonged.

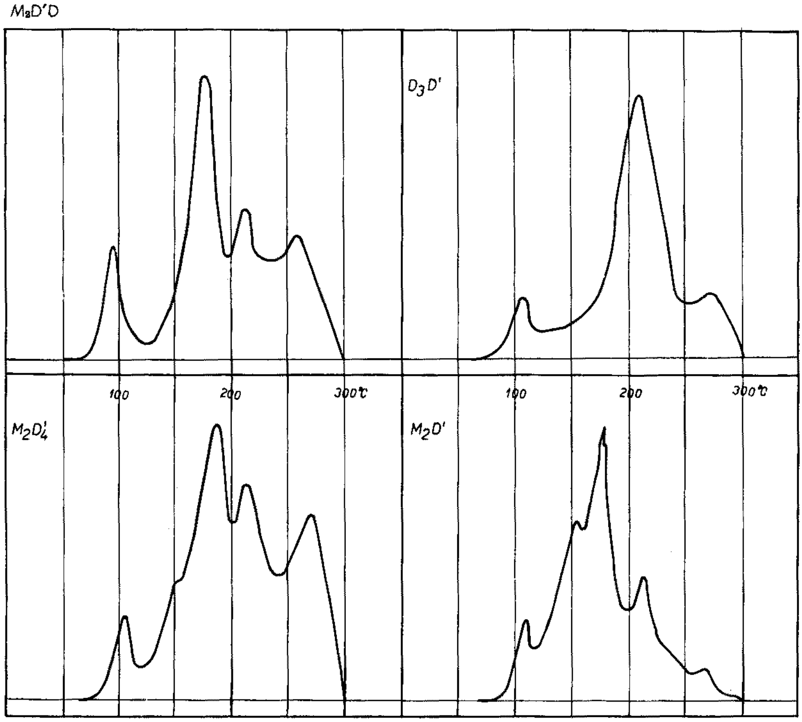
The Table indicates the following facts: in cleavage of organopolysiloxanes by sulphuric acid, the phenyl groups split first, the ease of removal of the groups being in the order $PhSi\equiv\ > Ph_2Si= \ > Ph_3Si-$. The second group is formed by methyl groups bound to silicon. It is interesting to note that if the molecule contains the organopolysiloxane group $-Si(CH_3)_3$, a total of three temperature values is obtained, at which the methyl groups separate in the form of methane. It can thus be concluded


M₂'D'
100
200
300 °C
M₂'''
100
200
300 °C
D₄''
D₃' TRANS.

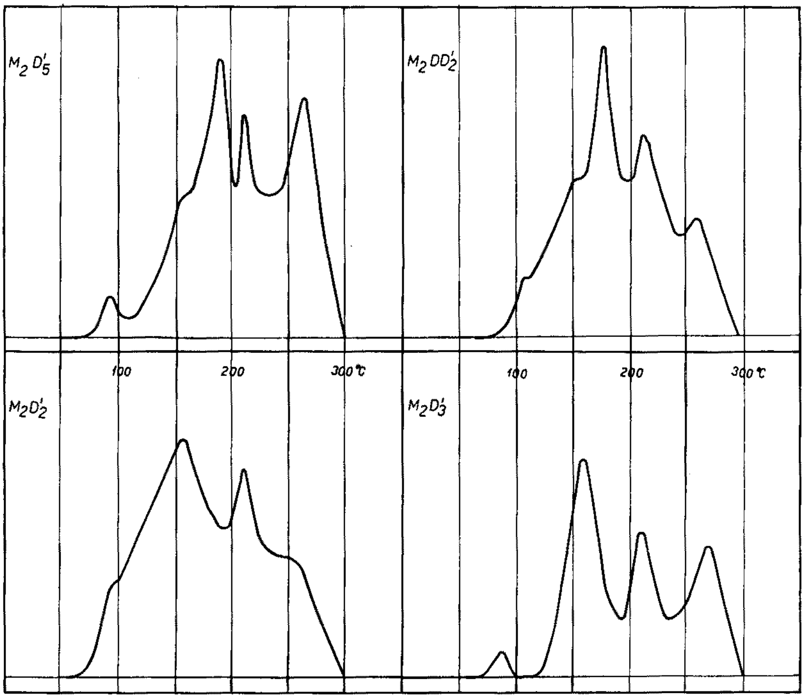
(a)


D₃'' CIS
M₂D₂''
100
200
300 °C
100
200
300 °C
D₂''D₂
M₂D''

(b)


$M_2D'D$
D_3D'
100
200
300°C
100
200
300°C
$M_2D'_4$
M_2D'

(c)


$M_2D'_5$
$M_2DD'_2$
100
200
300°C
100
200
300°C
$M_2D'_2$
$M_2D'_3$

(d)

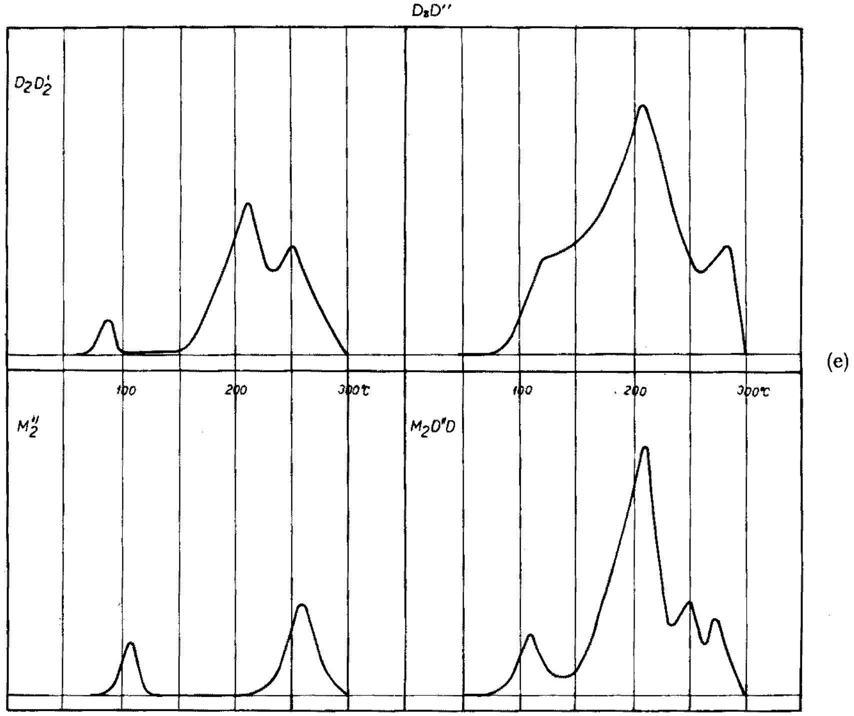


Fig. 3. Thermograms of organopolysiloxanes reacting with concentrated sulphuric acid. (For compound names, see footnote to Table I.)

that at a temperature of 155–185° the first methyl group separates, at about 215° the second and, finally, at 275° the third. In the course of the separation of the first methyl group a set of two temperatures can be observed: about 155° and about 185°. In some cases both may be observed, although one of them is less well defined. This may be explained by the fact that if a methyl group and a phenyl group are bound to silicon simultaneously, their spatial distribution is different, and in the case of sterically more accessible positions, the separation may take place at a lower temperature.

If the molecule contains only a $=Si(CH_3)_2$ group, the latter behaves like the last two methyl $-Si(CH_3)$ groups, *i.e.* the separation takes place at temperatures of about 215 and 275°. If only a $\equiv Si(CH_3)$ group is present, the splitting temperature is 255°, *i.e.* a little lower than the 275° corresponding to the last methyl group of $-Si(CH_3)_3$ or $=Si(CH_3)_2$.

The accuracy of the temperature record corresponding to the individual maxima of the thermogram, is determined by the instrumentation; in the arrangement used, the accuracy of the temperature maxima was ± 3–4°.

As can be seen from the EXPERIMENTAL, there is a certain delay between the time when the appropriate temperature is recorded and the signal of the detector, because the velocity of the carrier gas is 15 ml/min. Experimentally, it was found that this delay with the arrangement used amounted to 24 sec, which corresponds to a

TABLE I

SUMMARY OF TEMPERATURES (°) OF SPLITTING OF THE INDIVIDUAL FUNCTIONAL GROUPS OF ORGANOPOLYSILOXANES BY SULPHURIC ACID

No.	*Compound*[a,b]	*C or L*[c]	*Arrangement of functional groups*					
			$-Si(C_6H_5)_3$	$=Si(C_6H_5)_2$	$\equiv SiC_6H_5$	$-Si(CH_3)_3$	$=Si(CH_3)_2$	$\equiv SiCH_3$
1	$M_2'D'$	L			95		195	
2	M_2'''	L	130					
3	D_4''	C		127				
4	D_3' cis	C			105			260
5	D_3' trans	C			105			255
6	M_2D_2''	L		105		260 215 165		
7	$D_2''D_2$	C		125			275 210	
8	M_2D''	L		115		265 210		
9	M_2D_5'	L			90	265 210 185 155		
10	M_2DD_2'	L			110	270 215 175 155		
11	M_2D_2'	L			95	265 215 165		
12	M_2D_3'	L			85	275 210 160		
13	D_3D'	C			110		275 210	
14	M_2D_4'	L			105	275 215 185 155		
15	M_2D'	L			115	265 215 170 155		
16	D_2D_2'	C			90		250 215	
17	D_3D''	C		125			285 215	
18	M_2''	L		115				255
19	$M_2D''D$	L		110		275 215	250 215	
20	$M_2D_2'D$	L			105	265 225 170		

[a] For the sake of simplicity abbreviations for organopolysiloxanes used in specialized literature are applied in the Table:

M denotes	$(CH_3)_3SiO_{\frac{1}{2}}$
D	$(CH_3)_2SiO$
M′	$(CH_3)_2(C_6H_5)SiO_{\frac{1}{2}}$
M″	$(CH_3)(C_6H_5)_2SiO_{\frac{1}{2}}$
D′	$(CH_3)(C_6H_5)SiO$
D″	$(C_6H_5)_2SiO$
M‴	$(C_6H_5)_3SiO_{\frac{1}{2}}$

[b] Numerical index indicating the number of these formations in a molecule.

[c] C means cyclic and L linear arrangement of the molecule.

difference of 6°, considering the temperature increase of 15°/min, which must be subtracted from the recorded temperature in order to obtain the correct value.

Reaction thermal analysis can be exploited in analytical chemistry in various ways. Firstly, substances can be characterized, because only very similar substances possess the same thermograms. Secondly, a certain type of structural analysis is possible, which is especially convenient, *e.g.*, for organopolysiloxanes, as a supplement to reaction gas chromatography of these substances[12]. The authors are of the opinion that this method could be used in identifying very varied organic substances contained in a certain set. Further research into this field should provide further possibilities of structural analysis.

Other advantages of this method are found in the comparatively simple equipment required and in the fact that the whole analysis can be carried out with a small amount of the substance; only milligram or even smaller amounts are required, depending on the type of splitting reaction and on the sensitivity of the thermal-conductivity detector available. In some cases it should even be possible to operate with μg-amounts. The splitting of a comparatively small sample, which is suitably distributed (glass beads), is not subject to the errors found with larger amounts owing to imperfect heat transfer. Moreover, the gas-chromatographic detectors usually provide a differential record. This is another advantage, because with most thermoanalytical methods, special equipment is necessary to obtain a differential record.

Further differentiation can be achieved by suitable changes of the reaction media which cause the splitting (*e.g.*, at present the splitting of organopolysiloxanes by concentrated sodium hydroxide solutions is being studied).

In summarizing the above results, it can be stated that the reaction thermal analysis method could become another useful extension of the existing range of thermoanalytical techniques.

SUMMARY

A new method of thermal analysis based on the reaction of the test substance with a suitable reagent under programmed temperature conditions is described. The gaseous reaction products are detected by gas chromatography. The splitting of low-molecular-weight organopolysiloxanes by sulphuric acid is used as an example to illustrate the relationship between the structure of the test substance and the temperature at which the splitting of the individual functional groups occurs. The method seems applicable for identifying chemical groups and their location in certain types of molecules.

RÉSUMÉ

On décrit une nouvelle méthode d'analyse thermique basée sur la réaction de la substance à tester avec un réactif approprié dans des conditions de température programmées. Les produits de réaction gazeux sont décelés par chromatographie gazeuse. On a choisi comme exemple des organopolysiloxanes de faible poids moléculaire avec acide sulfurique. Cette méthode semble applicable pour l'identification de groupes chimiques et pour leur localisation dans certains types de molécules.

ZUSAMMENFASSUNG

Es wird eine neue Methode zur thermischen Analyse von organischem Polysiloxan beschrieben, die auf der Reaktion mit geeignetem Reagenz bei programmierten Temperaturbedingungen beruht. Die dabei auftretenden gasförmigen Reaktionsprodukte werden mit einem Gaschromatographen nachgewiesen. Die Aufspaltung niedrigmolekularer Polysiloxane durch Schwefelsäure dient als Beispiel, um die Beziehung zwischen der Struktur der geprüften Substanz und der Temperatur, bei der die Aufspaltung einzelner funktionaler Gruppen erfolgt, zu zeigen. Die Methode scheint geeignet zu sein, chemische Gruppen zu identifizieren und bei gewissen Typen von Molekülen zu lokalisieren.

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THE BROMOMETRIC DETERMINATION OF BULK ENOL CONTENT OF β-DIKETONES THAT UNDERGO RAPID TAUTOMERIZATION

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The determination of the bulk enol content of β-diketones and β-keto esters is of great importance in many physico-chemical investigations. Perhaps the most commonly used technique is that of MEYER[1,2] which has its basis in quantitative bromination of the enol "double bond". The overall validity of the results obtained in this manner is suspect because of the possibility of rapid keto–enol tautomerization during the analysis. Many attempts have been made to limit this possibility, notably the work of GERO[3] and of SCHWARZENBACH[4]. Several investigators have attempted to analyze for bulk enol content by infrared and ultraviolet techniques[5,6] but the results, while confirming previous trends, were generally only semi-quantitative. Perhaps the most promising spectral technique at present is high-resolution proton magnetic resonance[7-9].

Unfortunately, the more assuring chemical techniques[3,4] require buffers which often alter the solvent character from that found in the experiments wherein the enol data are used. Proton magnetic resonance techniques are also limited in that many solvents of experimental interest are protonic themselves and interfere with the measurement of the tautomer resonance. In the absence of time-averaging facilities, the p.m.r. technique is likewise noise-limited.

However, it is possible to obtain, in certain cases, enol content values by p.m.r. which are essentially unperturbed. An attempt was therefore made to evaluate the magnitude of the error arising as a consequence of rapid tautomerization during the bromination step, by making p.m.r. measurements in dioxane–water and alcohol–water mixed solvents where possible. It was initially hoped that the information obtained would aid in the evaluation of the enol content of systems not amenable to spectral measurements.

The compound 2,4-pentanedione was selected as a model for the study. This compound has many advantages in such an investigation. From the viewpoint of proton magnetic resonance measurements, the greatest superiority lies in the fact that at 60 MHz, the keto-methyl and enol-methyl protons give rise to two distinct and well defined resonance lines[7,8]. The findings of IOFFE AND KABACHNIK[10] would also seem to indicate that 2,4-pentanedione enol form is entirely in the "cis" configuration, which thus simplifies the stoichiometry of the bromination reaction.

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EXPERIMENTAL

Reagents

The compound, 2,4-pentanedione, reagent grade, was freshly distilled before each experiment. The solvents, *p*-dioxane and methanol, were spectral grade and were used as received. All other solvents and chemicals were analytical-reagent grade and were used without further purification.

Proton magnetic resonance measurements

All proton magnetic resonance measurements were made at 25.0 ± 1.5° with an upgraded Varian A-60 (60 MHz) spectrometer equipped with a standard Varian V-6040 variable temperature control. The average signal-to-noise ratio, as measured by the quartet of ethyl benzene (1% in carbon tetrachloride), was 13:1. The methyl resonances for the keto and enol forms were recorded in quintuplicate for each sample and the integrated intensities measured. The enol percent was calculated as:

$$k = \frac{\text{Average enol intensity}}{\text{Average keto intensity}}$$

$$\text{Enol \%} = (k/(1+k)) \cdot 100$$

The average relative mean standard deviation was of the order of 1% enol.

All solvents were degassed before use and all solutions were 0.100 *M* in 2,4-pentanedione. Before analysis the samples were thermostatted overnight at the experimental temperature in a constant temperature water bath.

Bromometric measurements

An established[11] indirect bromometric procedure was used for all measurements. The technique involves the addition of excess of bromine to a 0.1 *M* solution of 2,4-pentanedione, quenching the excess of bromine at a fixed time interval with an excess of phenol, reaction of the bromoketone with potassium iodide and titration of the liberated iodine with standard thiosulfate solution. In order to establish the effect of quench time on the observed results, five replicate determinations were made at an average of four different, equispaced quench time intervals. The standard deviation of the mean ranged from 0.4 to 0.6% enol.

All measurements were made at 25.0 ± 0.5° in a constant temperature water bath. The samples were equilibrated for 18–24 h at the experimental temperature before analysis. A blank consisting of the solvent alone was run at each quench time.

Determination of enol % at zero quench time

The enol content at zero quench time was determined by the extrapolation of the data obtained at various quench times to zero seconds. The extrapolation was accomplished by polynomial least-squares regression, by means of the IBM User's Library Program STUFF (Sixteen-Twenty Universal Function Fitter). The data were fitted to a function of the general form:

$$t = \text{time (sec)};\ t_0 = \text{enol \% at } t = 0 \text{ sec}$$

$$\text{Enol \%} = t_0 + a_1t_1 + a_2t_2^2 + a_3t_3^3 \ \ldots .$$

Several polynomial orders were tried for each sample and the results reported are those derived from the fit which gave the smallest residual sum of squares. The indeterminancy in the value of t_0 averaged 1% relative.

RESULTS AND DISCUSSION

The results of the bromometric determinations are contained in Table I. The strong dependence of the observed enol content on the time interval between the addition of bromine and the quenching agent, phenol, is quite evident. The effect (Fig. 1) is quite dramatic in the more polar solvents (*e.g.*, water) where a difference of 15 sec results in a relative increase of over 100%. If the bromination process is assumed to be "instantaneous" over the time period of the experiment then, it was reasoned, it is possible to extrapolate to zero seconds quench time from the data obtained at fixed, or real, quench times. This was done and results are reported in Table I under the heading "t_0". The results of the bromometric determinations at zero seconds quench time and of proton magnetic resonance measurements in similar solvents are contained in Table II.

TABLE I

OBSERVED ENOL % AT VARIOUS QUENCH TIMES FOR 2,4-PENTANEDIONE AT 25° IN VARIOUS SOLVENT MIXTURES

Wt.% org. solvent \ *Time (sec)*	*5*	*10*	*20*	*30*	*40*	t_0
Methanol–water mixtures						
100		74.6	75.6	76.7	77.6	74.1
76	61.9	67.3	77.4	—	—	56.8
56		58.4	73.3	86.4	97.3	42.6
43		50.5	67.5	81.8	94.1	29.9
32		45.2	63.4	79.8	93.4	25.8
21		41.9	61.7	80.0	96.7	21.2
0		44.3	70.2	92.1	109.1	15.3
Ethanol–water mixtures						
100		81.8	83.5	85.2	86.4	80.9
85		84.2	96.1	105.4	114.4	70.5
70		82.5	98.8	112.0	123.5	60.0
56		75.1	93.5	108.6	120.4	50.5
43		64.6	84.5	100.5	113.0	41.7
32		53.7	73.5	91.5	105.0	32.4
21		45.1	67.1	85.7	101.9	20.7
10		42.9	67.5	87.7	105.9	18.0
0		43.9	70.5	93.1	111.0	15.2
Dioxane–water mixtures						
100		80.7	80.9	81.1	81.8	80.7
87		67.6	68.4	69.2	—	66.8
77		60.8	63.1	64.7	66.6	57.0
67		56.3	59.2	62.3	65.4	53.6
58		49.9	54.5	58.3	63.3	42.5
48		44.5	50.4	55.5	—	38.3
39		39.6	46.4	53.5	59.8	34.0
29		38.5	48.3	56.5	64.7	25.5
20		35.8	46.6	57.1	66.3	22.5
10		33.7	46.7	58.5	68.7	19.7

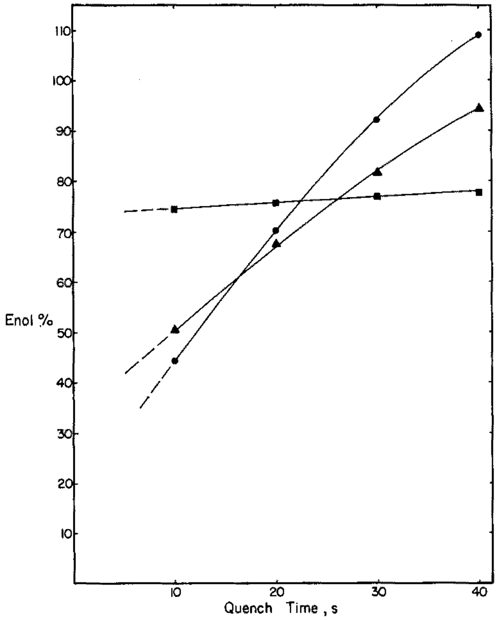

Fig. I. Enol % at various quench times for 2,4-pentanedione at 25° in (●) water, (▲) 43% by weight methanol–water and (■) methanol.

TABLE II

OBSERVED ENOL % BY THE BROMOMETRIC AND N.M.R. TECHNIQUES

Solvent (*% by wt. in* H_2O)	*Bromometric*	*N.M.R.*
Dioxane		
100	80.7	84.1
87	66.8	69.2[a]
78	57.0	61.6[a]
67	53.6	53.5[a]
58	42.5	45.9[a]
48	38.3	37.5[a]
39	34.0	31.1[a]
29	25.5	23.2[a]
20	22.5	20.8
10	19.7	16.1
Methanol		
76	56.8	54.5[a]
32	25.8	26.0[a]
21	21.2	20.3[a]
Ethanol		
85	70.5	68.9
32	32.4	28.9[a]
21	20.7	22.8[a]
10	18.0	19.5[a]
Water		
100	15.3	15.5

[a] These values were interpolated graphically over a very narrow range of solvent compositions which bracketed those of the bromometric determinations.

Although the results of both techniques are in surprisingly good agreement, certain trends should be noted. If the proton magnetic resonance measurements are taken as standard then it can be seen that the bromometric method resulted in values which are consistently low in solvents of low polarity and, conversely, high in solvents of high polarity.

The results in solvents of lower polarity might be explained in two ways. The liberation of iodine by the reaction of the bromoketone and potassium iodide is slower in solvents of low polarity than in solvents of higher polarity. If all of the bromoketone has not reacted at the time that the titration with thiosulfate is performed, a negative error might well be expected. Every effort was made to limit this error and no significant difference in the results was seen after 3 h or longer of standing before the titration with thiosulfate. A second explanation lies in the possibility that the bromination step in solvents of low polarity proceeds at a rate sufficiently slow to negate the assumption of instantaneous brominations. If this is the case then extrapolation to zero quench time would result in a negative error.

An examination of the results in the more polar solvents, where values in excess of 100% enol were observed at the longer quench times, suggests a mechanism which might explain the high values obtained bromometrically relative to the p.m.r. values. A value for bulk enol content in excess of 100% suggests a second enolization process involving the bromoketone. Any contribution to the observed enol percent by such a process would be in the form of a positive error. Extrapolation to zero time might then be expected to be in error and in a positive direction, as was observed.

A complete set of proton magnetic resonance measurements for the solvent systems methanol–water and ethanol–water proved impossible, owing to strong spectral interference arising from the main resonance and spinning side-bands of the solvent protons. The results reported in Table II appear adequate to demonstrate that over a wide range of solvent types and compositions, a good general agreement exists between the results of the two methods if certain precautions are taken. The proton magnetic resonance technique is the simplest if the measurement can be made. If not, then the technique of extrapolation to zero quench time can yield results which are generally valid.

We are grateful to the Atomic Energy Commission for support of this work under Contract No. AT(30-1)906.

SUMMARY

The bulk enol content observed for the model compound, 2,4-pentanedione as determined by bromometric methods depends on the time interval between addition of bromine and quenching with phenol. The largest influence on the results was observed in polar solvents. On the assumption that bromination occurs instantaneously, discrete quench-time results were extrapolated to zero time and compared with proton magnetic resonance measurements. Good general agreement was found between the methods in all cases, although definite relative error trends were observed in the bromometric results. The technique proposed permits the use of the chemical technique in cases where proton magnetic resonance is not applicable.

RÉSUMÉ

Les résultats obtenus lors des déterminations de la teneur en énol de la pentanedione-2,4 par dosage bromométrique dépendent de l'intervalle de temps entre l'addition de brome et la réaction avec le phénol.

La plus grande influence sur les résultats est observée en solvants polaires. On effectue une comparaison avec des mesures par résonance magnétique protonique; des valeurs concordantes sont obtenues. La technique proposée permet d'utiliser la méthode chimique lorsque la résonance magnétique n'est pas applicable.

ZUSAMMENFASSUNG

Der Hauptenolgehalt, der in der Modellverbindung 2,4-Pentandion mit Hilfe bromometrischer Methoden festgestellt wurde, hängt von dem Zeitintervall zwischen der Zugabe des Broms und der Reaktion mit Phenol ab. Der grösste Einfluss auf die Ergebnisse wurde in polaren Lösungsmitteln beobachtet. Unter der Annahme dass die Bromierung unverzüglich erfolgt, können die Ergebnisse der Zeitmessung auf Null extrapoliert und mit den protonenmagnetischen Resonanzmessungen verglichen werden. In allen Fällen wurde zwischen diesen Methoden eine gute Übereinstimmung gefunden. Die vorgeschlage Technik erlaubt die Verwendung der chemischen Methode in den Fällen, in denen die protonenmagnetische Resonanz nicht anwendbar ist.

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GRAVIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM, RHODIUM AND RUTHENIUM WITH THIOSALICYLAMIDE

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Various organic thio compounds have been used for the gravimetric and spectrophotometric determination of the platinum metals. 8-Mercaptoquinoline[1] has been employed for the precipitation of palladium, thionalide[2-4] for palladium, rhodium and ruthenium, and 2-mercaptobenzooxazole[5] and 2-mercaptobenzothiazole[5] for rhodium. Diphenylthiosemicarbazide[6] has been recommended for the colorimetric determination of ruthenium.

Thiosalicylamide was used by SHOME AND MAZUMDAR[7] for the spectrophotometric determination of thallium(III). In the present work this reagent was employed for the gravimetric and spectrophotometric determination of palladium, rhodium and ruthenium. Palladium, rhodium and ruthenium form bright yellow, yellowish brown and brown precipitates respectively with thiosalicylamide, which can be weighed directly after drying at 110°–120°. The palladium complex corresponds to $Pd(C_7H_7ONS)_4Cl_2$ and can be precipitated from highly acidic solutions. Rhodium and ruthenium react with thiosalicylamide in weakly acidic solutions. The rhodium complex can be represented as $Rh(C_7H_6ONS)_3$. The reagent reduces ruthenium(VI) and ruthenium(III) to the bivalent state, and the complex formed with the metal has the formula $Ru(C_7H_6ONS)_2$.

The palladium, rhodium and ruthenium complexes are soluble in ethanol and other common organic solvents and highly soluble in a mixture of isobutyl methyl ketone and ethanol. The rhodium and ruthenium complexes can be extracted with a mixture of isobutyl methyl ketone and alcohol for the spectrophotometric determination of the corresponding metals. Since the reagent solution in isobutyl methyl ketone decomposes slowly in highly acidic medium during extraction, palladium is determined spectrophotometrically in 50% ethanolic solution of the complex.

EXPERIMENTAL

Apparatus

A Carl Zeiss spectrophotometer, Model PMQ II, with 1-cm quartz cells, was used for absorbance measurements. A Cambridge Bench Model pH Meter equipped with glass and calomel electrodes was used for pH measurements.

Standard metal solutions

A standard palladium solution was prepared by dissolving pure palladium chloride in dilute hydrochloric acid, and standardizing by the dimethylglyoxime method. The rhodium solution was made by dissolving rhodium(III) chloride in dilute hydrochloric acid, and standardizing by precipitation of the metal with formic acid. The ruthenium solution was prepared by dissolving ruthenium(III) chloride monohydrate or sodium ruthenate in dilute hydrochloric acid, and standardizing by precipitation of the metal as sulphide and subsequent ignition to the metal in a current of hydrogen.

Diverse ion solutions

Solutions of diverse ions were prepared by dissolving known amounts of pure compounds in distilled water. Dilute hydrochloric acid was used where required.

Reagent solutions

A 1% solution of thiosalicylamide in 20% ethanol was used for the precipitation of palladium, rhodium and ruthenium. For spectrophotometric measurements, a 0.01 *M* reagent solution in ethanol was used.

Properties of metal complexes

The palladium, rhodium and ruthenium complexes with thiosalicylamide decompose at 193°, 162° and 210° respectively. The palladium complex is stable in dilute hydrochloric or sulphuric acid but decomposes in nitric acid. The rhodium and ruthenium complexes are stable in weakly acidic solutions (pH 3–7). All the complexes readily decompose in alkaline solution. The results of analysis of the pure complexes were as follows:

Palladium complex. Found: 13.4% Pd, 7.2% N, 16.3% S, 8.7% Cl; required for $Pd(C_7H_7ONS)_4Cl_2$: 13.5 % Pd, 7.1 % N, 16.2 % S, 9.0 % Cl.

Rhodium complex. Found: 18.4% Rh, 7.4 % N, 17.2 % S; required for $Rh(C_7H_6ONS)_3$: 18.4 % Rh, 7.5 % N, 17.2 % S.

Ruthenium complex. Found: 25.0 % Ru, 6.9 % N, 16.0 % S; required for $Ru(C_7H_6ONS)_2$: 24.9 % Ru, 6.7 % N, 16.0 % S.

GRAVIMETRIC DETERMINATION OF PALLADIUM, RHODIUM AND RUTHENIUM

Procedure

Dilute the metal ion solution to 125–150 ml and adjust its acidity to 2.0–2.5 *M* with dilute hydrochloric acid for the precipitation of palladium and to pH 4.5–5.5 with 1 *M* sodium acetate solution for the determination of rhodium or ruthenium. Warm the palladium or rhodium solution to 70–80° and add 3–4 times the theoretical amount of ethanolic 1% reagent solution for the precipitation of the metal. For ruthenium, heat the solution to boiling and add 8–10 times the theoretical amount of reagent solution with constant stirring for the formation of insoluble precipitate. Digest the precipitates of palladium, rhodium or ruthenium on a hot water-bath for 30 min, 1–2 h or 3–4 h, respectively. Filter the precipitate on a No. 4 sintered crucible. Wash the palladium complex with hot 1 : 10 hydrochloric acid and the rhodium or ruthenium complex with hot water. Dry at 110–120° for 2 h, cool in a desiccator and weigh. Typical results are shown in Table I.

Effect of pH

Palladium reacts with thiosalicylamide in strong acidic solution and the metal

TABLE I

DETERMINATION OF PALLADIUM, RHODIUM AND RUTHENIUM

Metal ion taken (mg)	*Wt. of complex (mg)*	*Metal found (mg)*	*Error (mg)*	*Metal ion taken (mg)*	*Wt. of complex (mg)*	*Metal found (mg)*	*Error (mg)*
Palladium							
5.05	37.50	5.055	+0.005	8.64	47.00	8.63	−0.01
10.10	75.00	10.11	+0.010	12.16	70.40	12.96	0.00
				Ruthenium			
15.15	112.40	15.16	+0.01	6.20	24.80	6.19	−0.01
Rhodium							
4.32	23.50	4.33	+0.006	12.40	49.70	12.39	−0.01

can be precipitated with the reagent from 2–8 *M* hydrochloric acid medium. In weaker acid the precipitate becomes slimy and does not coagulate.

The rhodium complex begins to coagulate above pH 3.8, the optimum pH range for the precipitation of the metal being 4.5–6.5.

Ruthenium(II) forms an insoluble precipitate with thiosalicylamide at pH 3.5 and the precipitation of the metal is complete between pH 3.8 and 6.0.

Effect of diverse ions

Palladium, rhodium or ruthenium was determined with thiosalicylamide in a mixture containing known amounts of Co, Ni, Mn, Zn, Ti, Al, In, Cd, Cr (as their sulphates), Fe(III), Ga, Ir, Au (as their chlorides), uranyl acetate, zirconyl chloride or ammonium molybdate. Palladium was precipitated from 6 *M* hydrochloric acid solution in order to avoid the interference of rhodium and ruthenium. Small amounts of platinum or gold could be tolerated when palladium was precipitated from 8 *N* hydrochloric acid solution. Copper, vanadium, nitric acid and other oxidising agents interfered with the determination of palladium. Cyanide interfered with the precipitation of rhodium and ruthenium. The results are recorded in Table II.

Separation of rhodium or ruthenium from palladium and platinum

Rhodium or ruthenium could be separated from palladium and platinum by means of thiosalicylamide. Palladium or platinum was first precipitated with thiosalicylamide from 3 *N* hydrochloric acid medium and filtered. The filtrate was adjusted to pH 5 and rhodium or ruthenium was subsequently determined with thiosalicylamide as before. The results are shown in Table III.

Rhodium and ruthenium could not be separated from each other with this reagent. However, ruthenium could be separated by the usual distillation method from rhodium and then rhodium and ruthenium could be determined separately as described above.

Separation from osmium

Palladium, rhodium or ruthenium could be separated from osmium by prior reduction of osmium(VI) or osmium(VIII) with sulphur dioxide to osmium(IV) and then palladium, rhodium or ruthenium could be determined by the described procedure. The results are given in Table III.

TABLE II

SEPARATION OF PALLADIUM, RHODIUM AND RUTHENIUM FROM DIVERSE IONS

Palladium		*Rhodium*		*Ruthenium*	
Foreign ion added (mg)	*Pd found (mg)*	*Foreign ion added (mg)*	*Rh found (mg)*	*Foreign ion added (mg)*	*Ru found*[i] *(mg)*
Co^{2+} (150)	5.05[a]	EDTA (20)	4.30[d]	EDTA (20)	6.19
Ni^{2+} (200)	5.05[a]	PO_4^{3-} (50)	4.31[d]	PO_4^{3-} (60)	6.21
Mn^{2+} (200)	5.05[a]	F^- (20)	4.31[d]	F^- (20)	6.20
Zn^{2+} (400)	5.05[a]	Tartrate (100)	4.32[d]	Tartrate (80)	6.21
Cd^{2+} (400)	5.05[a]	Co^{2+} (100)[e]	4.32[d]	Co^{2+} (80)[e]	6.20
Fe^{3+} (10)[b]	5.05[a]	Ni^{2+} (100)[e]	4.32[d]	Ni^{2+} (100)[e]	6.20
Al^{3+} (200)	5.05[a]	Zn^{2+} (100)[e]	4.32[d]	Zn^{2+} (100)[e]	6.19
Ti^{4+} (8)	5.06[a]	Mn^{2+} (100)[e]	4.32[d]	Mn^{2+} (80)[e]	6.20
Zr^{4+} (400)	5.05[a]	W^{6+} (100)[e]	4.31[d]	W^{6+} (80)[e]	6.21
Mo^{6+} (20)	5.05[a]	Mo^{6+} (80)[e]	4.33[d]	Mo^{6+} (80)[e]	6.20
Cr^{3+} (60)	10.10[c]	U^{6+} (30)[e]	4.32[d]	U^{6+} (30)[e]	6.19
In^{3+} (200)	10.10[c]	Al^{3+} (50)[e]	4.32[d]	Al^{3+} (60)[e]	6.21
Ga^{3+} (40)	10.10[c]	Cu^{2+} (15)[f]	4.33[d]	Cu^{2+} (10)[f]	6.20
U^{6+} (180)	10.15[c]	Fe^{3+} (15)[e]	8.63[g]	Fe^{3+} (15)[e]	6.21
Au^{3+} (2)	10.15[c]	Ga^{3+} (50)[e]	8.64[g]	Ga^{3+} (60)[e]	6.22
Pt^{4+} (2)	10.16[c]	In^{3+} (50)[e]	8.64[g]	In^{3+} (80)[e]	6.20
Rh^{3+} (5)	10.13[c]	Tl^{3+} (10)[e]	8.63[g]	Tl^{3+} (10)[e]	6.21
Ru^{3+} (5)	10.14[c]	V^{5+} (30)	8.66[g]	V^{5+} (15)[e]	6.19
Ir^{4+} (10)	10.12[c]	Th^{4+} (40)[e]	8.62[g]	Th^{4+} (45)[e]	6.20
		Ti^{4+} (20)[h]	8.64[g]	Ti^{4+} (30)[h]	6.21
		Ir^{4+} (10)	8.63[g]	Ir^{4+} (10)	6.22

[a] 5.05 mg Pd taken.
[b] In presence of phosphate.
[c] 10.10 mg Pd taken.
[d] 4.32 mg Rh taken.
[e] In presence of tartrate.
[f] In presence of EDTA.
[g] 8.64 mg Rh taken.
[h] In presence of fluoride.
[i] 6.20 mg Ru taken.

TABLE III

SEPARATION OF RHODIUM AND RUTHENIUM FROM PALLADIUM, PLATINUM AND OSMIUM, AND SEPARATION OF PALLADIUM FROM OSMIUM

Metal ion taken (mg)	*Foreign ions added (mg)*	*Metal found (mg)*	*Metal ion taken (mg)*	*Foreign ions added (mg)*	*Metal found (mg)*
4.32 (Rh)	10.10 (Pd)	4.30 (Rh)	5.05 (Pd)	9.50 (Os^{6+})	5.05 (Pd)
4.32 (Rh)	10.00 (Pt^{4+})	4.31 (Rh)	10.10 (Pd)	19.00 (Os^{8+})	10.09 (Pd)
4.32 (Rh)	10.10 (Pd) + 10.00 (Pt^{4+})	4.30 (Rh)	4.32 (Rh)	9.50 (Os^{6+})	4.33 (Rh)
6.20 (Ru)	10.10 (Pd)	6.19 (Ru)	8.64 (Rh)	19.00 (Os^{8+})	8.65 (Rh)
6.20 (Ru)	10.00 (Pt^{4+})	6.18 (Ru)	6.20 (Ru)	9.50 (Os^{6+})	6.22 (Ru)
6.20 (Ru)	10.10 (Pd) + 10.00 (Pt^{4+})	6.18 (Ru)	12.40 (Ru)	19.00 (Os^{8+})	12.41 (Ru)

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM, RHODIUM AND RUTHENIUM

Thiosalicylamide was employed for the spectrophotometric determination of palladium, rhodium and ruthenium. The palladium complex is appreciably soluble in 50% ethanol. The solution is yellow in colour and shows maximum absorbance at

350 nm in 0.1–3.5 *M* hydrochloric acid. The absorbance follows Beer's law at 350 nm over the palladium concentration range 0.5–1.06 μg/ml. The rhodium and ruthenium complexes can be extracted with isobutyl methyl ketone, the resulting solutions being yellow and greenish yellow in colour respectively. The solutions of rhodium and ruthenium complexes show maximum absorbance at 377 nm and 385 nm respectively. The absorbance of the rhodium complex follows Beer's law over the concentration range 1.25–4.5 μg/ml at 380 nm, and that of the ruthenium complex over the concentration range 1.10–5.20 μg/ml at 390 nm.

Procedure for palladium

Introduce a measured amount of palladium solution into a 25-ml volumetric flask and acidify the solution to 1 *M* by adding dilute hydrochloric acid. Cool the solution in ice-cold water, and add a few ml of ethanol followed by 10^{-3} *M* thiosalicylamide solution (2.5–3.0 ml). Mix the solution thoroughly and add a mixture of water and ethanol to make up to volume, adjusting the concentration of ethanol in solution to 50%. Allow the solution to stand for 30 min in order to attain the room temperature. Take the spectral transmittance measurements against an appropriate blank prepared under the same conditions with the same quantity of organic reagent.

Procedure for rhodium or ruthenium

Place a measured amount of the metal solution into 100-ml separating funnel. Adjust the rhodium solution to pH 4.2–5.6 and the ruthenium solution to pH 3.1–4.2 by adding the necessary amounts of 5% sodium acetate and 1 *M* hydrochloric acid. Shake vigorously with a measured amount of an ethanolic 10^{-2} *M* solution of thiosalicylamide, and place over a hot water-bath for about 10 min. Cool to room temperature and shake the precipitate 2–3 times with 5-ml portions of isobutyl methyl ketone followed by the addition of 10 ml of ethanol and 1 g of solid potassium chloride. Dilute the combined extract to 25 ml with isobutyl methyl ketone and measure the

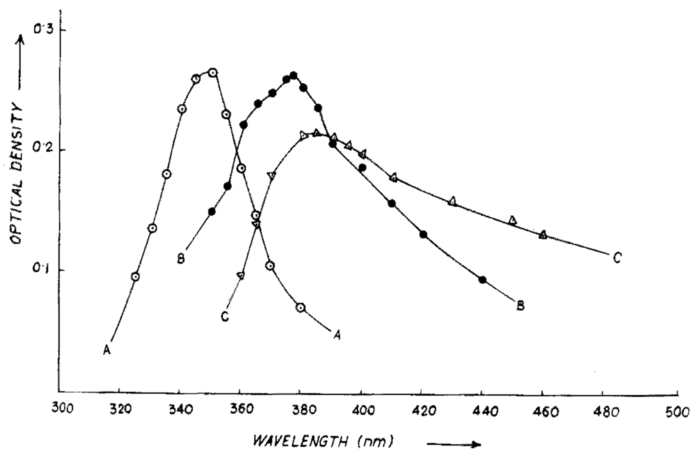

Fig. 1. Absorbance curves for palladium–, rhodium– and ruthenium–thiosalicylamide complexes. (⊙) Pd–TSA complex (0.798 μg Rh/ml), (●) Rh–TSA complex (3.90 μg Rh/ml), (△) Ru–TSA complex (3.25 μg/ml).

absorbance against an appropriate blank prepared under the same conditions with the same quantity of organic reagent.

Absorbance curves

The absorbance curves of solutions of the three metal complexes determined by the above procedure are shown in Fig. 1.

Effect of pH

The colour of the palladium complex is developed fully between pH 1.2 and 3.5 *M* with respect to hydrochloric acid. The acidity of the rhodium and ruthenium solutions was adjusted by adding varying amounts of 5% sodium acetate and dilute hydrochloric acid and the pH values of the aqueous layers were measured after extraction of the metal complexes. The results indicate that the rhodium and ruthenium ions are completely extracted in the pH ranges 4.2–5.6 and 3.1–4.2, respectively.

Effect of diverse ions

In the presence of known amounts of a large number of diverse ions, palladium, rhodium and ruthenium were separately determined following the procedures described above. The tolerance limits for various diverse ions (Table IV) represent the concentrations of foreign ions in presence of which the transmittance of the corresponding complex solution obtained was within ± 2% of the expected value.

TABLE IV

EFFECT OF DIVERSE IONS IN THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM, RHODIUM AND RUTHENIUM

Palladium (33.3 μg)		*Rhodium (203.8 μg)*		*Ruthenium (188.5 μg)*	
Diverse ion	*Amount tolerated (μg)*	*Diverse ion*	*Amount tolerated (μg)*	*Diverse ion*	*Amount tolerated (μg)*
Mn^{2+}	2500	Mn^{2+}	1000[b]	Mn^{2+}	1000[b]
Ni^{2+}	3000	Ni^{2+}	1000[b]	Ni^{2+}	2000[b]
Co^{2+}	1000	Co^{2+}	1000[b]	Co^{2+}	2000[b]
Cd^{2+}	2500	Cd^{2+}	1000[b]	Cd^{2+}	1500[b]
Zn^{2+}	1000	Zn^{2+}	2000[b]	Zn^{2+}	2000[b]
Fe^{3+}	1100[a]	Fe^{3+}	180[b]	Fe^{3+}	500[b]
Cr^{3+}	1000	Cr^{3+}	500[b]	Cr^{3+}	1000[b]
Al^{3+}	1200	Al^{3+}	500[b]	Al^{3+}	1000[b]
Rh^{3+}	1000	Mo^{6+}	2000[b]	Mo^{6+}	1000[b]
Ru^{3+}	500	W^{6+}	600[b]	W^{6+}	600[b]
Ga^{3+}	1000	Ti^{4+}	500[c]	Ti^{4+}	600[c]
Ti^{4+}	750	UO_2^{2+}	600	UO_2^{2+}	800
In^{3+}	1000	Ga^{3+}	400[b]	Ga^{3+}	1000[b]
Th^{4+}	1000	Cu^{2+}	100[d]	Cu^{2+}	200[d]
UO_2^{2+}	1000	Pd^{2+}	100	Pd^{2+}	100
Au^{3+}	0.6	Au^{3+}	70	Au^{3+}	75
Pt^{4+}	Interferes	Pt^{4+}	10	Pt^{4+}	10
		Th^{4+}	500[b]	Th^{4+}	1000[b]
		Ru^{3+}	Interferes	Rh^{3+}	Interferes
		Os^{6+}	Interferes	Os^{6+}	Interferes

[a] In presence of phosphate ions. [b] In presence of tartrate ions. [c] In presence of fluoride ions. [d] In presence of EDTA.

Nature of complex in solution and effect of reagent concentration

The empirical formula of the palladium–thiosalicylamide complex was determined by the mole ratio method[8]. The results clearly indicate that thiosalicylamide forms 1:4 and 1:3 complexes with palladium and rhodium respectively. These ratios were verified by the conventional slope ratio method.

Since the complex formation of the ruthenium takes place through prior reduction of ruthenium(VI) or (III) to ruthenium(II) by the reagent itself, neither slope ratio or mole ratio method is applicable in this case. If one starts with ruthenium(VI) and ruthenium(III), the reagent concentrations must be twelve times and six times, respectively, greater than the metal ion concentration for complete extraction.

Molar absorptivity, sensitivity, precision and accuracy

The molar absorptivities of the complexes and the sensitivity, coefficient of variation and relative mean error for the determinations are summarized in Table V.

TABLE V

MOLAR ABSORPTIVITY, SENSITIVITY, PRECISION AND ACCURACY

Complex	*Molar absorptivity*	*Sensitivity ($\mu g/cm^2$)*	*Coefficient of variation (%)*	*Relative mean error (%)*
Pd–TSA	$39.28 \cdot 10^3$	0.0027	0.547	0.26
Rh–TSA	$70.14 \cdot 10^2$	0.01480	0.720	0.28
Ru–TSA	$63.30 \cdot 10^2$	0.01603	0.770	0.23

DISCUSSION

A large number of organic thio compounds have been introduced for the determination of palladium, rhodium and ruthenium, but only a few of these are suitable for the precipitation of rhodium and ruthenium for direct weighing[9]. Thionalide has been employed for the precipitation of palladium, rhodium and ruthenium; the main disadvantages of thionalide are its low solubility in water and in dilute mineral acids, and its tendency to form polymers when heated with oxidants. Moreover, the thionalide–metal complexes are very slightly soluble in organic solvents, so that direct spectrophotometric determination of the metals is not possible. 2-Mercaptobenzothiazole and 2-mercaptobenzooxazole have been applied for the gravimetric determination of palladium and rhodium, but these metals cannot be separated by means of these reagents. The extract of the diphenylthiosemicarbazide complex of ruthenium is unstable towards light.

Thiosalicylamide is highly soluble in hot water, ethanol and other organic solvents, and is stable towards non-oxidising acids and dilute alkalies. It forms metal complexes of definite composition, which can be weighed directly. The complexes formed with palladium, rhodium and ruthenium are soluble in common organic solvents and hence can be employed in the spectrophotometric determination of these metals. Furthermore, the solutions of the complexes are fairly stable. The sensitivity of the palladium complex is very high. The main drawback of this new reagents is its susceptibility to oxidation with strong oxidising agents.

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SUMMARY

Thiosalicylamide is proposed for the gravimetric and spectrophotometric determination of palladium, rhodium and ruthenium. The precipitates formed with palladium, rhodium and ruthenium can be dried at 110°–120° for direct weighing and correspond to $Pd(C_7H_7ONS)_4Cl_2$, $Rh(C_7H_6ONS)_3$ and $Ru(C_7H_6ONS)_2$ respectively. Palladium can be separated from rhodium or ruthenium in highly acidic solution; under suitable conditions, Co, Ni, Mn, Fe, Zn, Mo(VI), W(VI), Al, Ga, In, V(V), Ir, etc., do not interfere. The metal–thiosalicylamide complexes form coloured solutions in common organic solvents, so that spectrophotometric determinations are possible. The Pd complex is dissolved in 50% ethanol whereas the rhodium or ruthenium complex is extracted with a mixture of isobutyl methyl ketone and ethanol. Maximum absorbance is obtained at 350, 380 and 390 nm, and the molar absorptivities are 39,300, 7000 and 6330 for the Pd, Rh and Ru complexes, respectively. Few ions interfere.

RÉSUMÉ

La thiosalicylamide (TSA) est proposée pour le dosage gravimétrique et spectrophotométrique du palladium, du rhodium et du ruthénium. Les précipités formés sont séchés à 110°–120° et pesés directement, correspondant respectivement à $Pd(C_7H_7ONS)_4Cl_2$, $Rh(C_7H_6ONS)_3$ et $Ru(C_7H_6ONS)_2$. Le palladium peut être séparé d'avec le rhodium ou le ruthénium en milieu fortement acide. Le dosage de ces 3 métaux est également possible en présence de nombreux autres éléments, soit en contrôlant le pH, soit en utilisant des réactifs masquants. On décrit également les conditions de dosage spectrophotométrique du palladium, du rhodium et du ruthénium, ces derniers donnant des complexes colorés avec la thiosalicylamide dans des solvants organiques.

ZUSAMMENFASSUNG

Thiosalizylamide (TSA) wird für die gravimetrische und spektralphotometrische Bestimmung von Palladium, Rhodium und Ruthenium vorgeschlagen. Die mit diesen Elementen gebildeten Niederschläge können nach Trocknung bei 110–120° direkt gewogen werden und haben folgende Zusammensetzung: $Pd(C_7H_7ONS)_4Cl_2$, $Rh(C_7H_6ONS)_3$, $Ru(C_7H_6ONS)_2$. Palladium kann in stark saurer Lösung von Rhodium oder Ruthenium abgetrennt werden. Unter geeigneten Bedingungen können die drei Metalle auch in Gegenwart folgender anderer Elemente gefällt werden: Co, Ni, Mn, Fe, Zn, Mo(VI), W(VI), W(VI), Al, Ga, In, V(V), Ir. Die Metall–TSA-Komplexe bilden gefärbte Lösungen mit organischen Lösungsmitteln, so dass spektralphotometrische Bestimmungen möglich sind. Der Pd-Komplex wird dazu in 50%igem Äthanol gelöst. Der Rhodium- oder Rhutenium-Komplex wird mit einer Mischung von Isobutylmethylketon und Äthanol extrahiert. Maxima werden bei 350, 380 und 390 nm erhalten mit Extinktionen von 39300, 7000 bzw. 6330 für die Komplexe der

Elemente Pd, Rh bzw. Ru. Nur wenige Ionen stören. Das Beersche Gesetz wird befolgt.

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N-BENZOYL-N-PHENYLHYDROXYLAMINE AS A COLORIMETRIC REAGENT FOR CERIUM

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Benzohydroxamic acids and substituted hydroxamic acids, particularly N-benzoyl-N-phenylhydroxylamine (BPHA) have received a great deal of attention as precipitation and colorimetric reagents for metals[1-7]. Among the rare earths, cerium(IV) is reported to form a gelatinous precipitate at pH 5, while cerium(III) is precipitated at pH 6.5–7.5. Extraction of cerium(IV) as the BPHA complex into chloroform from 3 N sulphuric acid has been reported by CZE-YUNG-SCHANG[5]. One of the present authors[8] found that a coloured species was extracted under these conditions, but the extract did not contain any cerium. In the course of a detailed investigation of the reactions of hydroxamic acids, cerium was found to give a stable coloured complex with BPHA which could be extracted quantitatively in the pH range 8–10. On the basis of these studies, a method has been developed for the determination of cerium in diverse samples of general interest.

EXPERIMENTAL

Reagents and equipment

N-Benzoyl-N-phenylhydroxylamine (BPHA). The reagent was prepared as described by SHOME[1] and was used as a 0.2% solution in ethanol.

Cerium standard solution. A stock solution was prepared by dissolving cerium(IV) ammonium sulphate (E. Merck, extra pure) in 5% (v/v) sulphuric acid. The solution was standardized gravimetrically by the precipitation of cerium as hydroxide and ignition to cerium(IV) oxide at 800–850°. This solution was used to prepare a working solution containing 0.1 mg CeO_2 per ml.

All other reagents used were of BDH AnalaR or E. Merck G.R. purity.

Absorption measurements were made with matched 1.00-cm corex cells on a Beckman DU spectrophotometer, with a tungsten lamp as the light source.

pH measurements were made with a Marconi pH meter, type TF 511 D.

General procedure

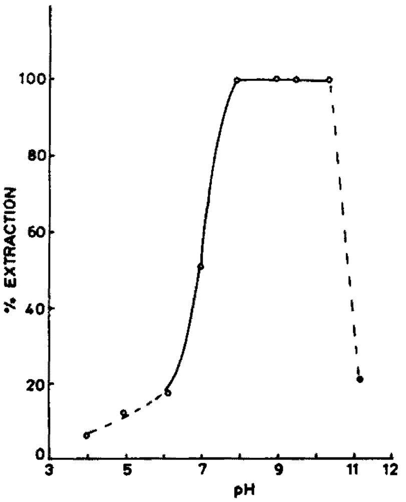
Dilute a suitable aliquot of the working solution of cerium(IV) (containing 0.50 mg of CeO_2) to 20 ml, add 5 ml each of the 0.2% reagent solution and 10%(w/v) ammonium nitrate solution and adjust the pH to the required value. Stir occasionally for 30 min and then transfer the solution to a 100-ml separating funnel, rinsing the beaker twice with 5 ml of chloroform. Shake the mixture vigorously for 3 min and collect the organic phase in a 25-ml volumetric flask. Wash the aqueous phase twice with 3 ml of the solvent, collect the washings in the same flask and then dilute to the mark with the solvent. Measure the absorbance at 460 nm against the corresponding reagent blank.

Effect of variables

The influence of the following parameters were studied to fix the optimum conditions for the spectrophotometric determination of cerium with BPHA.

Effect of pH. The extraction of cerium–BPHA complex into chloroform was studied in the pH range 4–11. The pH–extraction curve is given in Fig. 1 and the spectra of the cerium–BPHA complex in chloroform are given in Fig. 2. Above pH 10, unextractable precipitate was observed in the aqueous phase.

Effect of ethanol. BPHA is insoluble in water, hence the reagent was added as an alcoholic solution. In the final analytical procedure, the reagent was added at two stages. Hence the effect of alcohol was studied at two reagent concentrations following the general procedure. The results are shown in Table I.



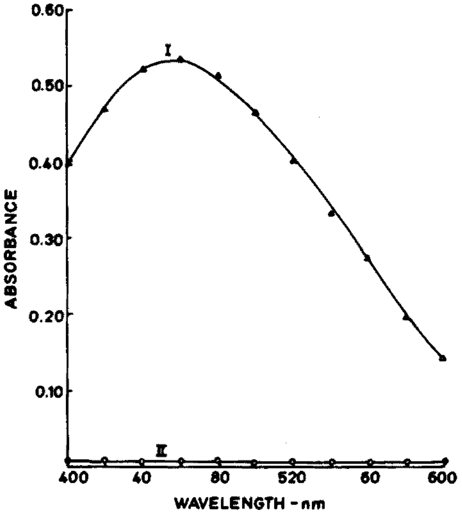


Fig. 1. Cerium–BPHA complex: % extraction *vs.* pH. CeO_2=0.50 mg; BPHA = 10 mg.

Fig. 2. Absorbance spectra: (I) Cerium–BPHA complex *vs.* $CHCl_3$ (20 p.p.m. CeO_2); (II) BPHA *vs.* $CHCl_3$.

TABLE I

EFFECT OF ETHANOL

(CeO_2 = 0.30 mg; pH = 9.5; volumes of aqueous and organic phases were *ca.* 50 ml and 25 ml, respectively)

Vol. of ethanol (ml)	*Reagent concentration (mg)*	*O.D. at 460 nm*
5	10	0.315
10	10	0.316
15	10	0.214
20	10	0.092
15	25	0.320
20	25	0.270

Effect of reagent concentration. To an aliquot of cerium(IV) solution, different volumes of an equimolar concentration of reagent solution were added, the pH of the solution was adjusted to *ca.* 9 and the general procedure was followed, the absorbance being measured at 460 nm. At least 9 times the molar concentration of metal ion was necessary for maximum complex formation. Any further addition of the reagent had no effect on the complex formation.

Effect of time on the extraction and stability of the complex. Extraction of the cerium–BPHA complex into chloroform was found to be complete within 3 min. The absorbance of the solution was found to be constant over a period of at least 20 days.

Choice of solvent. The cerium–BPHA complex was extracted into several organic solvents. The spectra of the complex extracted into various solvents were found to be similar in all non-polar solvents. The absorbances measured at 460 nm (λ_{max}) are given in Table II. No extraction was achieved with cyclohexane, hexane and heptane.

TABLE II

ABSORBANCE OF THE COMPLEX IN VARIOUS SOLVENTS

(CeO_2 = 0.50 mg; BPHA = 10 mg; pH = 9.3; volumes of aqueous and organic phases were *ca.* 50 ml and 25 ml, respectively)

Solvent	*O.D. at 460 nm*	*Solvent*	*O.D. at 460 nm*
Dichloromethane	0.560	Benzene	0.540
Chloroform	0.536	Toluene	0.350
Carbon tetrachloride	0.530	*o*-Xylene	0.470
Trichloroethylene	0.510		

Beer's law

The cerium–BPHA complex was found to obey Beer's law in the concentration range 4–40 p.p.m. of CeO_2 in chloroform. The mean optical density was found to be 0.106 ± 0.002/4 p.p.m. of CeO_2.

Effect of foreign ions

Among the anions, halides, nitrate, sulphate and acetate did not interfere, even when present in 1000-fold amounts; tartrate, oxalate, citrate, fluoride, phosphate and carbonate interfered.

The behaviour of polyvalent cations indicated that alkaline earths, Mg^{2+}, Zn^{2+}, Cd^{2+} Hg^{2+}, Pb^{2+}, rare earths and Th^{4+} when present at 20 times the cerium concentration, did not interfere with the colorimetric determination, while Zr^{4+}, Co^{2+}, Fe^{3+}, Ti^{4+} and UO_2^{2+} showed positive interference and Al^{3+}, Cu^{2+}, Ni^{2+}, Mn^{2+} and Be^{2+} prevented quantitative extraction.

The behaviour of common ions indicated that for the present method to be useful in the analysis of samples, prior separation of rare earths would be essential. Fluoride or oxalate precipitation was effective for this purpose. However, even traces of a common impurity like iron could give positive errors in the analysis, as the sensitivity for iron by Sandell's convention is 0.0026 μg Fe/cm^2. The extraction behaviour of BPHA complexes of elements[5] shows that many of the common elements can be extracted away from cerium with BPHA, in the pH region of 3–5, indicating the possibility of adopting a "two-stage extraction procedure" for the determination of cerium in samples.

Recoveries of cerium added to lanthanum oxide and analysis of lanthanum oxide samples

Weigh accurately 0.1 g of the sample into a beaker and dissolve in 25 ml of 1 *N* hydrochloric acid or sulphuric acid; warm if necessary. Add 5 ml of 25% ammonium chloride and 2 ml of 0.5% BPHA solution. Dilute to *ca.* 45 ml and adjust the pH to 4.5 ± 0.5 with pH paper. Transfer the solution to a 100-ml separating funnel and extract twice with 10 ml of chloroform. Discard the organic phase. Add 0.6 g of the reagent dissolved in 5 ml of ethanol and determine the cerium in the aqueous phase following the general procedure, after adjustment of the pH to *ca.* 9.

The recovery of different amounts of cerium added to pure lanthanum oxide and the analysis of a few typical samples are given in Table III.

TABLE III

RECOVERY OF CERIUM ADDED TO LANTHANUM OXIDE AND THE ANALYSIS OF SAMPLES

CeO_2 *added (mg)*	*O.D. at 460 nm*	*O.D. at 460 nm corrected for blank*	CeO_2 *found (mg)*	*Difference (mg)*
—	0.015	—	—	—
0.10	0.140	0.125	0.12	+0.02
0.40	0.423	0.408	0.39	−0.01
0.60	0.670	0.655	0.61	+0.01
0.49[a]	0.557	0.542	0.51	
	0.535	0.520	0.49	
	0.570	0.555	0.52	
	0.580	0.565	0.53	
	0.600	0.585	0.55	
			Mean 0.52	+0.03
0.46[a]	0.470	0.455	−0.43	−0.03
0.24[a]	0.275	0.260	0.24	0.00
0.26[a]	0.290	0.275	0.25	−0.01

[a] Analysed samples; cerium was determined by the persulphate method.

TABLE IV

ANALYSIS OF DIFFERENT SAMPLES

Sample	*Cerium content*	
	Other methods	*Present method*
Cerium glass 1	3.1 %[a]	3.0 %
Cerium glass 2	3.1 %[a]	3.1 %
G-1	214 p.p.m.[b]	190 p.p.m.
Carbonatite SWM	—	710 p.p.m.
Carbonatite C-1	—	695 p.p.m.
Carbonatite Aj-Sov	—	660 p.p.m.
Carbonatite CM	—	530 p.p.m.
Carbonatite ARB	—	2080 p.p.m.
Carbonatite BRC	—	730 p.p.m.

[a] W. R. Schoeller and A. R. Powell[19], volumetric, after fluoride separation.
[b] P. Murugaiyan *et al.*[20], isotopic dilution.

The general applicability of the present method was evaluated by analysing a variety of samples. The initial chemical separation of rare earths was carried out by the fluoride method[9]. The rare-earth fluoride precipitate was filtered, ignited to oxide and then converted to sulphate in order to avoid interference of fluoride. The cerium content was determined by the two-stage extraction procedure. The results obtained on these samples are given in Table IV.

RESULTS AND DISCUSSION

BPHA can be used as extractive spectrophotometric reagent for cerium. Excess of ethanol tends to reduce the percentage extraction but this effect can be compensated by increasing the reagent concentration. Common anions do not interfere. Beer's law is obeyed in the range 4–40 p.p.m. of CeO_2 in the organic phase. The colour is stable for at least 20 days. Another advantage of the method is that the colour development procedure itself takes care of the oxidation of cerium(III) to cerium(IV) by atmospheric oxidation during the 30-min period of occasional stirring.

TABLE V

COMPARISON OF SENSITIVITIES

Methods	*Sensitivity*[a]	*Ref.*
Persulphate	0.025	10
Carbonate	0.056	11–13
Tiron	0.031	14
Cerimolybdic heteropoly acid	0.045	15
TTA	0.015	16–18
Present method	0.030	—

[a] $\mu g/cm^2$ for $A = 0.001$.

The sensitivity of the present method is compared with those of some other methods reported in the literature in Table V. The present method, though less sensitive than the persulphate and TTA methods, is simple. The Table does not include the indirect methods because they require the quantitative oxidation of cerium(III) and the destruction of excess oxidant without concurrent reduction of cerium(IV).

A number of common elements interfere in the spectrophotometric determination of cerium with BPHA. However, group separation of rare earths as fluoride, with the addition of lanthanum as the carrier, if need be, followed by the selective extraction of trace impurity elements with BPHA at lower pH, eliminates the interference from most of these elements. The applicability of the present method to samples like lanthanum oxide was demonstrated. The residual absorbance of the sample blank (0.015 at 460 nm) is the main factor that prevented the application of the method to the determination of cerium at limits lower than 100 p.p.m. The method was applied successfully for the determination of cerium at 100-μg levels in mineral samples of interest to analytical chemists and geochemists.

SUMMARY

N-Benzoyl-N-phenylhydroxylamine is recommended as a spectrophotometric reagent for cerium. It extracts cerium in the pH range 8–10. Beer's law is obeyed in the concentration range of 4–40 p.p.m. of CeO_2. Cerium(III) is oxidised automatically to cerium(IV) during the colour development stage. The method has been applied to samples such as lanthanum oxide, cerium glass, G-1 and carbonatites.

RÉSUMÉ

Les auteurs proposent la N-benzoyl-N-phénylhydroxylamine comme réactif spectrophotométrique du cérium. On effectue l'extraction du cérium entre les pH 8 et 10. La loi de Beer s'applique pour des concentrations comprises entre 4 et 40 p.p.m. de CeO_2. Le cérium(III) est oxydé automatiquement en cérium(IV) au cours du développement de la coloration. Cette méthode a été appliquée à des échantillons tels que: oxyde de lanthane, verre de cérium, G-1 et carbonatites.

ZUSAMMENFASSUNG

N-Benzoyl-N-phenylhydroxylamin wird als spektralphotometrisches Reagenz für Cer empfohlen. Es extrahiert Cer beim pH 8–10. Das Beersche Gesetz wird im Konzentrationsbereich von 4–40 p.p.m. CeO_2 befolgt. Während der Farbentwicklung wird Cer(III) automatisch zum Cer(IV) oxydiert. Diese Methode wurde bei Proben wie Lanthanoxide, Cerglas, G-1 und Carbonatit angewandt.

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DIE PHOTOMETRISCHE BESTIMMUNG VON WISMUTSPUREN UNTER VERWENDUNG VON 7-[α-(*o*-CARBOMETHOXYANILINO)BENZYL]-8 HYDROXYCHINOLIN

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(Eingegangen den 10. Juni, 1969)

In einer vorangegangenen Mitteilung[1] wurde berichtet über die photometrische Bestimmung von Blei mit 7-[α-(*o*-Carbomethoxyanilino)benzyl]-8-hydroxychinolin (CMAB-Oxin). Nach der bis dahin bekannten Eigenschaft des CMAB-Oxins[2], mit Kationen der Ladung $\geqq 3+$ im Verteilungssystem Wasser/Chloroform keine extrahierbaren Komplexe zu bilden, war die starke Störung der getesteten Bleibestimmung durch Mitbestimmung des Wismut(III)-Ions völlig überraschend. Wir haben daraufhin die Möglichkeit der Extraktion von Wismut sowie die eventuelle Extraktion einiger weiterer dreiwertiger Kationen vor allem unter den "Blei[1]-Magnesium[3]-Extraktionsbedingungen" untersucht und dabei gefunden, dass sich CMAB-Oxin gut für eine hochselektive extraktionsphotometrische Bestimmung von Wismut eignet.

EXPERIMENTELLER TEIL

Geräte

Spektralphotometer VSU 1 des VEB Carl Zeiss, Jena. pH-Meter OP 201/1 der Fa. Radelkis, Budapest mit Einstab-Glaselektrode.

Reagenzien

Salzlösungen. Gearbeitet wurde mit sauren Lösungen von $Al_2(SO_4)_3$, $BiONO_3$, $KCr(SO_4)_2$, $Fe_2(SO_4)_3$, $GaCl_3$, $In_2(SO_4)_3$, $La(NO_3)_3$ und $TlNO_3$.

CMAB-Oxin-Lösung. Entsprechende Mengen CMAB-Oxin, hergestellt nach[1], lösten wir in Chloroform p.a., das durch fünfmaliges Schütteln mit dem gleichen Volumen Wasser und anschliessende Destillation von Alkohol befreit war, um eine etwa lösungsvermittelnde Wirkung des Alkohols auszuschliessen. Glykokollpuffer pH = 12.60. Boratpuffer pH = 8.00. KCN-Lösung 1.25 *M*. Natriumcitratlösung 1.25 *M*. Natronlauge 6 *N*. Salzsäure 6 *N*.

Extraktionsversuche

25 ml wässrige Phase, enthaltend jeweils 10 µmol des Ions (Tl^+ nur 3 µmol, Bi^{3+} nur 1.25 µmol), 0.1 *M* an Kaliumcyanid und 0.1 *M* an Natriumcitrat, schüttelten wir nach Einstellen des gewünschten pH-Wertes (unter Verwendung von Pufferlösung, Natronlauge oder Salzsäure) mit 25 ml chloroformischer Reagenzlösung mindestens

15 min. Der Reagenzüberschuss betrug mindestens das Zehnfache. Nach der Phasentrennung wurde der pH-Wert der wässrigen Phase erneut bestimmt (diese Werte sind im folgenden angegeben) und die Extinktion der organischen Phase bei einer Schichtdicke von 3 cm im Wellenlängenbereich von 390 bis 410 nm gegen Reagenzlösung gemessen. Bei den Versuchen mit Eisen(III) und bei pH-Werten <8 wurde kein Cyanid zugesetzt.

Die Versuche haben wir im pH-Bereich von 5 bis 13 durchgeführt.

Die bisherigen Untersuchungen ergaben, dass von den eingesetzten dreiwertigen Kationen (und Tl^{+}) Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+} und La^{3+} unter den angegebenen Bedingungen nicht mit CMAB-Oxin/Chloroform extrahiert werden können. Dagegen verursachen Bi^{3+}, In^{3+} und Tl^{+} hohe Extinktionen in der organischen Phase, sie werden demnach als CMAB-Oxinate extrahiert. Für Wismut und Indium ist die Abhängigkeit der Extinktion der organischen Phase vom pH-Wert der wässrigen Phase in Abb. 1 wiedergegeben. Der gefundene sehr niedrige Wert für den praktischen Extinktionskoeffizienten des Indium-CMAB-Oxinats ($\varepsilon \approx 650$) lässt bei der in dieser Untersuchung angewandten Arbeitsmethodik die Frage offen, in welchem Ausmass Indium extrahiert wurde. Für Wismut ist aus der Abb. 1 (Kurve I) zu ersehen, dass für seine Extraktion ein enges pH-Bereich von 12.2 ± 0.4 eingehalten werden muss. Ab pH >12.6 steigt die Extinktion, wie das beim Magnesium ähnlich gefunden wurde[3], wieder an. Die Ursache dieses Anstiegs liegt wahrscheinlich in der Oxydation des CMAB-Oxins.

Im Falle des Thallium nahm die Extinktion der organischen Phase so schnell

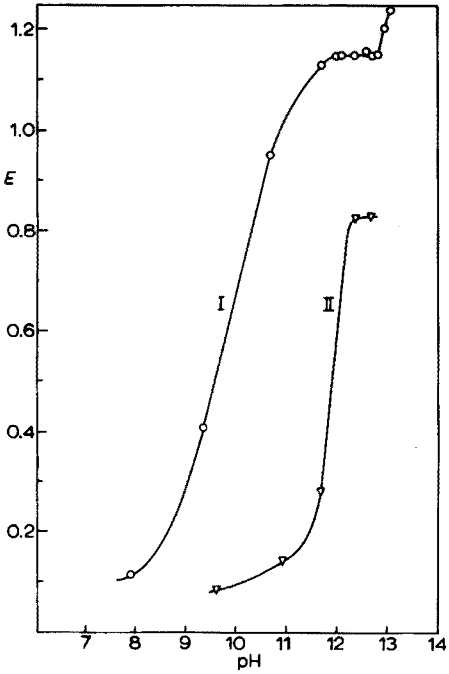

Abb. 1. Abhängigkeit der Extinktion der organischen Phase vom pH-Wert der wässrigen Ph
$\lambda = 400$ nm. (I) Bi-CMAB-Oxinat; Bi:Reagenz = 1:30. (II) In-CMAB-Oxinat; In:Reagenz = 1:10.

ab, dass eine einwandfreie Messung nicht möglich war. Der Maximalwert lag bei pH$\approx$12.6, der Wellenlänge von 400 nm und ergab einen praktischen Extinktionskoeffizienten von $\varepsilon \approx 2200$.

Absorptionsspektren

Die Absorptionsspektren der CMAB-Oxinate des Wismuts und des Indiums für das sichtbare Bereich, gemessen gegen Reagenzlösung, zeigt die Abb. 2. In beiden Fällen liegen die Maxima bei 395 nm.

Als Messlicht für die weiteren Versuche mit Wismut wurde wegen der beim Absorptionsmaximum des Komplexes noch hohen Eigenextinktion der Reagenzlösung Licht der Wellenlänge $\lambda = 400$ nm festgelegt.

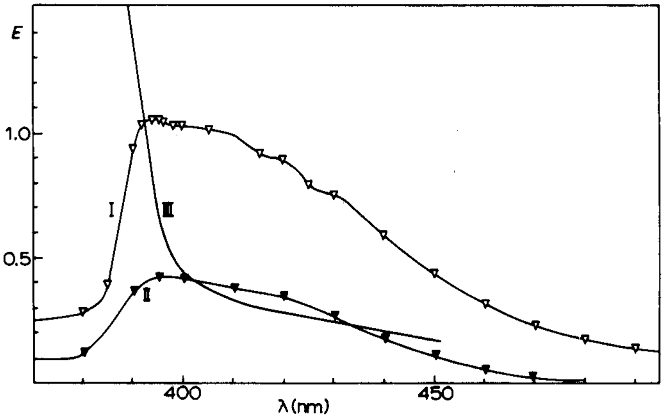

Abb. 2. Absorptionsspektren der CMAB-Oxinate des Wismuts (I:0.05 m*M*, CN^- und Citrat je 0.1 *M*, Bi:R = 1:30, pH = 12.4) und des Indiums (II:0.24 m*M*, sonst wie I), gemessen gegen Reagenzlösung, *d* = 3 cm. (III) Absorption der Reagenzlösung (1.5 m*M*) gegen Chloroform.

Abhängigkeit der Extinktion des Wismut-CMAB-Oxinats von den Arbeitsbedingungen

Ein mindestens zehnfacher Reagenzüberschuss ist zur Erreichung der maximalen Extinktion erforderlich und ein weiterer Überschuss (gemessen wurde bis zum hundertfachen) wirkt sich nicht aus. In Anwesentheit von Cyanid (0.1 *M*) und Citrat (0.1 *M*) reicht eine Schütteldauer von 3 min aus. Bei Erhöhung der Konzentrationen der Hilfskomplexbildner und Tarnreagenzien muss die Schüttelzeit verlängert werden. Hohe Tartratkonzentrationen ($\approx$1 *M*) verhindern die Wismutextraktion vollständig. Auch bei den Wismut-CMAB-Oxinat-Lösungen nimmt die Extinktion mit der Zeit langsam, im Sonnenlicht schneller, ab.

Die Testung der Wismutbestimmung

Die Testung erfolgte im Arbeitsbereich von 0.2 bis 2 μmol Wismut in der gleichen Weise wie die der extraktionsphotometrischen Bestimmung von Blei mit CMAB-Oxin[1].

Reagenzien. Wismutstandardlösung (0.2 m*M*). Als Standardsubstanz diente $BiONO_3$ p.a. (VEB Berlin-Chemie), dessen Formelmasse komplexometrisch (gegen Xylenolorange)[4] zu 292.78$\pm$0.08 ermittelt wurde. In einem 1 l-Messkolben lösten wir unter Erwärmen 1 mmol der Substanz in 300 ml 5 M HNO_3 und füllten dann unter Temperieren (20°) mit Aqua bidest. bis zur Marke auf. Diese Lösung wurde mit Aqua bidest. auf das Fünffache verdünnt. CMAB-Oxin-Lösung (1.2 mM). 115.3 mg (0.3 mmol) CMAB-Oxin wurden in 250 ml Chloroform p.a. gelöst. Die Lösung wird im Dunkeln aufbewahrt und täglich frisch angesetzt.

Arbeitsbedingungen

In einem Schütteltrichter gibt man zu a ml ($a=1$, 2, 4, 6, 8, 10) Wismutstandardlösung, 2 ml 1.25 M Natriumcitratlösung, b Tropfen ($b=1$ bis 8) 12 M Natronlauge, 2 ml 1.25 M Kaliumcyanidlösung, 5 ml Glykokollpuffer pH 12.6 und ergänzt mit Aqua bidest. auf 25 ml. Der pH muss bei 12.2 ± 0.4 liegen. Nach gutem Vermischen setzt man 25.0 ml Reagenzlösung zu und schüttelt 5 min. Nach der Phasentrennung wird die organische Phase durch ein trockenes Filter filtriert und in einer 2 cm-Küvette die Extinktion bei 400 nm gegen Reagenzlösung gemessen.

Ergebnisse

Das Lambert–Beersche Gesetz ist im getesteten Arbeitsbereich 0.2–2.0 µmol Wismut erfüllt. Als praktischer Extinktionskoeffizient wurde der Wert $\varepsilon_{400} = 7.2 \cdot 10^3$ l mol^{-1} cm^{-1} gefunden.

Das Verfahren wird durch folgende (aus 24 Messdaten erhaltene) Fehlerangaben charakterisiert:

Standardabweichung s_K	± 0.010 µmol
Variationskoeffizienten V (b_o bis b_u)	$\pm$(0.5 bis 5.2) Rel-%
Fehlerbereich T ($S=99\%$)	± 0.029 µmol
T ($S=99.9\%$)	± 0.039 µmol

Die untere Bestimmungsgrenze ($b_N = \sqrt{2} \cdot |T99.9|$) liegt bei 0.05 µmol Bi (in 25 ml); $E_N = 0.029$ ($d=2$ cm).

Die Eichgerade geht nicht durch den Koordinatenursprung, es gilt ein erweitertes Lineargesetz. Die Berechnung der in der Probe gefundenen Wismutmenge erfolgt nach: $E \cdot [\omega] + c_A$ mit $[\omega] = 1.728$ µmol Bi und $c_A = -0.038$ µmol Bi.

Einfluss von Fremdionen

Wismut und Blei verhalten sich bei der Extraktion mit CMAB-Oxin sehr ähnlich. Unter Beachtung aller Hinweise, die über den Einfluss von Fremdionen auf die photometrische Bestimmung von Blei mit CMAB-Oxin in einer vorangehenden Untersuchung[1] gegeben wurden, ergibt sich folgendes:

Keine Störung ergeben bis 1000 b_o: Alkalimetalle, Ca, Mg, Al, Ga, Cu, Zn, Cd, La, Cr, Mn, Co, Ni; bis 100 b_o: Tl, In, Fe.

Blei stört stark durch Mitbestimmung und muss daher durch Vorextraktion entfernt werden.

Bestimmung der Zusammensetzung des Bi-CMAB-Oxin-Komplexes

Die Untersuchung wurde durchgeführt nach der von KORENMAN[5] für Zweiphasensysteme variierten Jobschen Methode. Die für Wismut erhaltenen Werte und —zum Vergleich—die nach der gleichen Methode für den Blei-CMAB-Oxin-Komplex gemessenen zeigt die Abb. 3. Während, wie bekannt[2], für den Bleikomplex das Verhältnis Pb:R = 1:2 gefunden wurde, zeigt der Wismutkomplex die Zusammensetzung Bi:R = 1:3. Kurve I und III erhielten wir bei konstantem Volumenverhältnis der beiden Phasen und der üblichen kontinuierlichen Variation des Konzentrationsverhältnisses der Reaktionspartner. Beim Messen der Kurve II waren die Konzentrationen der Reaktionspartner in den beiden Phasen konstant und gleich und das Volumenverhältnis der beiden Phasen wurde kontinuierlich variiert.

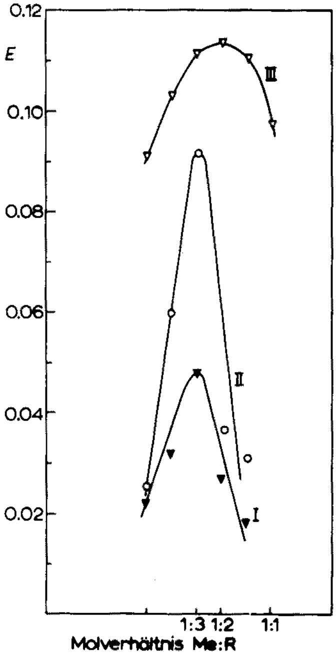

Abb. 3. Job'sche Kurven. (I und II) Bi und CMAB-Oxin; 0.1 *M* Citrat; pH = 12.2 ± 0.4; λ = 400 nm. (III) Pb und CMAB-Oxin; 0.1 *M* Tartrat; pH = 9.5; λ = 410 nm.

DISKUSSION DER ERGEBNISSE

Phillips und Duckwall[6] stellten schwerlösliche Chelate von nach der Art des CMAB-Oxins in 7-Stellung substituierten Oxinen durch Vermischen wässriger Metallsalzlösungen mit den äthanolischen Reagenzlösungen her. Sie erhielten dabei auch Chelate mit Metallionen der Ladung > 2+ und beobachteten in den Verbindungen im wesentlichen Molverhältnisse, wie sie auch in den Komplexen aus diesen Metallionen und dem unsubstituierten Oxin bekannt waren. Sie sahen deshalb diese substituierten Oxine als zweizähnige Liganden an.

Mit dem Ziel, die Selektivität des Oxins als organisches Reagenz für die extraktionsphotometrische Bestimmung von Metallen zu erhöhen, untersuchten Umland und Meckenstock[2] die in 7-Stellung substituierten Oxine, deren Substituenten über zum Teil mehrere Elektronendonatoratome (N,O,S) verfügen, in der Annahme, dadurch Dreizähnigkeit zu erreichen und die so gross sind, dass

Selektivitätserhöhung durch sterische Hinderung bei der Komplexbildung zu erwarten ist. Sie stellten fest, dass diese in 7-Stellung substituierten Oxine bei Abwesenheit von Lösungsvermittlern im Verteilungssystem Wasser/Chloroform nur noch mit Kationen der Ladung 2+ reagieren. Wir fanden hingegen, dass Bi^{3+}, In^{3+} (und Tl^{+} bzw. Tl^{3+}) mit CMAB-Oxin in chloroformischer Lösung, auch nach sorgfältiger Entfernung des Äthanols aus dem Chloroform, aus der wässrigen Phase extrahiert werden können, während dies bei Al^{3+}, Ga^{3+}, La^{3+}, Cr^{3+} und Fe^{3+} unter den überprüften Bedingungen nicht gelingt.

Die bisher untersuchten dreiwertigen Ionen von Al, Ga, In, Tl, Bi, La, Cr (nur bei erhöhter Temperatur) und Fe lassen sich mit Oxin extrahieren[7], bei Verwendung von CMAB-Oxin trifft das für Al, Ga, La, Cr und Fe(III) nicht zu. Unterschiede zwischen den CMAB-Oxinaten und den 2-Methyl-Oxinaten zeigen sich bei Ga, La, Cr und Fe(III), die wohl mit 2-Methyloxin[7], aber nicht mit CMAB-Oxin extrahierbar sind. (Fe(III) stört aber beim Arbeiten mit CMAB-Oxin durch seine oxydierende Wirkung, besonders bei gleichzeitiger Anwesenheit von Cyanid.)

Zwischen dem Oxin, dem 2-Methyloxin und dem CMAB-Oxin bestehen demnach deutliche Selektivitätsunterschiede, die für Trennungen gut nutzbar sein sollten. Das CMAB-Oxin (als Modellsubstanz für etwa 25 bisher dargestellte analoge Verbindungen[2,8,9]) besitzt eine merklich höhere Selektivität als das Oxin, die Unterschiede lassen sich aber nicht in der einfachen Weise ausdrücken, wie UMLAND UND MECKENSTOCK[2] das ursprünglich annahmen.

Das Verhältnis Bi:R=1:3 im Wismut-CMAB-Oxinat lässt auf Zweizähnigkeit des Liganden schliessen.

Weitere Untersuchungen über das komplexchemische Verhalten des CMAB-Oxins sind im Gange.

Frau KARIN GOLDMANN danke ich für die gewissenhafte Durchführung der zahlreichen Versuche.

ZUSAMMENFASSUNG

Die Möglichkeit der Extraktion von Al, Ga, In, Tl, Bi, La, Cr und Fe(III) mit CMAB-Oxin wird untersucht. Von den eingesetzten dreiwertigen Ionen (und Tl^{+}) lassen sich Bi (sehr gut) und In und Tl extrahieren. Auf Selektivitätsunterschiede zwischen Oxin, 2-Methyloxin und CMAB-Oxin wird hingewiesen. Die Zusammensetzung des Wismut-CMAB-Oxinats ist 1:3. Die extraktionsphotometrische Bestimmung von Wismut wird getestet. Wismut lässt sich mit CMAB-Oxin hochselektiv und mit guter Reproduzierbarkeit bestimmen.

SUMMARY

The possibility of extracting trivalent metals (Al, Ga, In, Tl, Bi, La, Cr, Fe(III)) with CMAB-oxine was examined; only bismuth, indium and thallium could be extracted. Differences in the selectivities of oxine, 2-methyloxine and CMAB-oxine are discussed. The composition of the bismuth-CMAB-oxinate is 1:3. Bismuth can be extracted and determined spectrophotometrically at pH 12.2 ± 0.4; the molar absorptivity at 400 nm is $7.2 \cdot 10^{3}$. The method is selective and reproducible.

RÉSUMÉ

On examine les possibilités d'extraction de métaux trivalents: Al, Ga, In, Tl, Bi, La, Cr, Fe, au moyen de CMAB-oxine (7-[α-(*o*-carbométhoxyanilino)benzyl]-hydroxy-8-quinoléine). Il est possible d'extraire ainsi bismuth, indium et thallium. On examine également les différences de sélectivité de l'oxine, de la méthyl-2-oxine et de la CMAB-oxine. La composition du bismuth-CMAB-oxinate est 1:3. Le bismuth peut être extrait et dosé spectrophotométriquement à pH 12.2 ± 0.4, coefficient d'extinction molaire: $7.2 \cdot 10^3$ à 400 nm. Cette méthode est sélective et reproductible.

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GAS CHROMATOGRAPHIC QUALITATIVE AND SEMIQUANTITATIVE ANALYSIS OF APPLE AROMA BY MEANS OF RETENTION INDEXES

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The separation and identification of the components in a complex mixture such as fruit aromas is a difficult problem which has been studied in many ways and with different techniques. CRIPPEN AND SMITH[1] have reviewed the gas–liquid chromatographic identification systems. This technique not only achieves the separation of components but also gives retention data for identification, which has to be completed by instrumental techniques such as infrared spectroscopy[2,3], mass spectrometry[4], ultraviolet spectrophotometry[5], nuclear magnetic resonance[6], and derivative formation for functional group identification[7]; organoleptic evaluation has also been employed[8,9]. Retention data in several chromatographic columns of different polarity also provide reliable identification.

In this work, retention indexes, affected with minor errors[10], are employed. The qualitative analysis is based on a comparison of retention indexes of apple aroma components with those of standard compounds previously identified[11]. To avoid aroma changes, head-space gas technique is employed for sample collection[12], and, as the olfactory threshold is lower than the flame-ionization detection limit, a flash low-pressure distillation in a nitrogen stream to concentrate the aroma, is used[13]. Semi-quantitative analyses are based on the linear relation between detector responses and the concentration of aqueous solutions of the components, and on the constant values of mV/p.p.m. for each compound. The differences in aroma between two varieties of apples have been studied.

EXPERIMENTAL

Apparatus

Conventional gas chromatographs with flame-ionization detectors were used.

The columns were copper tubes, 2 m in length and of 4.8 mm inner diameter. Stationary phases were 2% Ucon 50 LB 1200X, 2% Squalane, and 2% Squalane: Ucon 50 LB 1200X (1:1). Supports were Chromosorb G a.w. 80–100 mesh, deactivated by acetic acid digestion and 0.05 % tetrahydroxyethylethylenediamine (THEED). Another column used consisted of Porapak Q 80–100 mesh (without stationary phase).

Column temperatures were 50° and 70° for conventionally packed columns, and 150° and 190° for Porapak Q columns. The carrier gas flows were 60 ml/min for argon, 35 ml/min for hydrogen, and 625 ml/min for air.

Preparation of apple juice concentrate

The juices of "verde doncella" and "reineta" apples were obtained by pressing and filtering the fresh fruits. To concentrate the juice, a flash distillation method, with reduced pressure and nitrogen as an inert carrier gas was utilized. This system allowed concentration at room temperature, thus avoiding changes in the original aroma. Concentrates containing the juice aroma were collected in two traps cooled with liquid air. The mean yield was 0.30% for "verde doncella" and 0.22% for "reineta". Approximately 5 g of concentrate was obtained from 2 kg of fruit juice in 2 h. This quantity of concentrate was enough to obtain aroma chromatograms during one or two months depending on storage characteristics.

Sampling

In a 250-ml Erlenmeyer flask provided with a ground-glass stopper and a side hole fitted with a rubber diaphragm, 5 ml of aroma concentrate was placed and thermostatted at 30°. Samples of 3 ml of head-space gas were collected and then injected into the chromatograph.

TABLE I

IDENTIFICATION OF PEAKS OBTAINED IN "REINETA" APPLE AROMA CHROMATOGRAMS, BY MEANS OF RETENTION INDEXES[a]

Compound	*Squalane*		*Squalane : Ucon*		*Ucon*	
	Apple	*Standard*	*Apple*	*Standard*	*Apple*	*Standard*
Acetaldehyde	358	346	409	387	482	482
Proprionaldehyde	435[b]	437	494	497	585	580
Methanol	435[b]	420	540	537	651	648
Ethanol	435[b]	422	567	574	690[c]	686
1-Propanol	537[c]	521	676	675	793[c]	795
Butyraldehyde	537[c]	535	592	592	690[c]	680
Ethyl acetate	551	548	618	617	704	700
2-Butanol	569	567	682	690	807[b]	802
2-Methyl-1-propanol	597	589	737[c]	737	860	858
2-Methyl-2-butanol	613	614	708[b]	710	807[b]	809
1-Butanol	632	625	777	778	903[c]	901
Valeraldehyde	648[c]	640	708[b]	701	783	785
Ethyl propionate	648[c]	646	708[b]	707	793[c]	791
Methyl butyrate	660[c]	660	723[c]	722	807[b]	807
Butyl formate	660[c]	660	723[c]	723	826[b]	823
2-Pentanol	670	665	795[c]	788	903[c]	902
Isobutyl methyl ketone	682	680	737[c]	733	826[b]	826
Ethyl isobutyrate	697	695	748	749	826[b]	825
3-Methyl-1-butanol[d]	706	697	846	845	973[b]	973
2-Methyl-1-butanol	706	700	846	847	973[b]	972
Ethyl butyrate	739[c]	737	795[c]	795	877	877
Caproaldehyde	739[c]	742	802	803	887	887
2-Hexen-1-al	781	(781)	862	(863)	973[b]	(974)
Propyl butyrate[d]	837[c]	834	(888)	890	973[b]	970
Ethyl valerate	837[c]	837	(888)	893	973[b]	976
1-Hexanol	837[c]	831	(963)	(966)	(1107)	(1099)
Ethyl caproate	(935)	(935)	(990)	(991)	(1075)	(1073)

[a] Indexes in brackets were measured at 70°, and the others at 50°.
[b] Retention indexes employed in identification of three components.
[c] Retention indexes employed in identification of two components.
[d] Compounds presenting close values of retention indexes in the three columns.

Retention index measurement

The retention indexes of all compounds in a complex mixture such as apple aroma were obtained by means of the equation

$$I_x = 100\left(z + \frac{\log r_{xz}}{b}\right) \qquad (1)$$

where $b = \log V'_{(z+1)}/V'_z = \log r_{(z+1)z}$ ($V'_{(z+1)}$ and V'_z are n-alkane adjusted retention volumes of $(z+1)$ and z carbon atoms) and $r_{xz} = V'_x/V'_z$ for any compound x.

The value of b was calculated as the mean of the logarithm of relative retention for successive n-alkanes from $z=5$ to $z=10$.

Every r_{xs} value was calculated for the peaks of the aroma chromatogram. Internal standard S was n-nonane for Squalane and Squalane: Ucon columns and n-decane for Ucon. r_{sz} can be computed from another chromatogram of the internal standard which was utilized to measure the b value; r_{xz} was therefore obtained from the relation $r_{xz} = r_{xs}\, r_{sz}$. When these values are substituted for the terms in eqn. (1), the retention indexes can be obtained for all compounds in a complex mixture with only one standard.

TABLE II

IDENTIFICATION OF PEAKS OBTAINED IN "VERDE DONCELLA" APPLE AROMA CHROMATOGRAMS, BY MEANS OF RETENTION INDEXES[a]

Compound	*Squalane*		*Squalane : Ucon*		*Ucon*	
	Apple	*Standard*	*Apple*	*Standard*	*Apple*	*Standard*
Acetaldehyde	351	346	410	387	498	482
Methanol	431[b]	420	535[c]	537	647	648
Ethanol	431[b]	422	568	574	691	686
Acetone	431[b]	426	494	499	593	594
Methyl acetate	471	470	535[c]	534	628	623
1-Propanol	528[c]	521	676	675	801[d]	795
Butyraldehyde	528[c]	535	586	592	681	680
Ethyl acetate	552	548	615	617	707	700
2-Butanol	574, 586	567	682	690	801[d]	802
2-Methyl-1-propanol	596	589	737[c]	737	854[c]	858
2-Methyl-2-butanol	614	614	712[c]	710	801[d]	809
Methyl propyl ketone[e]	633[c]	624	692	692	784	781
Valeraldehyde	633[c]	640	692	701	784	785
1-Butanol	633[c]	625	777[c]	778	900[b]	901
Propyl acetate	648	646	712[c]	712	801[d]	800
2-Pentanol	671[c]	665	786	788	900[b]	902
Isobutyl methyl ketone	671[c]	680	737[c]	733	828	826
3-Methyl-1-butanol[e]	706[c]	697	846	845	970[c]	973
2-Methyl-1-butanol	706[c]	700	846	947	970[c]	972
Isobutyl acetate[e]	706[c]	708	777[c]	769	854[c]	852
Methyl isovalerate	706[c]	716	777[c]	774	854[c]	855
Caproaldehyde	749[c]	742	804	803	888	887
Butyl acetate	749[c]	745	810	811	900[b]	901
2-Hexen-1-al	782	(781)	(863)	(863)	970[c]	(973)
Isoamyl acetate	814	812	873	872	959	956
1-Hexanol	837	831	(963)	(966)	(1106)	(1099)
Hexyl acetate	(945)	(946)	(1006)	(1007)	(1098)	(1096)

[a] Indexes in brackets were measured at 70°, and the others at 50°.
[b] Retention indexes employed in identification of three components.
[c] Retention indexes employed in identification of two components.
[d] Retention indexes employed in identification of four components.
[e] Compounds presenting close values of retention indexes in the three columns.

RESULTS AND DISCUSSION

Retention index values were obtained for all peaks detected in aroma chromatograms of "verde doncella" and "reineta" apples. Retention indexes were also measured for 70 standard compounds selected from fruit aroma constituents (esters, alcohols, aldehydes and ketones).

These retention values for the aroma peaks and standards were compared for each of the three columns employed (Tables I and II). The reliability of identification increases when the retention indexes of the aroma components are equal to the indexes of standards in all columns, but if some standards give retention values close to each other in every column, it cannot be definitely said which of them is present in the fruit, on the basis of this comparative procedure. In the "verde doncella" apple there were three unresolved peaks: 3-methyl-1-butanol/2-methyl-1-butanol; methyl propyl ketone/valeraldehyde and isobutyl acetate/methyl isovalerate. In the "reineta" apple the doubtful pairs were 3-methyl-1-butanol/2-methyl-1-butanol and propyl butyrate/ethyl valerate.

Some components appeared in only one peak; this fact is marked in the Tables. If a component was not present in a pure peak in some of the three columns, its identification was more uncertain. This occurred in the "reineta" apple with methyl butyrate, butyl formate and ethyl proprionate; in the "verde doncella" apple with 1-butanol and isobutyl acetate or methyl isovalerate.

Sources of errors in determination

Errors in the determination of retention indexes increased as the retention volumes decreased, and when the differences between the retention volumes of internal standard and component were large. Thus, variations in the index were bigger from acetaldehyde up to 2-butanol, than in the other components. Another important source of error was peak masking, for example, the index on Squalane for possible methyl propyl ketone in "verde doncella" was 9 units different from the index of methyl propyl ketone standard, because the aroma peak was masked with 1-butanol and 2-pentanol, but the other two discrepancies were smaller because the peaks were probably pure. Likewise, errors resulted when overlapping of peaks occurred.

An auxiliary functional group identification method

Aroma chromatograms were made at two temperatures: 50° and 70° both for samples and standards. The $\delta I/\delta T$ values were calculated for standard alcohols, ketones, aldehydes and esters. Alcohols gave 20 $\delta I/\delta T$ mean values of -9 ± 1.7 (Squalane), -21 ± 1.6 (Squalane:Ucon) and -11 ± 0.9 (Ucon), but the other homologous series showed no typical values. For example, in the Ucon phase, the values were: 3 ± 2.9 for aldehydes, 4 ± 3.4 for ketones and 2 ± 1.7 for esters. Such data can be utilized to identify alcohols, in the presence of –CO– and –COO– in a complex mixture, when chromatograms are recorded at two temperatures. The special behavior of the –OH group, the most polar among the groups studied, can be related to the disturbance of the molecular dipoles with increasing temperature, which produces a decreased polarization orientation. Consequently, a diminution of the solute–solvent interactions occurs which results in lower column retention values.

Confirmation of the aroma components identified, by means of quantitative response

In a complex mixture such as apple aroma, there are overlapping peaks. It was not possible to measure peak areas accurately, therefore it was necessary to relate the quantity of component to the peak height. The response depended on column selectivity and efficiency, and consequently, on retention, decreasing in the order: Squalane, Squalane: Ucon, Ucon, for alcohols with increasing retention volumes. The diminution was least important for aldehydes, ketones, esters and volatile alcohols, because the differences in retention volumes were smaller in the three columns.

Porapak Q in the separation of the most volatile components of the apple aroma

The chromatographic characteristics of some polymer porous beads have already been studied[14]. Porapak Q was the most efficient packing tested; the retention volumes of aroma components were larger than with the three packed columns used, although the operating temperature was higher. This property is quite important in the separation and identification of the most volatile fraction of the aroma.

Table III shows the identification of the aroma components of the most volatile fraction of "verde doncella" and "reineta" apples. It should be noted that the variation between the indexes of the aroma peak and the standard peaks is smaller than in the other columns employed. Compounds with larger retention indexes were not detected; for example, 3-methyl-1-butanol or 2-methyl-1-butanol was identified in "reineta" but not in "verde doncella" because it was present in a smaller quantity. Indexes at 150° were compared with those at 190° in some cases, because the constancy of the indexes was demonstrated, even for alcohols, in this range of temperature.

TABLE III

RE-IDENTIFICATION OF THE MOST VOLATILE COMPONENT OF APPLE AROMA BY MEANS OF RETENTION INDEXES IN PORAPAK Q AT 150°[a]

Compound	*"Verde doncella"*	*"Reineta"*	*Standard*
Methanol	291	289	292
Acetaldehyde	339	338	336
Ethanol	383	383	379
Propionaldehyde	—	444	441
Acetone	445	—	442
1-Propanol	487	487	485
Isobutyraldehyde	524	519	(524)
Butyraldehyde	543	543	542
Ethyl acetate[b]			562
2-Butanol	559	563	(561)
2-Methyl-1-propanol	—	572	(575)
1-Butanol	595	595	(600)
Ethyl propionate[b]			(657)
2-Pentanol	—	660	(660)
2-Pentanol[b]			(660)
Propyl acetate	659	—	(661)
3-Methyl-1-butanol[b]			(684)
2-Methyl-1-butanol	—	680	(687)

[a] Indexes in brackets are measured at 190°, the others at 150°.

[b] Compounds showing close values of retention index.

Semiquantitative analysis

In order to calculate the quantity of every component identified, the peak height in mV was measured in those columns where the peak of the component was probably pure. As a head-space gas technique was utilized in sampling, and as the concentrates were very dilute aqueous solutions, the quantity of every component injected depended on the concentration and vapor pressure of the solution. To fix these variables, aqueous solutions containing p.p.m. amounts of the compounds identified were prepared and thermostatted at 30°. All chromatographic conditions were also fixed to avoid retention time variations. The detector responses for each aqueous solution of each component at various concentrations were measured. When detector response was plotted against the concentration of the solutions in p.p.m.,

TABLE IV

COMPONENTS IDENTIFIED AND SEMIQUANTITATIVELY MEASURED

(Concentration in apple juice expressed in p.p.m.)

Component	*"Verde doncella"*	*"Reineta"*
Acetaldehyde	7	9.7
Propionaldehyde	—	0.03
Isobutyraldehyde	0.003	0.003
Butyraldehyde	0.08	0.1
Valeraldehyde	0.02	0.005
Caproaldehyde	0.2	0.8
2-Hexen-1-al	0.2	0.2
Acetone	0.05	—
Isobutyl methyl ketone	0.009	0.001
Methanol	15	3.4
Ethanol	3	26
1-Propanol	0.4	1
2-Methyl-1-propanol	0.07	0.4
2-Butanol	0.06	0.04
1-Butanol	2.5	1.7
2-Methyl-2-butanol	0.04	0.05
2-Pentanol	0.9	0.07
3-Methyl-1-butanol	0.3	5.1
2-Methyl-1-butanol		
1-Hexanol	1.6	0.9
Methyl acetate	0.006	—
Ethyl acetate	0.3	0.6
Ethyl propionate	—	0.4
Propyl acetate	0.04	—
Ethyl butyrate	—	1.4
Butyl acetate	0.7	—
Isobutyl acetate	0.002	—
Methyl isovalerate		
Ethyl isobutyrate	—	0.01
Methyl butyrate	—	0.01
Butyl formate	—	0.003
Isoamyl acetate	0.2	—
Ethyl valerate		
Propyl butyrate	—	0.06
Hexyl acetate	0.3	—
Ethyl caproate	—	0.02

linear relations passing through the origin were obtained. In this manner, values of mV/p.p.m., constant for each compound, were calculated. With these values, it was possible to measure concentrations in aroma by dividing the response of a compound in an aroma chromatogram by its mV/p.p.m. constant.

In Table IV, the calculated p.p.m. quantities of every aroma component in the fruit juices are given.

CONCLUSION

The results given in Table IV indicate that the aromas of "verde doncella" and "reineta" apples have almost the same components and have similar quantitative composition in regard to alcohols, aldehydes and ketones. The fundamental differences of aroma must be attributed to the esters. It can be seen that in "verde doncella" apples, the major part of these compounds are acetates, whereas in "reineta" apples there are more ethyl esters.

Synthetic concentrates of both juices were prepared from alcohols, aldehydes and ketones. The difference in aroma was very slight, but when esters were added, the synthetic concentrates showed aroma characteristics very similar to the concentrate of the natural fruit juice.

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SUMMARY

The components of two varieties of apples were investigated by gas chromatography. After a flash distillation method to concentrate the apple juice, aroma chromatograms were obtained in four columns of different polarity. When the values of the peak retention indexes were compared with the indexes of standard compounds, 25–26 volatile components could be identified. These constituents were semiquantitatively measured by means of peak heights. Fundamental differences in the aroma of the two apple varieties were established by this method.

RÉSUMÉ

Deux variétés de pommes ont été examinées par chromatographie gazeuse. Après distillation flash pour concentrer le jus de pommes, des aromagrammes ont été obtenus dans quatre colonnes de différente polarité. On a pu ainsi identifier 25 composants volatiles. Ces constituants ont été dosés semiquantitativement en constantes mV/p.p.m. Des différences fondamentales dans l'arome de ces deux variétés de pomme ont pu être établies par cette méthode.

ZUSAMMENFASSUNG

Die Bestandteile verschiedener Apfelsorten wurden mit Hilfe der Gaschromatographie qualitativ und halbquantitativ untersucht. Nach Konzentration des Apfelsaftes wurden mit 4 Kolonnen verschiedener Polarität Chromatogramme der Aromen erhalten. Die Werte für die Retention der Peaks und der Vergleich dieser mit Standardverbindungen führten zur Identifizierung von 25 bzw. 26 Komponenten. Über die grundsätzlichen Unterschiede bei den Aromen verschiedener Apfelsorten wird berichtet.

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POLAROGRAPHIC CHARACTERISTICS OF COPPER IONS IN AZIDE SOLUTIONS

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Investigations on the reactions between copper and azide ions[1,2] have been almost entirely confined to studies of the CuN_3^+ species, although other aspects of the copper–azide reaction are well known, mainly those concerning the isolation of solid compounds or the formation of azide–amine complexes. Information on these studies can be found in excellent reviews[3–5].

Information obtained from some preliminary investigations[6,7] led to the study of the behavior of aqueous solutions of copper and azide ions, which is reported in the present paper. The results are mainly concerned with the characteristics of the polarographic waves obtained in concentrated azide solutions of copper(II) ions. These results made it possible to draw definite conclusions regarding the maximum number of azide ligands involved in complex formation between copper(II) and copper(I) ions with azide ions in aqueous solutions.

EXPERIMENTAL

The apparatus and reagents used were of the same specifications as reported in previous papers[6,7].

Conductometric titrations were carried out with the help of an "Industrial Instruments" Model R C 16B2 bridge.

Copper(II) perchlorate was prepared by reaction of C. P. perchloric acid with excess of C. P. copper carbonate. The solution was standardized by electrolytic gravimetric deposition and checked by iodometric titrations; some free perchloric acid was added to avoid hydrolysis during storage.

Copper(I) in azide supporting electrolyte was obtained by reduction of the corresponding copper(II) solution with finely powdered metallic copper, under a nitrogen atmosphere in the polarographic cell. The polarograms were taken after settling of the copper.

Precision of $E_{1/2}$ measurements was achieved by means of the interpolation procedure previously described[1], with some modifications, as discussed below.

All measurements were made at $25 \pm 0.1°$.

RESULTS AND DISCUSSION

Polarograms obtained in sodium azide solutions of copper(II) ions (Fig. 1) show two waves that should correspond to the reduction of copper(II) to copper(I) and of copper(I) to the amalgam, respectively. It may be clearly observed that the higher the azide concentration, the better is the separation of the two waves. Accordingly, more concentrated supporting electrolytes were used in all later work in order to obtain more precise results. The lower part of the first wave is strongly affected by the interference of an anodic mercury dissolution wave[8], which creates problems in measuring the i_d and $E_{1/2}$ values. Measurements of cathodic current in the separating region between the two waves (Fig. 1) is the most convenient method of obtaining $i_{d(1)}$, inasmuch as it is not possible to draw the whole wave free from anodic interference.

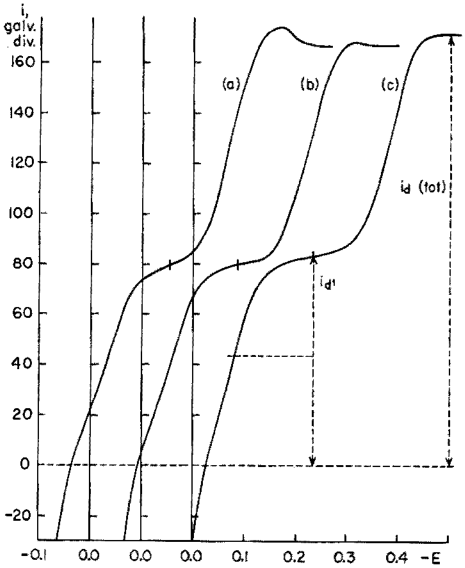

Fig. 1. Polarograms of 3.0 mM copper(II) in the prsence of 0.10% gelatin at ionic strength 4.0. Sodium azide concentration: (a) 1.0 M, (b) 2.0 M, (c) 3.0 M.

The usual procedure of taking the half i_d value for the determination of $E_{1/2}$ worked reasonably well only for high copper concentrations. For low copper(II) concentrations, a high anodic current correction in the $E_{1/2}$ region affected the measurements. A large number of experiments showed that if a blank solution containing some copper(II) was used, the $E_{1/2}$ values determined at different copper concentrations were quite consistent. The choice of copper content in the blank solutions was based on the minimum value capable of promoting a cathodic current in the $E_{1/2}$ region. Measurements of $E_{3/4}$ and $E_{1/4}$ were also obtained by this procedure.

The same procedure was also extended to measurements of the slope of the polarographic wave for the usual test of reversibility, because very high discrepant values were obtained at low copper concentrations (less than 1 mM), because of anodic interference. When a copper-containing blank was used as described above, the slope values obtained from many solutions were of the same order of those of the 3–7.5 mM copper(II) solutions.

It is interesting to note the strong tendency to polarographic maxima in the second wave, in contrast with the first wave where the phenomenon is not observed, even in the total absence of maximum suppressors. The presence of sodium perchlorate used to adjust ionic strength, at low azide concentration solutions, increased markedly the tendency to form maxima in the second wave.

TABLE I

TESTS OF REVERSIBILITY FOR THE FIRST POLAROGRAPHIC WAVE, IN ABSENCE OF MAXIMUM SUPPRESSORS

(7.5 mM copper(II); ionic strength 4.0)

[N_3^-]	[HN_3]	$i_{d(tot)}$ *(galv. div.)*	$-E_{1/2}$ *(V)*	*Slope (V)*	$-E_{3/4}$ *(V)*	$-E_{1/4}$ *(V)*	$E_{3/4}$–$E_{1/4}$ *(V)*	*pH*
4.00	0.00	456.0	0.0775	0.0621	0.1100	0.0491	−0.0609	9.0
3.50	0.00	456.0	0.0740	0.0615	0.1041	0.0436	−0.0605	8.8
3.50	0.25	454.0	0.0748	0.0621	0.1053	0.0445	−0.0608	5.5
3.50	0.50	452.5	0.0740	0.0616	0.1053	0.0460	−0.0585	5.3

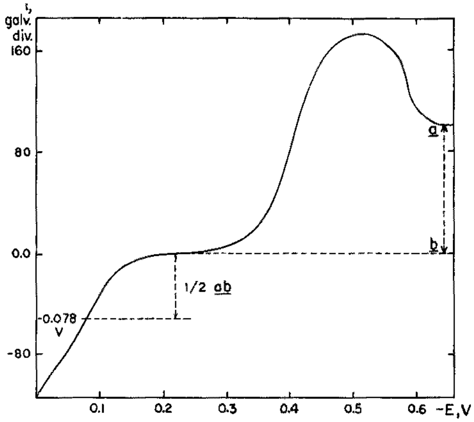

Fig. 2. Polarogram of reduced solution in 4.0 M sodium azide. Copper(I) is *ca.* 6.2 mM.

Table I presents data on the first wave. The one-electron reduction and the reversibility of the process either in acidic or alkaline solutions were shown by the calculated slope. Acceptable values for the differences ($E_{3/4}$–$E_{1/4}$) confirmed this reversibility[8,9]. The total i_d (sum of the first and second wave heights) showed only a slight decrease with increasing hydrazoic acid concentration and the $E_{1/2}$ values were not affected.

Similar calculations of the slope for the second wave also showed reversibility of the electrode process, with the expected one-electron reduction. The copper reduction can thus be characterized as stepwise.

The tendency of azide ion to stabilize copper(I) is also evidenced by the easy reduction of copper(II) solutions with metallic copper. This reduction was achieved in absence of air, with finely powdered copper, and total decolorization of the intensely brown initial solutions was observed on the formation of the copper(I) complexes. When the concentration of the azide solution was less than 0.5 *M* and that of the copper(II) higher than 3 m*M*, some white CuN_3 was formed during the reduction.

The polarogram of the reduced solution (Fig. 2) shows clearly an anodic wave corresponding to the oxidation of copper(I) to copper(II), followed by the normal second cathodic wave. The measurement of $E_{1/2}$ of this anodic wave, calculated from the half $i_{d(2)}$ value, led to exactly the same value as that determined for the cathodic wave. The reversibility of the process was thus again confirmed.

TABLE II

DIFFUSION CURRENT CONSTANT I_1 AND I_{tot}, IN 4.0 *M* SODIUM AZIDE WITH NO MAXIMUM SUPPRESSOR

$C_{Cu(II)}$ (m*M*)	$m_1^{2/3} \cdot t_1^{1/6}$ ($mg^{2/3} \cdot sec^{-1/2}$)	$m_2^{2/3} \cdot t_2^{1/6}$ ($mg^{2/3} \cdot sec^{-1/2}$)	I_1	$2I_1$	I_{tot}
1.088	1.83	1.85	1.33	2.66	2.63
2.176	1.82	1.85	1.34	2.68	2.67
4.352	1.81	1.85	1.32	2.64	2.61
9.722	1.70	1.84	1.308	2.616	2.616

Table II shows that the diffusion current constant, *I*, for the first wave has approximately half the value of the I_{tot} constant, corresponding to the sum of the two waves. This means that the two copper waves are of equal height when corrected for the same capillary characteristics, as expected for such stepwise reduction[10].

As previously pointed out, the behavior of azide and thiocyanate ions have been frequently compared, because of the analogies of their reactions with several metal ions. In this connection, it seems interesting to note that the polarographic characteristics described here for copper(II) are very different from those observed by MEITES[11] in thiocyanate supporting electrolyte of concentration higher than 0.57 *M*;

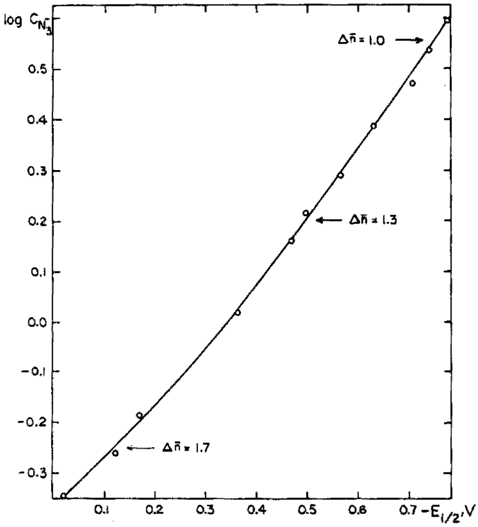

Fig. 3. Shift of $E_{1/2}$ with increasing sodium azide concentration for the first polarographic wave. 7.5 m*M* copper(II); ionic stength 4.0.

two waves of unequal heights were observed, the second being in the region of about -1.4 V *vs.* S.C.E. The first wave was shown by coulometric measurement to correspond to the direct reduction of copper(II) to the amalgam and the second was considered to be of catalytic nature[11].

The mean ligand number $\bar{n}$, or the difference of mean ligand number, $\Delta\bar{n}$, may be calculated with the help of $\Delta E_{1/2}$ values[12]. In order to obtain precise measurements, solutions of high copper concentration must be used. The plot of $E_{1/2}$ *vs.* log $[N_3^-]$ in Fig. 3 shows a slight curvature. The value of $\Delta\bar{n}$ tends to unity as the azide concentration increases.

All the i_d values of this series are the same, after correction for the drop time. This may indicate that copper(II) is quantitatively present as a definite complex species in the range studied. The observed $\Delta\bar{n}$ with decreasing azide concentration (Fig. 3), would thus be related to a corresponding decrease of $\bar{n}$ for copper(I).

The data given in Table II were obtained in the absence of a maximum suppressor, the total current being measured at -0.9 V, far beyond the second wave maximum. The presence of suppressors like gelatin, polyacrylamide and especially Triton X100, was found to decrease the total diffusion current, as usual.

Similar precise studies were not carried out for the second wave, because the increased tendency to maxima, induced by the perchlorate present at lower azide concentrations, requires lowering of the copper concentration, with consequent lack of precision. However, a few measurements at 3–4 *M* azide concentrations (Table III) were considered. From these data it can be seen that if a deviation of only 1 mV is admitted for each $\Delta E_{1/2}$ determined, recalculation of both $\bar{n}$ values leads to 3.0 ligands. Furthermore, the average of the two tabulated $\bar{n}$ values is almost exactly 3.00. As the azide concentration is very large, it can be inferred that the maximum number of azide ligands on the copper(I) ion is three. As has been already discussed[2], the sum of this integer $\bar{n}$ value with the limiting unitary $\bar{n}$, from the first wave, indicates clearly four ligands for copper(II) ions. It can thus be concluded that for azide concentrations up to 4 *M*, the contribution of any copper(II) and copper(I) species richer in azide ligands than four and three, respectively, is very improbable.

TABLE III

SECOND POLAROGRAPHIC WAVE: $\bar{n}$ VALUES FOR COPPER(I) IONS, IONIC STRENGTH 4.0

$C_{Cu(II)}$ *(mM)*	*Max. supp.*	$[N_3^-]$	$E_{1/2}$ *(V)*	$\Delta E_{1/2}$ *(mV)*	$\bar{n}$
1.5	Gelatin	3.95	0.3810	23.5	3.14
	0.1%	2.95	0.3575		
0.9	Triton X100	3.95	0.3805	21.5	2.87
	0.01%	2.95	0.3590		

Some experiments were carried out in 1.0 *M* and 4.0 *M* sodium azide supporting electrolyte, in order to observe the dependence of the $E_{1/2}$ values for both waves with copper concentration. Despite the decrease in the precision of the measurements caused by the lowering of the copper concentration, the $E_{1/2}$ values were found to be reproducible within 2 mV, after *iR* correction, in the studied range of 0.4–7.5 m*M* copper for the first wave, and 0.2–0.9 m*M* for the second wave. This excludes any significant contribution of a polynuclear species.

Mixtures of 1 m*M* copper(II) solutions containing a ten-fold excess of azide ion become much more strongly colored on addition of organic solvents miscible with water, especially acetone. The phenomenon is similar to that observed in the cobalt-(II)–thiocyanate and cobalt(II)–azide systems[13]. This suggested that additional and valuable information could be obtained by means of conductometric titrations in acetone–water medium.

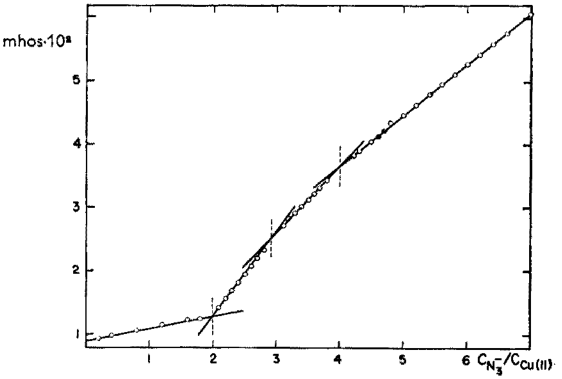

Fig. 4. Conductometric titrations in water–acetone solutions. 0.04346 *M* copper(II); 0.4346 *M* NaN_3; volume ratio of water/acetone: 1/5.55.

Figure 4 shows the results of one of the several conductometric titrations, performed in suitable proportion of water and acetone. The slight solubility of $Cu(N_3)_2$ in the solvent mixture masked completely the first expected step of CuN_3^+ formation. The following steps, however, show clearly the formation of species with three and four ligands. There is no evidence for the presence of polynuclear species or complexes with more than four ligands.

These facts were considered as definite confirmation of the nonexistence of significant concentrations of species with more than four azide ligands in copper ions, or even polynuclear complexes. One may thus conclude that the isolated solid compounds, such as $Li_4Cu(N_3)_6$[3], probably contain in the crystal lattice, $Cu(N_3)_4^{2-}$ and N_3^- ions, rather than $Cu(N_3)_6^{4-}$ anions.

The thermodynamic formation constants of the successive copper(II) azide complexes have been determined by making use of solubility measurements and will be reported later.

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SUMMARY

The stepwise and reversible reduction of copper(II) ions in supporting electrolytes consisting of 0.5–4.0 *M* sodium azide at constant ionic strength was studied; the behavior was different from that observed in thiocyanate solutions. The diffusion current constant for the sum of the two waves, in 4.0 *M* sodium azide supporting electrolyte, is 2.62 and is exactly twice the value for the first wave. The maximum number of azide ligands was found to be 4 and 3 for copper(II) and copper(I), respectively. No evidence was found for polynuclear species.

RÉSUMÉ

On examine les paliers et la réduction réversible des ions cuivre(II) dans des solution d'azoture de sodium 0.5 à 4.0 *M* comme électrolyte de base, à force ionique constante. Le comportement est différent de celui observé dans des solutions au thiocyanate. Le courant de diffusion, constant pour la somme des deux vagues, dans l'azoture de sodium 4.0 *M* est de 2.62; il est exactement le double de la valeur du premier palier. Le nombre maximum de ligands azoture est de 4 pour le cuivre(II) et 3 pour le cuivre(I). On n'a pas de preuve de la présence de groupes polynucléaires.

ZUSAMMENFASSUNG

Es wurde die schrittweise, reversible Reduktion von Kupfer(II)-Ionen in Trägerelektrolyten mit 0.5–4.0 *M* Natriumazid bei konstanter Ionenstärke untersucht. Das Verhalten unterschied sich von demjenigen, welches in Thiocyanatlösungen beobachtet wurde. Die Diffusionstromkonstante für die Summe zweier Stufen in 4.0 *M* Natriumazid beträgt 2.62 und ist genau doppelt so gross wie für die 1. Stufe. Die maximale Zahl der Azid-Liganden beträgt für Kupfer(II) vier und Kupfer(I) drei. Anzeichen für polynukleare Spezies wurden nicht gefunden.

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SHORT COMMUNICATIONS

Determination of sulfide with crystal violet–tetraiodomercurate(II) ion-association reagent

Trace concentrations of sulfide, as H_2S or HS^- in solution below pH 13, are commonly determined iodimetrically, or colorimetrically by the formation of methylene blue[1]. Newer methods include the sulfide-induced reaction of azide ion with iodine[2], and potentiometric determination with the sulfide-selective solid state electrode[3].

The ion-association compound formed between crystal violet and tetraiodomercurate(II) ion is sufficiently insoluble to be useful in column techniques, and is responsive to sulfide in the range 0–6.0 p.p.m. It would also be responsive to metal ions whose iodide salts are extremely insoluble, but those cations usually are incompatible with sulfide. If necessary, cations present can be replaced by an innocuous alkali-metal cation by ion exchange.

In the first report of an insoluble ion-association compound as an analytical reagent, BOUILLOUX[4] described a compound formed between methylene blue and tetraiodomercurate(II) ions as a colorimetric reagent for silver ion. This reagent is not sufficiently insoluble for use in a column technique. LAMBERT AND MANZO[5] recently described the insoluble compound formed between tris(1,10-phenanthroline)iron(III) and triiodide ions as a colorimetric reagent for cyanide ion.

Reagent and apparatus

Tetraiodomercurate(II) ion is prepared by reaction of the proper stoichiometric ratio of potassium iodide and mercury(II) nitrate in solution. Crystal violet (Fisher Scientific Co. reagent grade, 99%) in 0.5% solution is added to an equal volume of 0.5% solution of tetraiodomercurate(II) ion with stirring. The precipitate is digested overnight in warm solution, filtered with suction on a Buchner funnel for 3 h, and air dried overnight.

A 10–15 mm column of the precipitate is prepared in an 8-mm outside diameter glass tube above a plug of borosilicate glass wool held in place by a constriction in the tube. A funnel is attached to the column by *ca.* 75 cm of transparent flexible tubing at a height sufficient to provide a flow rate of one drop of solution every 2–3 sec. The column is thoroughly washed with deionized water until the blank is decreased to a constant low value.

Calibration curve and results

A calibration curve is prepared for the concentration range 0–6 p.p.m. sulfide. A freshly prepared *ca.* 500-p.p.m. stock solution of sodium sulfide is prepared by the method of BUDD AND BEWICK[6], from which a 20-p.p.m. working solution is made. All solutions are prepared fresh daily with water which has been deaerated by boiling or by purging with nitrogen gas. Sample solution is added to the funnel to maintain an approximately constant drop rate. The first 20-ml portion of eluent is discarded, after which a 10-ml portion is collected and its absorbance measured at 590 nm.

Samples for analysis should be collected with the usual precautions against air oxidation[1]. The calibration curve is a straight line in the region 0–6.0 p.p.m. sulfide ion and 0–0.80 absorbance. Table I shows the experimental results.

TABLE I

EXPERIMENTAL RESULTS FOR CALIBRATION CURVE

Concn. S^{2-} (p.p.m.)	*No. detns.*	*Absorbance*		
		Average	*Range*	*Std. dev.*
0	5	0.013	0.010–0.018	0.003
2.0	5	0.258	0.240–0.270	0.012
3.0	5	0.389	0.370–0.410	0.018
4.0	5	0.503	0.480–0.520	0.018
5.25	6	0.668	0.640–0.700	0.023

Interferences

The following ions (500 p.p.m.) produce no appreciable interference in deionized water: sodium, potassium, ammonium, calcium, sulfate, chloride, nitrate, bicarbonate, fluoride, iodide, phosphate, sulfite and hydroxide. No interference was observed from 450-p.p.m. concentrations of the above ions in the analysis of a solution containing 2.5 p.p.m. of sulfide. The reagent also reacts with cyanide ion in low concentration, but the response is non-linear. Reagent response is relatively unaffected by variations in pH near the neutral range. Strong oxidants and reductants should be absent.

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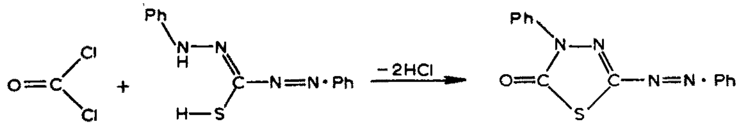
Studies with dithizone
Part XIX*. A photochemical oxidation product of dithizone

In an extended study of the causes underlying the deterioration of solutions of dithizone (1,5-diphenyl-3-mercaptoformazan; I) in organic solvents on keeping, the photochemically induced reaction in chloroform has been investigated.

When green solutions of dithizone in dry chloroform are irradiated with ultraviolet light the colour gradually becomes brownish-red. Reduction of the bulk of the reaction mixture followed by column chromatography led to the isolation of a brownish-yellow crystalline product (m.p. 138°; composition $C_{14}H_{10}N_4OS$) which was identified as 5-phenylazo-3-phenyl-1,3,4-thiadiazole-2-one (II) by mixed melting point, and a comparison of its visible and infrared spectra with those of an authentic sample prepared as described much earlier by Preund and Kuh[1] by the action of phosgene on dithizone. The phosgene clearly originated from the familiar photochemical decomposition of the solvent chloroform, a process accompanied by the formation of hydrogen chloride which caused the reaction product to fume in moist air. The reaction proceeds as follows:

$$CHCl_3 \xrightarrow[h\nu]{[O]} COCl_2 + HCl$$



I II

Experimental

Purified dithizone (2.0 g) dissolved in chloroform (500 ml) was irradiated in the flask of a Hanovia 1L photochemical reactor with a medium-pressure mercury vapour lamp (Cat. No. 12771/1). After 14 h the spectrum of a suitably diluted aliquot portion of the reaction mixture showed a complete change from that of the parent dithizone solution: there was no further change after irradiation for another hour. The solvent was removed from the reaction mixture under reduced pressure: acid fumes of hydrogen chloride were noted at this stage. The brownish-yellow residue was purified by chromatography on an alumina column and eluted with chloroform–benzene mixture (1:1). Recrystallisation from ethanol gave brownish-yellow crystals (yield 65%) m.p. 138°. (Found: C, 58.8; H, 3.0; N, 19.9; S, 11.5%. Calcd. for $C_{14}H_{10}N_4OS$(II): C, 59.5; H, 3.6; N, 19.8; S, 11.4%.)

An authentic sample of 5-phenylazo-3-phenyl-1,3,4-thiadiazole-2-one (II), m.p. 139°, was prepared by the reaction of phosgene on dithizone[1] (Found: C, 59.2; H, 3.7; N, 19.4; S, 11.2%). A mixture with the irradiation product from dithizone melted at 138°. The visible spectrum of (II) in carbon tetrachloride shows a broad shoulder ($\sim$ 305 nm) and a single sharp peak (λ_{max} 375 nm; $\varepsilon_{max} = 19{,}300$). The infrared spectrum unambiguously shows the presence of the $\rangle C=O$ group by a strong band at 1670 cm^{-1} and there is no absorption in the $\rangle NH$ region.

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* W. S. McDonald, H. M. N. H. Irving, G. Raper and D. C. Rupainwar, *Chem. Commun.*, 392 (1969) is regarded as Part XVIII of this series.

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Some chemical interferences of calcium in atomic absorption spectrophotometry

As in flame emission spectroscopy, numerous concomitants influence the production of neutral atoms of calcium in atomic absorption spectroscopy. It is generally recommended that a fuel-rich air–acetylene flame condition should be used to improve the sensitivity for calcium. However, during recent work[1] on the determination of atmospheric calcium by atomic absorption spectroscopy, it was found that a lean air–acetylene flame generally reduces or eliminates the chemical interferences on calcium from the possible atmospheric concomitants studied, while a fuel-rich flame gives the most chemical interferences. Absorption measurements of calcium were made in various flame conditions at different burner heights.

Experimental

Apparatus. All absorption measurements were made with an Instrumentation Laboratory (Model 153) dual double-beam atomic absorption spectrophotometer. For studies with air–acetylene flames, the standard laminar-flow Boling burner head was used throughout. Calcium hollow-cathode lamps (Westinghouse, high-intensity lamps) were used as radiation sources.

Instrumental conditions. These were selected for the study of chemical interferences rather than study of sensitivity for calcium.

Investigation of flame profiles and interferences. The absorbances of aqueous solutions of calcium (10 μg/ml) were measured in the various flame conditions at different burner heights in an attempt to seek optimum flame conditions for chemical interferences for calcium. In order to study the chemical interferences, possible concomitants in the atmospheric samples were added to calcium solutions; 100 μg/ml of interfering cation was added to 10 μg/ml of analyte, and, for interfering anions, 0.3 M solutions of the relevant acids were added to 10 μg/ml of analyte. For the preparation of the samples, reagent-grade chemicals and distilled deionized water were used throughout.

Results

Under the instrumental conditions developed (Table I), the flame profiles of calcium in various flame conditions were obtained (Fig. 1). Figure 2 shows the anionic interferences on calcium in various flame conditions at different burner heights. A similar study of cationic interferences is shown in Fig. 3. Various flame conditions

TABLE I

INSTRUMENTAL CONDITIONS

Element	Ca	422.7 nm				
H.C. lamp	7 mA					
Flame (psi)	Lean air:	5.0	Stoich. air:	5.0	Fuel-rich air:	5.0
	acetylene	3.5	acetylene	4.0	acetylene	4.5
Slit width	160 μ					
Burner height	7 mm					
Detector	RCA lp 28 PM tube, 700 V					

and burner heights were used to seek an optimum flame condition for minimal cationic interference from concomitant ions.

Flame profiles

If the height of the area of maximum absorption in the flame depends on the rates of formation and depletion of the neutral atoms as stated by RANN AND HAMBLY[2], the formation of the calcium atoms near the burner head must be extremely high in a lean flame compared to other flame conditions. This may be attributed to less expansion of flame gases and higher flame temperature in that region of a lean flame. The sensitivity for calcium measured under this condition is quite comparable with that obtained in an optimum fuel-rich flame condition.

The sensitivity, however, decreases rapidly with the increase in the burner height in a lean flame. It appears that the recombination of the calcium atoms takes place very rapidly because of an abundance of oxygen and apparent greater expansion of flame gases in a higher region of the lean flame.

Anionic interferences

For the comparison of chemical interferences, a % difference in absorbances

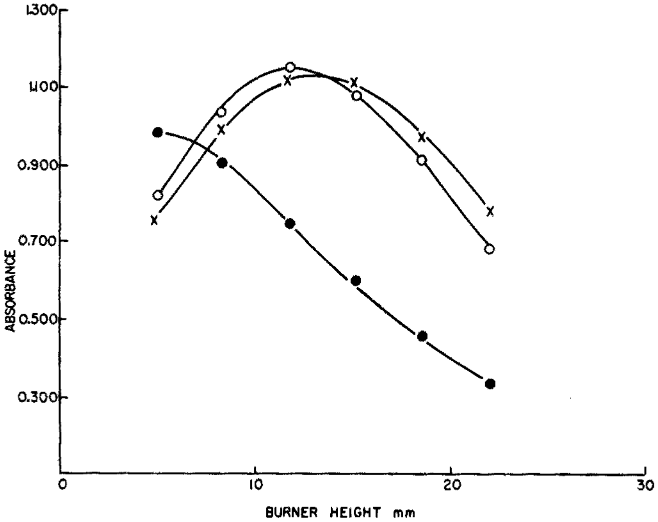

Fig. 1. Flame profiles of calcium absorbance in various flame conditions. (●) Lean flame; (×) stoichiometric flame; (○) fuel-rich flame.

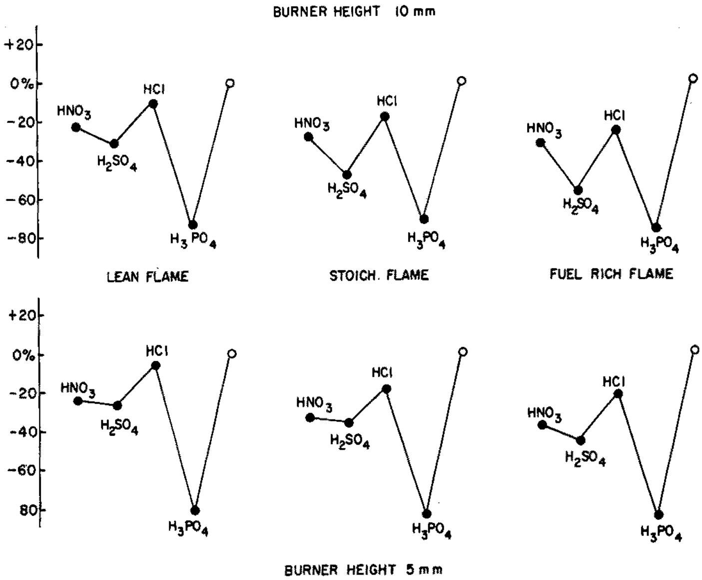

Fig. 2. Variations of the anionic interferences on calcium absorbances in various flame conditions at different burner heights.

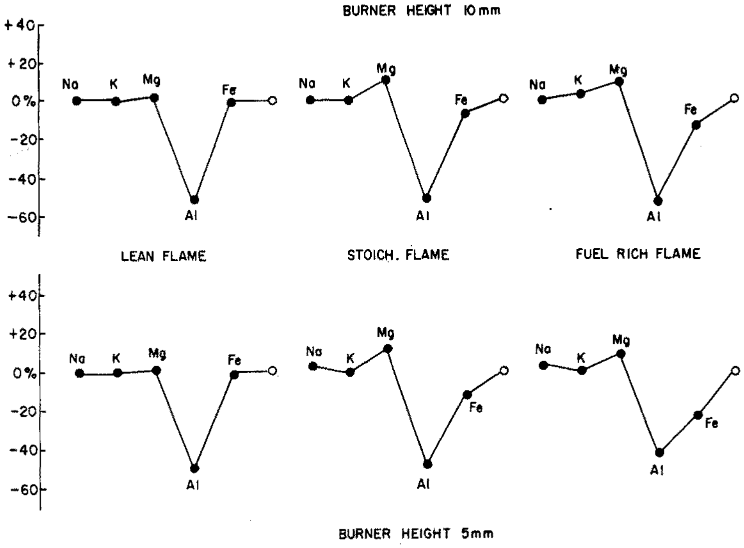

Fig. 3. Variations of the cationic interferences on calcium absorbances in various flame conditions at different burner heights.

greater than ±2 was considered significant. The depressive effects by anions were observed most in a fuel-rich flame, which gives the best sensitivity for calcium, and were reduced in a lean flame possibly owing to higher flame temperature, although the reduction of the anionic interferences was not as spectacular as that of cationic interferences in a lean flame. The burner height seemed to have no significant effect on chemical interferences.

The present work also confirms the previous observation[3] that the depressive effects decrease in the order: $PO_4^{3-} > SO_4^{2-} > NO_3^- > Cl^-$. It was found that this order remains the same regardless of the flame condition and burner height.

Cationic interferences

The depressive effects by aluminum and iron were observed in all flame conditions. The apparent higher flame temperature in a lean flame does not seem to be high enough to break the probable spinel structure, $CaO \cdot X_2O_3$. However, sodium, potassium and magnesium have no effect on calcium in a lean flame. In an attempt to explain the reduction or elimination of the chemical interferences, it is suggested that a higher flame temperature, reducing environment and shorter residence time of the oxide formed occur in a lean air–acetylene flame. Similar observations were also made for chromium, nickel, and manganese[4] in a lean flame.

Higher flame temperature could be expected because of the higher ratio of oxygen (air) to fuel (acetylene) in a lean flame. But elimination of the interference by a slight increase in flame temperature still needs justification. The overexcitation[5] process which takes place in flame emission spectroscopy appears to play an important role in furnishing higher flame temperature in a lean flame condition as follows: $C + XO \rightarrow CO + X$. If the flame temperature is high enough to prevent analyte atoms from oxide formation (analyte and analyte-interferent), minimum oxide formations can be logically expected, despite an abundance of oxygen from a lean flame, compared to a fuel-rich flame, in accordance with the mass-action law.

If, on the other hand, the primary reaction zone which was apparently utilized in the present study behaves as an arc, the higher populations of electrons will undoubtedly favor the existence of the neutral atoms. Finally, the reduction of interferences could also be explained by the incomplete evaporation of spray droplets near the burner head. Considering the largeness of the droplets and the higher flame temperature near the burner head in a lean flame, incomplete evaporation is not unusual and as a consequence a quicker evaporation leaves little chance for oxides formed to interact to cause the interelement effects.

In conclusion, a lean air–acetylene flame was found to be preferable to a fuel-rich flame in order to reduce chemical interferences, although the latter flame gives better sensitivity. More elaborate studies on flame temperature and flame environment of a lean flame are desirable in the application of the flame in atomic absorption spectroscopy.

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(Received June 21st, 1969)

Determination of rhenium and molybdenum and their separation from each other and other ions by internal electrolysis

Internal electrolysis is a very simple technique for the electrogravimetric determination of certain metal ions. In order to prevent cementation on the anode and to have a smooth and adherent deposit on the cathode in cells without a diaphragm, the choice of anode is restricted to those which have an electrode potential value about 0.4 V less than those of the metals to be deposited. These restrictions have limited the use of this technique to only a few separations.

When zinc, with an electrode potential of -0.76 V (*vs.* hydrogen electrode), is used as the anode, smooth adherent deposits of copper (electrode potential value of $+0.34$ V) cannot be obtained on a platinum cathode, unless a suitable complexing agent is present to reduce the potential to a more negative value. The complexing agent also masks the effect of interfering ions. Thus the use of complexing agents under proper pH conditions has allowed a few successful methods to be developed for determinations and separations of copper, cadmium, silver, bismuth, lead, antimony, cobalt, nickel, selenium, tellurium from each other and other ions[1].

In the present paper, methods are described for the separation and determination of rhenium and molybdenum in the presence of a large number of foreign ions, such as iron, aluminium, chromium, titanium, thorium, zirconium, uranium(VI) beryllium, zinc, manganese, tungsten(VI), vanadium(V), lanthanum, tantalum(V), alkali and alkaline earths, lead and cadmium.

Apparatus

The Cambridge pH indicator and the apparatus assembly consisting of a platinum gauze cathode and a zinc plate anode were the same as used earlier[1].

Standard solutions

Rhenium solution. By external electrolysis, rhenium is usually completely deposited from a 5% (v/v) sulphuric acid solution at room temperature by electrolysis overnight[2,3] or from a 1 *M* sulphuric acid solution maintained at 70–75° in 60–75 min with a rotating anode[4]. It was found that with a 2-V source, rhenium could be quantitatively deposited without stirring in 5 h from a 1 *M* sulphuric acid solution at room temperature. This observation was utilized in the standardisation of the rhenium solution prepared by dissolving potassium perrhenate in 1 *M* sulphuric acid solution.

Molybdenum solution. A standard solution was prepared by dissolving *ca.* 0.1362 g of ammonium molybdate in 100 ml of water containing about 2 ml of liquid ammonia (0.88), and standardizing by the oxine method[5].

Solutions of other metal ions were prepared and standardised as described previously[1].

Determination of rhenium

To the potassium perrhenate solution in a 400-ml beaker add 5 ml of concentrated hydrochloric acid and 2–3 g of potassium iodide, and boil to reduce rhenium(VII) to rhenium(IV). Remove the free iodine liberated with a few drops of 0.1 *N* sodium thiosulphate solution. Dilute to 250 ml and add EDTA (disodium salt) in an amount at least ten times the total quantity of metal ions present. Adjust the pH to 9–10 by dropwise addition of ammonia solution. Place the Pt–Zn electrode assembly in the solution for 2 h during which time rhenium is completely deposited on the platinum gauze cathode. Remove the electrode assembly and wash over the solution with a jet of water. Wash the cathode separately with ethanol, dry at 80–90° and weigh.

For all subsequent separations, the platinum cathode was cleaned with concentrated nitric acid, washed with water and alcohol, dried and weighed before use.

Typical results for pure rhenium solutions are shown in Table I. In studies of the separation of rhenium from mixtures of the foreign ions mentioned above, 20–40 mg of each diverse metal ion was added; in studies of the influence of a particular ion, at least 100–400 mg of the relevant metal ion was used. To this solution was added 4–5 g of potassium iodide and 10 ml of concentrated hydrochloric acid, and the above procedure was carried out, 2–3 g of EDTA being added. The results obtained for rhenium showed the same order of precision as those obtained for pure solutions (Table I).

TABLE I

DETERMINATION OF RHENIUM

pH	*Rhenium present (mg)*	*Rhenium found (mg)*	*pH*	*Rhenium present (mg)*	*Rhenium found (mg)*
9.0	4.3	4.28	9.5	2.15	2.12
9.0	2.15	2.11	10.0	4.3	4.28
9.5	4.3	4.27	10.0	4.3	4.27

Separation and determination of rhenium, lead and cadmium

To the solution containing the three metals, 5 ml of concentrated hydrochloric acid and 2 g of potassium iodide were added, and the procedure recommended for pure rhenium solutions was followed. After the deposition of rhenium, the residual solution containing lead and cadmium was evaporated to 250 ml and its pH was adjusted by dilute sulphuric acid to 2.5 for the deposition of lead and thence to 4.0 to remove cadmium[1]. The results are shown in Table II.

TABLE II

SEPARATION AND DETERMINATION OF RHENIUM, LEAD AND CADMIUM

Rhenium (mg)		*Lead (mg)*		*Cadmium (mg)*	
Present	*Found*	*Present*	*Found*	*Present*	*Found*
4.3	4.3	2.64	2.64	2.66	2.66
4.3	4.28	2.64	2.63	2.66	2.65
6.45	6.43	1.32	1.30	1.33	1.32

Determination of molybdenum

To the molybdate solution add dilute hydrochloric acid to make the solution 0.6 *M* in acid, and stir in 2–3 g of potassium iodide to reduce molybdenum(VI) to molybdenum(V). Remove the free iodine with 0.1 *N* sodium thiosulphate and add about 0.5 g of EDTA (disodium salt). Neutralize the solution with ammonia, dilute to 250 ml, adjust the pH to 8.0–10.0 and electrolyze for 12 h, during which time molybdenum is completely deposited. Remove, wash, dry and weigh the platinum cathode as described for rhenium.

Typical results are shown in Table III. Studies of the separation of molybdenum from other ions were made in the same way as described for rhenium; after adjustment of the acidity to 0.6 *M* hydrochloric acid and addition of 4–5 g of potassium iodide, the above method was followed, except that 2–3 g of EDTA was added. The results obtained were very similar to those shown in Table III.

TABLE III

DETERMINATION OF MOLYBDENUM

pH	*Molybdenum present (mg)*	*Molybdenum found (mg)*
8.0	7.2	7.16
8.0	7.2	7.15
9.0	3.6	3.55
9.0	3.6	3.57
10.0	7.2	7.18
10.0	7.2	7.2

Separation and determination of rhenium and molybdenum

To a solution containing potassium perrhenate and ammonium molybdate, add 5 ml of concentrated hydrochloric acid and 5 g of potassium iodide, and boil. Remove the liberated iodine with 0.1 *N* sodium thiosulphate solution. Add EDTA (disodium salt) and ammonium thiocyanate, each in amounts 10 times the total quantity of ions present, and boil again. Molybdenum forms the red thiocyanate complex. Dilute to 250 ml, and adjust the pH to 9.0–10.0; the colour changes to yellow. Then electrolyze the solution with the electrode assembly for 2 h for the deposition and determination of rhenium.

Dilute the remaining solution to 500 ml in a volumetric flask. Boil a suitable aliquot with 2 ml of concentrated nitric acid to decompose the thiocyanate complex of molybdenum; then fume with 2 ml of concentrated sulphuric acid. Dilute with water to give an acid strength of 3.6–5.4 *N*. Add 1 g of potassium iodide and titrate the liberated iodine with 0.1 *N* sodium thiosulphate solution.

TABLE IV

SEPARATION AND DETERMINATION OF RHENIUM AND MOLYBDENUM

Molybdenum present (mg)	*Molybdenum present in aliquot (mg)*	*Molybdenum found (mg)*	*Rhenium present (mg)*	*Rhenium found (mg)*
72.0	7.2	7.16	4.3	4.28
144.0	7.2	7.17	4.3	4.27
36.0	3.6	3.58	2.15	2.13

After the addition of 0.5 g of EDTA (disodium salt), dilute the solution to 250 ml, adjust the pH to 8.0–10.0, and deposit and determine molybdenum as described above.

Typical results for the separation of the metals are shown in Table IV.

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BOOK REVIEW

Electron Microscopy and Microanalysis of Metals, edited by J. A. BELK AND A. L. DAVIES, Elsevier Publishing Company, Amsterdam, 1968, xiv+264 pp., price Dfl. 47.50.

This book is primarily intended for student metallurgists and arises from two series of postgraduate lectures given at the University of Aston. It consists of twelve chapters by nine different authors. A grasp of basic physical principles is required of the reader but no prior knowledge of the techniques is assumed.

Almost inevitably in this type of compilation there are risks of omission and duplication. A consistent clarity of presentation is essential in a book intended for the non-specialist and is not always achieved in this case. On the one hand, the chapters on the use of the electron microscope for deformation and precipitation studies are very well presented; on the other, the description and illustration of the function of the condenser lens in the chapter on electron optics is confused and appears to be incorrect. Some of the photographs are poorly reproduced; what is described as "a simple transmission electron diffraction pattern" appears to consist of only two spots.

Whereas there are numerous other text books on electron microscopy to which the student can be directed, the same is not true of electron probe microanalysis. Shortcomings in this part of the book are thus doubly unfortunate, and no text on this subject can be complete without an adequate description of the correction theory required for quantitative measurements. Only in the last two years have opinions on this aspect converged and Chapter 10—evidently written before 1965, to judge by the references—has unhappily been overtaken by events. Some old errors are perpetuated (*e.g.* μ/ϱ for Al Kα in Al is given as 300 on one page and as 380 on another; 385 is a better value) and no clear guidance is given on the *preferred* correction method. The standard of presentation in this part of the book is again patchy. X-Ray images of a field are frequently displayed on different pages so that comparison is made difficult. The identity of the radiation used is not attached to each image as it should be and may be separated by as much as three pages.

A text of this nature is badly needed at the present time and in many respects this volume will be very helpful to students. It could have been more so.

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Short Communications

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