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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	
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SUMMARIES OF PAPERS PUBLISHED IN
ANALYTICA CHIMICA ACTA
Volume 45, No. 2, April 1969

THE ATOMIC FLUORESCENCE SPECTROSCOPY OF COBALT
WITH A HIGH-INTENSITY HOLLOW-CATHODE LAMP AND
A MICROWAVE-EXCITED ELECTRODELESS DISCHARGE
TUBE AS SOURCES

The fluorescence of cobalt atoms in air-hydrogen, air-propane and air-acetylene flames is described. Resonance fluorescence is obtained at 240.73, 242.49 and 252.14 nm with a high-intensity hollow-cathode lamp or a microwave-excited electrodeless discharge tube as source. Cobalt may be determined by E.D.T. excitation in the range 0.01-7.0 p.p.m. in aqueous solution with a detection limit of 0.005 p.p.m. at the 240.73 nm line. An oxidizing air-propane or air-hydrogen flame is best for atomic fluorescence measurements.

B. FLEET, K. V. LIBERTY AND T. S. WEST,
Anal. Chim. Acta, 45 (1969) 205-211

NEUTRON ACTIVATION ANALYSIS OF TRACES IN
ELECTROLYTIC ZINC SULPHATE SOLUTION

PART IV. SIMULTANEOUS DETERMINATION OF COBALT, CADMIUM, IRON
AND INDIUM

A neutron activation analysis for the simultaneous determination of cobalt, iron, indium and cadmium in electrolytic zinc sulphate solutions is described. The chemical separation, in hydrochloric acid medium, involved anion exchange followed by solvent extraction. Concentrations of 0.3 $\mu\text{g Co/ml}$, 25 $\mu\text{g Fe/ml}$ and 0.4 $\mu\text{g Cd/ml}$ were found. The concentration of indium was below the detection limit (0.01 $\mu\text{g/ml}$).

L. J. LIESSENS, R. DAMS AND J. HOSTE,
Anal. Chim. Acta, 45 (1969) 213-218

THE DETERMINATION OF CALCIUM AND MAGNESIUM IN
STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

A study was made of the determination of 1-200 $\mu\text{g/g}$ of total calcium and magnesium in steel by atomic absorption spectrophotometry. A direct procedure which avoided the use of glass apparatus was selected in order to avoid contamination problems which can occur with dissolution, separation and concentration techniques. Sodium and strontium ions are used to eliminate interferences and control the ionization of calcium and magnesium atoms in the nitrous oxide-acetylene flame. Investigations showed that although maximum sensitivity occurred in mixed air/nitrous oxide-acetylene flames, the higher temperature nitrous oxide-acetylene flame is required to overcome interferences. Results are presented for selected standard samples.

M. L. TAYLOR AND C. B. BELCHER,
Anal. Chim. Acta, 45 (1969) 219-226

ADHESION AND ADHESIVES

2nd, completely revised, edition

edited by R. Houwink and G. Salomon

Volume 1

Adhesives

7 × 10", xvi + 548 pages, 72 tables, 150 illus., 1965, £ 8.0.0, Dfl. 67.50, US \$24.00

The introductory chapter of this first volume is a concise guide to the scientific background of all adhesive processes. Surface science and bulk properties of solids, as related to adhesive bonding, are discussed and illustrated by recent examples from the technology of metals, glass, rubber and plastics. An annotated bibliography is provided for the reader who wants access to more highly specialized works. The further nine chapters, making up the volume, cover the basic materials used in adhesion technology. Greatest attention is paid to synthetic adhesives, especially the classical thermohardening and the new epoxy resins. Fields previously examined in the first edition have been extended, and a brief contribution added on the adhesion of glass and on glass-to-metal bonding.

CONTENTS:

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

Volume 2

Applications

7 × 10", xiv + 580 pages, 21 tables, 300 illus., 1966, £ 8.0.0, Dfl. 67.50, US \$24.00

In this second volume the main trends in industrial application are outlined by sixteen specialists. Assessment of surface geometry, choice of surface treatment, and selection of the most economical bonding process — the correct decision in each case is the basis for any successful engineering process. The introductory chapter deals with the general background; it links the two volumes and extends the annotated bibliography to 1966. Two compact "adhesives charts" facilitate the choice of a candidate adhesive and of processing methods. The work also contains a Subject Index to Volume 2 and an Author Index to both volumes.

CONTENTS:

Introduction. 11. Surface texture. 12. Surface treatment of adherends. 13. Adhesive bonding processes. 14. Wood, reconstituted wood and glued laminated structures. 15. Adhesive-bonded metal structures. 16. Bonded composite structures. 17. Pressure-sensitive adhesive tapes. 18. Rubber-textile structures. 19. The tack printing inks. 20. Adhesion in paint technology. 21. Miscellaneous applications. 22. Testing of adhesive joints. 23. Mechanical testing of bonded joints. Appendix: Adhesives charts. Subject index. Author index. Volumes 1 and 2.



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CATHODE-RAY-EXCITED EMISSION SPECTROSCOPIC
ANALYSIS OF TRACE RARE EARTHS
PART III. DETERMINATION OF TERBIUM

The technique of trace analysis of rare earths by cathode-ray-excited emission spectroscopy has been applied to the determination of terbium in an yttrium oxide matrix. With the 544-nm emission from terbium as the detection wavelength, and with high-resolution spectrometry, a detection limit of about 2 p.p.b. can be attained. The effect of sample firing temperature during diffusion and crystallization is treated in detail. Effects of other rare earth and first transition group interferences are discussed.

S. LARACH AND R. E. SHRADER,
Anal. Chim. Acta, 45 (1969) 227-232

THE POTENTIOMETRIC DETERMINATION OF FLUORINE
IN NUCLEAR FUEL REPROCESSING SOLUTIONS

The determination of fluoride in zirconium decladding (Zirflex) solutions, uranium feed solutions and uranium final product solutions is described. The procedures are based on potential measurements of a fluoride-sensitive electrode *versus* a saturated calomel electrode after a relatively simple pre-treatment of the sample, *e.g.* dilution, complexing of metal constituents or separation by a cation-exchange column.

H. H. PH. MOEKEN, H. ESCHRICH AND G. WILLEBORTS,
Anal. Chim. Acta, 45 (1969) 233-241

STUDIES WITH DITHIZONE. PART XIII. THE
EXTRACTION OF METHYL-, BENZYL-, AND
p-BROMOPHENYL-MERCURY(II) DITHIZONATES

1:1 Complexes are formed between dithizonate ions, HDz⁻, and certain organomercury cations, RHg⁺ (R = methyl, benzyl, and *p*-bromophenyl). Their absorption spectra in carbon tetrachloride and the effects of pH on the percentage extracted from aqueous buffers containing, or free from, auxiliary complexing agents have been studied. The anomalous behaviour previously reported could not be confirmed.

H. M. N. H. IRVING AND A. M. KIWAN,
Anal. Chim. Acta, 45 (1969) 243-248

A NEW OXIDATION PRODUCT OF DITHIZONE

The oxidation of dithizone with hydrogen peroxide in strongly alkaline solutions yields 1,5-diphenylformazan-3-sulphonic acid as a violet compound which loses a proton to give yellow solutions of the corresponding sulphonate ion and reddish-violet solutions on removal of a second proton from an imino-group. The acid dissociation constants $pK_1 = -0.92$ and $pK_2 = 12.9$ ($\mu = 1 M NaNO_3$) were determined spectrophotometrically.

H. M. N. H. IRVING, D. C. RUPAINWAR AND S. S. SAHOTA,
Anal. Chim. Acta, 45 (1969) 249-254

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INTRODUCTION TO NUCLEAR CHEMISTRY

by D. J. CARSWELL

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

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STATISTICAL THERMODYNAMICS

An Introduction to its Foundations

H. J. G. HAYMAN

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

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

THE STRUCTURE OF INORGANIC RADICALS

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

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

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


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

FUNDAMENTALS OF METAL DEPOSITION

by E. RAUB and K. MÜLLER

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

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

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STUDIES WITH DITHIZONE. PART XV. FURTHER REACTIONS WITH ORGANOMERCURY COMPOUNDS

The reactions between dithizone and a wide variety of organomercurials of general formula $R \cdot Hg^+ X^-$ have been investigated. The intensely coloured complexes of formula $R \cdot Hg(HDz)$ that are formed in acid solution can be extracted quantitatively in an organic phase and used for the absorptiometric determination of the parent mercurial. Extractabilities, absorption spectra and molar extinction coefficients are reported and discussed in relation to the nature of the organic radical R attached to the mercury(II) ion.

H. M. N. H. IRVING AND A. M. KIWAN,
Anal. Chim. Acta, 45 (1969) 255-269

STUDIES WITH DITHIZONE. PART XVI. WATER-SOLUBLE ARYLMERCURY(II) DITHIZONATES AND SECONDARY ARYLMERCURY(II) DITHIZONATES

Arylmercury(II) cations containing carboxy groups form with dithizone yellow 1 : 1 complexes of the type $HOOC \cdot R \cdot Hg(HDz)$ which can be extracted quantitatively into carbon tetrachloride over a wide pH range. In alkaline media, water-soluble yellow complexes $-OOC \cdot R \cdot Hg(HDz)$ are formed and in strongly alkaline solutions these ionise further to give magenta-coloured anions, $-OOC \cdot R \cdot Hg(Dz)^-$. Phenylmercury(II) dithizonate, $PhHg(HDz)$, ionises in very alkaline solution to give the magenta anion $PhHg(Dz)^-$ and the acid dissociation constant, $pK = 11.5$ (in 36-53% v/v ethanol-water; $\mu = 0.1 M NaClO_4$) was determined spectrophotometrically. In alkaline solution and in the presence of excess of organomercurial, dithizone yields a series of secondary dithizonates which are less stable and less soluble in organic solvents than the corresponding primary complexes; their spectra were recorded.

H. M. N. H. IRVING AND A. M. KIWAN,
Anal. Chim. Acta, 45 (1969) 271-277

1-[(5-BROMO-2-PYRIDYL)AZO]-2-NAPHTHOL AS A POSSIBLE NEW CHROMOGENIC REAGENT

The heterocyclic azo compound, 1-[(5-bromo-2-pyridyl)azo]-2-naphthol (5-Br- β -PAN), forms various coloured metal chelates, which can be extracted with different organic solvents. Most of the reacting metals form reddish chelates, except for cobalt(III) and palladium(II) (green), and vanadium(V) (olive). Chelate stability is greatly affected by pH. The molar absorptivities are usually considerably greater than those of the β -PAN chelates. A correct choice of pH, solvent and masking reagents allows 5-Br- β -PAN to be made reasonably selective.

S. SHIBATA, K. GOTO AND E. KAMATA,
Anal. Chim. Acta, 45 (1969) 279-288

Molecular Vibrations and Mean Square Amplitudes

by SVEN J. CYVIN

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

The book reviews completely the previous work on mean amplitudes of vibration, including 476 references. Furthermore the spectroscopic analysis of harmonic vibrations of polyatomic molecules is reconsidered. The survey includes

known methods based on the Wilson G and F matrices, but also supplementary aspects and new material, particularly as regard to the compliants ('inverse' force constants), Coriolis coupling and Σ matrices.

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

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

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

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

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

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



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THE USE OF TERTIARY AROMATIC AMINES IN THE EXTRACTION OF URANIUM FROM NEUTRAL AND ACIDIC MEDIA

(in German)

Tertiary aromatic amines behave in different ways in the extraction of uranium(VI). In neutral media all the amines tested show more or less high extractabilities. In acidic media, turbidities are obtained in some cases, and reasonable extractions in other cases. The more distant the nitrogen from the amine nucleus, or the more ramified the chain, the better is the extraction. Out of 21 amines examined, 3-(dimethylamino)-methylindole in chloroform proved to be the best extracting agent.

E. GAGLIARDI AND G. HEROLD,
Anal. Chim. Acta, 45 (1969) 289-296

EXTRACTION OF PLATINUM METALS BY HIGH-MOLECULAR-WEIGHT AMINE-RHODIUM(III) SYSTEMS

The complexes formed by rhodium(III) and tin(II), and by rhodium(III) in hydrochloric acid solutions and their extractability by tri-*n*-octylamine have been studied. Hydrochloric acid solutions of rhodium(III) developed a red colour when heated with tin(II) chloride, but a yellow species was obtained by dilution of solutions of the red complex with water. By heating rhodium(III) with tin(II) in 7-11.6 *M* hydrochloric acid, the yellow species was obtained directly in aqueous solution. A procedure was developed for the extraction of the yellow complex from aqueous solution with tri-*n*-octylamine. A mechanism for the extraction of both species is proposed. The extractabilities of the Rh(III)-HCl, Pt(IV)-HCl and Pd(II)-HCl systems by tri-*n*-octylamine depend on the hydrochloric acid concentration; rhodium could be separated from platinum and palladium leading to a sensitive, reproducible analytical method for the determination of rhodium by means of the extracted yellow complex in tri-*n*-octylamine.

M. A. KHATTAK AND R. J. MAGEE,
Anal. Chim. Acta, 45 (1969) 297-304

VOLATILE CHELATES OF THE ALKALI METALS

Alkali metal derivatives of pentafluorodimethylheptan-3,5-dione and heptafluorodimethyloctan-4,6-dione are described. Their mass spectra were examined and the integrated ion-current technique was used to determine quantities of the alkali metal chelates down to 10^{-9} g. The volatility and stability of these chelates were studied. Gas chromatographic separation of mixtures of alkali metal β -diketonates does not appear to be feasible because of undesirable exchange reactions.

R. BELCHER, J. R. MAJER, R. PERRY AND W. I. STEPHEN,
Anal. Chim. Acta, 45 (1969) 305-309

SPOT TESTS IN ORGANIC ANALYSIS

Seventh English Edition, completely revised and enlarged

by FRITZ FEIGL in collaboration with VINZENZ ANGER

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

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

Comparison with the 6th edition reveals the following differences:

	Number in	
	6th Edn.	7th Edn.
Preliminary tests	32	45
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In total the book now gives in 561 sections information on more than 900 tests compared with 600 tests in 346 sections in the preceding edition.

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

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

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THE USE OF TRILAURYLAMINE IN PARTITION CHROMATOGRAPHY

PART I. THE SEPARATION OF NEPTUNIUM FROM CONCENTRATED URANIUM SOLUTIONS

(in French)

The partition of neptunium(IV) between nitric acid-uranyl nitrate solutions and Kel-F powder coated with a trilaurylammonium nitrate solution has been studied in order to determine the optimum operating conditions for separating neptunium from uranium. The reversed-phase partition chromatography was performed by passing a 2 N HNO₃-0.1 M iron(II) solution containing up to 100 g.l⁻¹ of uranium, through a column of TLA-HNO₃-Kel-F beads. After washing the column with N nitric acid containing iron(II) sulphamate, the neptunium is eluted with a sulfuric acid-nitric acid mixture. The method is very selective for neptunium(IV), and allows a good separation from fission products, plutonium and uranium. It has been applied to solutions in which the weight ratio U/Np is greater than 10¹⁰, and to the preparation of radiometrically pure ²³⁹Np.

D. GOURISSE AND A. CHESNÉ,
Anal. Chim. Acta, 45 (1969) 311-319

THE USE OF TRILAURYLAMINE IN PARTITION CHROMATOGRAPHY

PART II. SIMULTANEOUS SEPARATION OF NEPTUNIUM AND PLUTONIUM FROM URANIUM

(in French)

A simultaneous separation of neptunium and plutonium from uranium is proposed, involving the partition of these two elements between a column of Kel-F coated with a trilaurylammonium nitrate solution and aqueous nitrate solutions. Neptunium(IV) and plutonium(IV) are fixed from a nitrate solution containing iron(II)-iron(III) to adjust the valence states. After washing the column with nitric and chlorhydric solutions, the neptunium and plutonium are eluted with a sulfuric-nitric acid mixture, and the analysis is completed by α -radiometry.

D. GOURISSE AND A. CHESNÉ,
Anal. Chim. Acta, 45 (1969) 321-325

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF COBALT IN VARIOUS MATERIALS WITH ZINC DIETHYLDITHIOCARBAMATE

Cobalt is extracted with a benzene solution of zinc diethyldithiocarbamate. The excess of reagent and metals such as copper and nickel extracted with cobalt are removed by washing the organic phase with potassium cyanide solution. Other metals such as bismuth and lead are replaced by copper by shaking the organic phase with copper sulfate solution; the copper in the organic phase is removed by potassium cyanide solution. The absorbance of cobalt diethyldithiocarbamate in the organic phase is then measured at 325 nm. Down to 1 μ g of cobalt in a few grams of uranium, thorium, aluminum, beryllium and zirconium can be readily determined.

K. MOTOJIMA AND N. TAMURA,
Anal. Chim. Acta, 45 (1969) 327-332

INORGANIC ELECTRONIC SPECTROSCOPY

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

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

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

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

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

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

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

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

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



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SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN
MIXED OXIDE (U-Pu)O₂ SAMPLES

(Short Communication; in French)

T. ARNAL,
Anal. Chim. Acta, 45 (1969) 333-336

NEUTRON ACTIVATION ANALYSIS OF HIGH-PURITY
SELENIUM. PART IV. SIMULTANEOUS DETERMINATION OF
CHLORINE, BROMINE AND IODINE

(Short Communication)

C. BALLAUX, R. DAMS AND J. HOSTE,
Anal. Chim. Acta, 45 (1969) 337-340

A RAPID METHOD FOR THE DETERMINATION OF
FLUORINE IN SILICATE ROCKS AND MINERALS

(Short Communication)

A. HALL AND J. N. WALSH,
Anal. Chim. Acta, 45 (1969) 341-342

A RAPID DIMETHYLGLYOXIME METHOD FOR THE
DETERMINATION OF NICKEL(II) IN SEA WATER

(Short Communication)

E. KENTNER, D. B. ARMITAGE AND H. ZEITLIN,
Anal. Chim. Acta, 45 (1969) 343-346

UTILIZATION OF SURFACTANTS IN A.C. POLAROGRAPHIC
ANALYSIS

(Short Communication)

N. GUNDERSEN AND E. JACOBSEN,
Anal. Chim. Acta, 45 (1969) 346-350

DETERMINATION OF NITRATE IN SEA WATER

(Short Communication)

K. MATSUNAGA AND M. NISHIMURA,
Anal. Chim. Acta, 45 (1969) 350-353

DETERMINATION OF TRACES OF SELENOCYANATE

(Short Communication)

K. VASUKI, M. L. SHANKARANARAYANA AND S. K. MAJUMDER,
Anal. Chim. Acta, 45 (1969) 353-354

Photoluminescence of Solutions

With Applications to Photochemistry and Analytical Chemistry

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

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

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

Comprehensive Analytical Chemistry

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

VOLUME IIB: Physical Separation Methods

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

Volume Two, Part B is devoted to physical separation methods. After an account of the theory and practise of liquid chromatography in columns, the volume continues with a lengthy treatment of gas chromatography.

The next chapter, on ion exchangers, is notable for the account it gives of analytical applications, while distillation (theory and technique) is the last topic to be treated in the present volume.

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

Atomic-Absorption Spectroscopy

and Analysis by Atomic-Absorption Flame Photometry

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

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

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



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RAPID SOLVENT EXTRACTION OF TITANIUM(IV) WITH
TRIBUTYL PHOSPHATE

(Short Communication)

A. A. YADAV AND S. M. KHOPKAR,
Anal. Chim. Acta, 45 (1969) 355-357

DETECTION OF HALOGEN-SUBSTITUTED ALDEHYDES

(Short Communication)

T. J. NOVAK AND E. J. POZIOMEK,
Anal. Chim. Acta, 45 (1969) 358-360

OSCILLOPOLAROGRAPHIC DETERMINATION OF GERMANIUM

(Short Communication)

H. ALFARO J., G. DONOSO N. AND O. PLATTEAU V.,
Anal. Chim. Acta, 45 (1969) 360-363

Pigments

An Introduction to their Physical Chemistry

edited by **David Patterson**

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

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

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

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

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

by H. R. C. Pratt

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

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

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

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

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

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



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Other sections are planned on heterogeneous reactions, solid state reactions, and kinetics and technological processes.

THE ATOMIC FLUORESCENCE SPECTROSCOPY OF COBALT WITH A HIGH-INTENSITY HOLLOW-CATHODE LAMP AND A MICROWAVE-EXCITED ELECTRODELESS DISCHARGE TUBE AS SOURCES

B. FLEET, K. V. LIBERTY AND T. S. WEST

Chemistry Department, Imperial College, London, S.W. 7 (England)

(Received January 10th, 1969)

It has been demonstrated in recent years that atomic fluorescence spectroscopy (a.f.s.) in flames may be expected to provide an analytical technique of greater sensitivity than atomic absorption spectroscopy (a.a.s.) for a wide range of elements.

The choice of the irradiating source is of primary importance and two main solutions have been offered.

1. A source of continuous radiation emitted over a wide spectral region, *e.g.* the high-pressure xenon-arc lamp which has been utilized in the determination of a large number of elements^{1,2}.

2. A source emitting the atomic line spectrum characteristic of the specific element concerned, *e.g.* vapour discharge lamps^{3,4}, hollow-cathode lamps^{5,6} and microwave-excited electrodeless discharge tubes^{7,8}.

Of these alternatives, it was clear that continuous sources, although offering wide utility, could not for obvious reasons compete in terms of sensitivity with the more intense atomic line sources. Employing a 150-W xenon-arc lamp as source, for example DAGNALL, THOMPSON AND WEST² obtained detection limits for cobalt, at the 240.7 nm resonance line, of 1.5 p.p.m. and 1.0 p.p.m. in the air-propane and air-hydrogen flames respectively.

Vapour discharge lamps are not generally applicable as they may be obtained only for a very limited number of elements, *e.g.* Cd, Zn, and Hg. These lamps may also be unsatisfactory as they may suffer from substantial self-reversal of the resonance lines.

High-intensity hollow-cathode lamps of the type designed by SULLIVAN AND WALSH⁹ have been used with considerable success in the a.f.s. determination of silver and magnesium^{6,10} and also in the a.f.s. determination of nickel⁵.

The apparatus necessary for the construction of microwave-excited electrodeless discharge tubes has been described previously⁷. WINEFORDNER *et al.*⁸ have used a cobalt iodide electrodeless discharge tube to obtain fluorescence signals for cobalt in the oxyhydrogen flame, achieving a detection limit of 2 p.p.m.

It was decided in this work, therefore, to use a high-intensity hollow-cathode lamp and to explore further the potentialities of microwave-excited electrodeless discharge tubes for cobalt. Various flame compositions were investigated in order to attain maximum sensitivity.

EXPERIMENTAL

Apparatus

The apparatus consisted of a Techtron AA4 atomic absorption spectrometer fitted with a 3 nm/min wavelength scan motor and with the output coupled to a Servoscribe flat-bed potentiometric strip-chart recorder. For experiments involving electrodeless discharge tubes (2450 MHz), the Techtron indicator unit was modified to receive unmodulated signals, and for experiments with a hollow-cathode lamp both source and amplifier were modulated at 285 Hz. Sources used were an ASL high-intensity cobalt hollow-cathode lamp operated by the Techtron power supply units, and discharge tubes operated by a 2450 MHz "Microtron 200" high-frequency generator, employing a model 210 L ($\frac{3}{4}$ wave) microwave cavity.

The burner heads used were the Techtron air-propane emission head and the Unicam air-acetylene emission head fitted to the instrument by a suitable adapter.

Reagents

Cobalt chloride hexahydrate, analytical grade; cobalt metal, electrolytic grade.

A 100 p.p.m. cobalt stock solution was prepared by dissolving 0.4037 g of cobalt chloride hexahydrate in distilled water and diluting to 1 l. More dilute solutions were prepared, as required, by appropriate dilution of the stock.

Preparation of electrodeless discharge tubes

Discharge tubes were prepared⁷ containing cobalt iodide or cobalt chloride both with argon filler gas. The cobalt chloride was preferred as these tubes were more intense and stable, also there was less attack on the inner walls of the tube with, accordingly, a longer operating lifetime. A suitable discharge tube was prepared by placing *ca.* 1.5 mg of cobalt chloride hexahydrate and 0.1 mg of cobalt metal in a sealed-off quartz tube of 0.8-cm nominal internal bore and dehydrating the material under vacuum with gentle warming. After dehydration was complete, the cobalt chloride was sublimed 1 cm up the walls of the tube and the bulb was sealed-off under 5-torr argon pressure. The total length of the bulb was 5 cm. The small amount of metallic cobalt was added in order to minimise decomposition of the cobalt chloride at the high operating temperatures employed.

Operating conditions of atomic spectral sources

In order to maintain a stable and intense discharge, the discharge tube was operated at *ca.* 60 W. Below *ca.* 50 W the output became unstable and the tube flickered, whilst above *ca.* 70 W an air-blast cooling of the cavity was required and this tended to reduce stability of operation.

Maximum intensity of emission was obtained from the high-intensity hollow-cathode lamp by using the maximum operating currents recommended by the manufacturers, *i.e.* 20 mA cathode current and 400 mA secondary current. Table I clearly shows that the ratio between lamp output (on the 240.7 nm line), with and without secondary electrode operation, increases at lower slit widths. Thus the effect of the secondary discharge was to increase overall light output and also to achieve a sharper line source, both being advantageous factors in a.f.s. work.

TABLE I

COMPARISON OF LAMP OUTPUT AT 240.7 nm WITH AND WITHOUT SECONDARY CURRENT OPERATION AT DIFFERENT SLIT WIDTHS

Slit width (μ)	Lamp output ^a (meter deflection in scale divisions)		Ratio B/A
	A ^b	B ^c	
100	20.0	100	5.0
50	17.5	100	5.7
25	15.0	100	6.7
10	11.0	100	9.1

^a The E.H.T. supply to the photomultiplier tube was constant for each pair of readings.^b Operation of hollow cathode only.^c Operation of hollow cathode and secondary discharge.

TABLE II

MAJOR RESONANCE LINE EMISSION FROM THE COBALT CHLORIDE MICROWAVE-EXCITED DISCHARGE TUBE AND THE ATOMIC FLUORESCENCE SPECTRUM PRODUCED BY COBALT ATOMS IN AN AIR-PROPANE FLAME^a

Atomic line (nm)	Relative intensity	A.f.s. relative intensity
240.73 ^b	62	100
241.16	35	
241.45 ^c	37	
241.53		
242.49 ^b	34	50
243.22	20	
252.14 ^b	47	39
252.90	27	
340.51 ^b	82	
341.23 ^d ^e	82	
341.26		
345.35 ^b ^c	100	
345.52		
352.68 ^c	110	
352.90		
352.98		
353.34 ^b	32	

^a The values of relative intensity are uncorrected for detector response, and the two scales of relative intensity are not directly comparable.^b Line used in a.a.s.^c Lines unresolved by monochromator.^d Intercombination line.

Both sources emitted a typical cobalt atomic line spectrum with similar *relative* line intensities, but the discharge tube exhibited less extraneous background radiation and sharper line profiles, and presented a cleaner overall spectrum in the range 220–366 nm. A direct comparison of the emission intensity, at 240.7 nm, of these two sources when focussed directly on a 25- μ slit from a distance of 38 cm showed a ratio of *ca.* 20:1 in favour of the discharge tube.

The output stability of the sources on the 240.7 nm line was measured by allowing each source to warm up under full operating conditions for 45 min followed

by recording a time *vs.* intensity plot for 1 h. The electrodeless discharge tube had zero drift over 1 h with a $\pm 1.25\%$ scatter, whereas the high-intensity hollow-cathode lamp had *ca.* 3% drift over 1 h with very little deviation from the straight line.

Choice of atomic line

Atomic cobalt possesses a large number of resonance lines of which several have been used in atomic absorption studies, *e.g.* the lines at 240.73, 242.49, 252.14, 340.51, 345.35 and 353.34 nm. Of these the 240.7 nm line is most sensitive in absorption and is the only line for which fluorescence measurements have previously been made^{2,8}.

Table II shows the major resonance lines emitted by the cobalt discharge tube; the cobalt atomic fluorescence spectrum obtained for a discharge tube, with an air-propane flame by aspirating cobalt chloride solution is also given. It is immediately clear that the most sensitive signals are obtained by resonance fluorescence at 240.7 nm. Other strong fluorescence lines occur at 242.5 nm and 252.1 nm, but signals obtained in the region 340–360 nm are weak and the lines are ill-defined.

Where resonance lines occur close together, they may be resolved, when viewed directly, with a 25- μ slit width (equivalent to 0.08 nm optical slit width), but the atomic fluorescence produced by these lines may not be resolved at the 300- μ slit width (0.99-nm optical slit width) which was used in the analytical procedure. Additionally further line broadening would be expected to occur because of the nature of the flame as an atom reservoir. Thus the strong resonance lines at 240.73, 241.16, 241.45 and 241.53 appear as one broad line in analytical fluorescence as measured here, with the 242.49 nm line being resolved.

Choice of flame

Three flame compositions were considered suitable for the a.f.s. study of cobalt. Of these, the air-propane and air-acetylene flames were known to afford approximately equal sensitivity in atomic absorption, whilst the air-hydrogen flame has shown wide utility in atomic fluorescence work. The air-propane flame was maintained on the standard Techtron air-propane emission burner head, and the air-acetylene and air-hydrogen flames on a Unicam air-acetylene emission burner head modified with a brass collar to fit the Techtron atomiser-burner unit.

The emission spectrum for each type of flame was recorded over the region 220–360 nm, the same burner position and the same instrumental settings being used where possible. It was found that above *ca.* 260 nm the air-propane flame displayed considerably higher background radiation than the air-hydrogen flame; however, at 240–250 nm both flames exhibited a very low and almost identical background plot. In contrast, the background arising from the air-acetylene flame was very much higher in all regions of the spectrum and considerable backing off of the meter was required even at 240 nm. It was considered, therefore, that the air-propane and air-hydrogen flames would be more suitable for use with the Techtron in an unmodulated mode, *i.e.* with discharge tubes which at 2450 MHz appear as virtually continuous sources to the Techtron AA4 detection system, whereas all three flames should be suitable for a modulated source and detector, *e.g.* with the hollow-cathode lamp.

In all cases it was found that a lean (oxidizing) flame afforded optimal fluorescence signals.

Photomultiplier gain and slit width

Because the cobalt fluorescence emission was spread over a region of *ca.* 0.8 nm, and because the flame background emission in this narrow region was relatively low, it was advantageous to use the maximum available slit width of 300 μ . Maximum photomultiplier E.H.T. supply was used to obtain best sensitivity and detection limits could be improved by a factor of *ca.* 3 employing the $\times 5$ scale expansion facility provided.

Atomic fluorescence measurements for a hollow-cathode lamp

For both types of burner used, the centre of the head was placed 2.5 cm from the monochromator slit and the area just above the primary cones was viewed. This area of the flame, which was found to give best sensitivity, was irradiated by the hollow-cathode lamp situated in a position such that it subtended a 90° angle with the slit at the centre of the flame. The quartz window of the lamp was situated at a distance of *ca.* 2.5 cm from the centre of the flame. Because of the crowded geometrical arrangement required, attempts to focus the source emission at the centre of the flame by lenses proved impracticable and no improvement in sensitivity was achieved thereby.

Instrumental settings. Primary lamp current, 20 mA; booster current, 400 mA; wavelength, 240.7 nm; slit width, 300 μ ; E.H.T., maximum; scale expansion, $\times 5$; air pressure, 15 p.s.i.g.; fuel gas pressure, sufficient to give a stable, lean flame.

Calibration curves were prepared in the usual way for aqueous solutions; figures for analytical range and limit of detection are given in Table III.

TABLE III

ANALYTICAL RANGE AND DETECTION LIMITS* FOR THE A.F.S. OF COBALT AT 240.7 nm IN AIR-PROPANE, AIR-HYDROGEN AND AIR-ACETYLENE FLAMES

<i>Hollow cathode</i>			<i>Discharge tube</i>		
<i>Fuel gas</i>	<i>Limit of detection (p.p.m.)</i>	<i>Analytical range (p.p.m.)</i>	<i>Fuel gas</i>	<i>Limit of detection (p.p.m.)</i>	<i>Analytical range (p.p.m.)</i>
Propane	0.20	0.5-4.0	Propane	0.005	0.01-0.20
Hydrogen	0.20	0.5-4.0	Hydrogen	0.005	0.01-0.20
Acetylene	0.33	0.8-7.0	Acetylene	0.01	0.02-0.35
			Propane	0.015 ^b	0.03-1.00

* Detection limit defined as that concentration of cobalt, in p.p.m., which corresponds to a signal: noise ratio of 2:1.

^b Without scale expansion.

Atomic fluorescence measurements for a discharge tube

The burner arrangement used with the hollow-cathode lamp was retained, with the electrodeless discharge tube and microwave cavity placed opposite the flame in the same 90° angle arrangement as before. The source was distant *ca.* 11 cm from the centre of the flame, *i.e.* the shortest light path compatible with the construction of the Techtron atomiser-burner unit and the 210 L microwave cavity.

In this case, it was beneficial to focus the radiation from the source into the flame by means of a fused silica lens of 6.4 cm focal length; a 2-fold increase in sensitivity was obtained.

Instrument settings. E.D.T. operated at 60 W; instrument unmodulated in the amplifier stage and used with and without $\times 5$ scale expansion; all other settings as before.

Results are recorded in Table III.

Effect of foreign ions

The effect was studied of a 100-fold excess (by weight) of a selected range of cations on the a.f.s. determination of a 0.1-p.p.m. cobalt solution in the air-propane flame with a discharge tube as source. The results are summarized in Table IV. No negative interference was noticed and the small positive interferences can probably be ascribed to increased background radiation in the flame.

TABLE IV
INTERFERENCE EFFECTS IN A.F.S. OF COBALT (0.1 p.p.m.) AT 240.7 nm IN AIR-PROPANE FLAME

<i>Element (100-fold excess)</i>	<i>Signal intensity</i>	<i>Error (%)</i>	<i>Element (100-fold excess)</i>	<i>Signal intensity</i>	<i>Error (%)</i>
—	40	—	Sr ²⁺ (Sr(NO ₃) ₂)	40	0
K ⁺ (KNO ₃)	40	0	Zn ²⁺ (ZnSO ₄)	41	+2.5
Fe ³⁺ (FeCl ₃)	40	0	Cu ²⁺ (CuSO ₄)	42	+5
Cr ³⁺ (CrCl ₃)	42	+5	Sn ²⁺ (SnCl ₂)	42	+5
Ca ²⁺ (Ca(NO ₃) ₂)	40	0	Mn ²⁺ (MnSO ₄)	42	+5
Al ³⁺ (AlCl ₃)	41	+2.5	Ni ²⁺ (NiSO ₄)	40.5	+1.25

Atomic absorption of cobalt

In previous work with the same instrumentation¹¹, the sensitivity achieved by atomic absorption with the Techtron AA4 with 10-cm slot burner and the air-propane flame was 0.10 p.p.m. cobalt (aqueous) for 0.005 absorbance unit. A slit width of 25 μ was employed. It was thought that a further decrease in the slit width to (say) 10 μ would achieve even greater sensitivity, and the discharge tube would provide the very intense line source required. Unfortunately, no improvement in absorption sensitivity was obtained, although it was possible to use a lower E.H.T. setting, and obtain a better detection limit.

DISCUSSION AND CONCLUSIONS

The atomic fluorescence determination of cobalt is possible by means of the resonance re-radiation at the 240.73, 242.49 and 252.14 nm lines; the lines are listed in order of decreasing sensitivity. Determinations were made with a modulated source (hollow-cathode lamp) and tuned amplifier and also an unmodulated source (an E.D.T.) and amplifier. The expected improvement in noise levels when modulation was used, was not realised and the far greater intensity of the microwave-excited electrodeless discharge tube proved to be decisive in obtaining highest sensitivity.

The air-hydrogen flame offered no advantage over the air-propane flame in the spectral region used, but both surpassed the air-acetylene flame which possessed much higher background noise.

The method described provides a very sensitive technique for the trace determination of cobalt with relative freedom from interference. The limit of detection

(0.005 p.p.m.) compares favourably with those previously quoted for atomic fluorescence (1.0 and 1.5 p.p.m. and 2.0 p.p.m.) and atomic absorption (0.1 p.p.m.).

We are grateful to A.W.R.E. (Aldermaston) for financial support for this programme and to the Courtauld Educational Trust for a grant for the purchase of the atomic absorption spectrophotometer used in this study.

SUMMARY

The fluorescence of cobalt atoms in air-hydrogen, air-propane and air-acetylene flames is described. Resonance fluorescence is obtained at 240.73, 242.49 and 252.14 nm with a high-intensity hollow-cathode lamp or a microwave-excited electrodeless discharge tube as source. Cobalt may be determined by E.D.T. excitation in the range 0.01–7.0 p.p.m. in aqueous solution with a detection limit of 0.005 p.p.m. at the 240.73 nm line. An oxidizing air-propane or air-hydrogen flame is best for atomic fluorescence measurements.

RÉSUMÉ

On décrit la fluorescence des atomes de cobalt dans les flammes air-hydrogène, air-propane et air-acétylène. La fluorescence de résonance est obtenue à 240.73, 242.49 et 252.14 nm avec, comme source, une lampe à cathode creuse de forte intensité ou un tube à décharge excité sans électrode (E.D.T.). Par excitation E.D.T. le cobalt peut être dosé entre 0.01–7.0 p.p.m. en solution aqueuse avec une limite de détection de 0.005 p.p.m. à 240.73 nm. Ce sont les flammes air-propane ou air-hydrogène qui conviennent le mieux pour ces mesures de fluorescence atomique.

ZUSAMMENFASSUNG

Die Fluoreszenz von Kobaltatomen in Luft-Wasserstoff-, Luft-Propan-, und Luft-Acetylen-Flammen wurde beschrieben. Bei Verwendung einer hochintensiven Hohlkathodenlampe und einer durch Mikrowellen angeregten elektrodenlosen Entladungsröhre, treten Resonanzfluoreszenzen bei 240.73, 242.49 und 252.14 nm auf. Kobalt kann durch E.D.T.-Anregung im Bereich von 0.01–7.0 p.p.m. in wässriger Lösung mit einer Nachweisgrenze von 0.005 p.p.m. bei 240.73 nm bestimmt werden. Die oxydierenden Luft-, Propan- oder Wasserstoff-Flammen sind für die Atomfluoreszenz am besten geeignet.

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NEUTRON ACTIVATION ANALYSIS OF TRACES IN ELECTROLYTIC ZINC SULPHATE SOLUTION

PART IV. SIMULTANEOUS DETERMINATION OF COBALT, CADMIUM, IRON AND INDIUM

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In previous studies¹⁻³ of the analysis of zinc sulphate solutions, the determinations of mercury, uranium, ytterbium, molybdenum, rhenium, tellurium, selenium, arsenic and antimony by activation analysis have been described, because several of these elements are known as inhibitors in the electrolysis of zinc. Empirically^{4,5}, it has been shown that the presence of cadmium and cobalt also affects unfavourably the deposition of zinc. In the present work the determination of cobalt and cadmium was studied simultaneously with the determination of iron and indium.

Activation analyses for cadmium, indium and cobalt in zinc, and for indium in zinc salts, have been described in the literature⁶⁻¹⁰. No determination of these elements in zinc sulphate solutions appears to have been reported and no simultaneous determination of the four elements in a zinc matrix has been described. Nevertheless, neutron activation analysis for cobalt, iron, indium and cadmium in presence of zinc can be performed simultaneously if adequate chemical separation methods are elaborated. Elution from anion-exchange resin with successively more dilute hydrochloric acid allows a separation of these four elements. Radiochemically pure fractions are obtained through further chemical separations.

Nuclear data

From Table I it is obvious that activation of cobalt gives rise to the isotope ⁶⁰Co

TABLE I
 MOST IMPORTANT NUCLEAR PROPERTIES

<i>Natural isotope</i>	<i>Abundance</i>	<i>Thermal activation cross section (barn)</i>	<i>Isotope formed</i>	<i>Half-life</i>	<i>Most important γ-energies (keV)</i>
⁵⁹ Co	1.00	20	⁶⁰ Co	5.2 y	1173; 1332
		12	^{60m} Co	10.2 min	58; 1332
⁵⁴ Fe	0.0581	2.3	⁵⁵ Fe	2.9 y	206
⁵⁸ Fe	0.0034	1.0	⁵⁹ Fe	45 d	143; 192; 1099; 1291
¹¹³ In	0.045	56	^{114m} In	49 d	190
		2	¹¹⁴ In	72 sec	558; 725; 1300
		155	^{116m} In	54 min	137; 417; 819; 1097; 1293; 2112
¹¹⁵ In	0.955		^{115m} Cd	43 d	485; 934; 1290
¹¹⁴ Cd	0.28	0.14	¹¹⁵ Cd	2.3 d	231; 261; 492; 527
		1.1	^{115m} In	4.5 h	336
		Daughter			

which can easily be measured. Neutron activation of iron by means of the isotope ^{59}Fe is not very sensitive, but relatively large concentrations of iron were present in the samples. Because the respective full energy peaks at 1173 and 1132 keV due to ^{60}Co , and at 1099 and 1291 keV due to ^{59}Fe , are not sufficiently resolved by scintillation γ -ray spectrometry, a radiochemical separation is required. Indium was expected to be present in very low concentrations in the sample, but fortunately, activation analysis for indium is very sensitive. As the half-life of the isotope ^{114}In is too short to allow its measurement after the chemical separation, the isotope $^{114\text{m}}\text{In}$ was measured. Activation of cadmium yields the isotopes $^{115\text{m}}\text{Cd}$ and ^{115}Cd . The isotope ^{115}Cd with a half-life of 2.3 d is usually measured, because its induced activity is 180 times higher than that of $^{115\text{m}}\text{Cd}$ after an irradiation time shorter than 2 days. As the isotope ^{115}Cd is a pure β -emitter in 62% of its decay mode to indium, measurement of the shorter-lived, 4.5-h, daughter isotope $^{115\text{m}}\text{In}$, 95% of which decays by an isomeric transition of 336 keV, was applied. Therefore, the cadmium should be measured 30 h after the chemical separation of cadmium to allow for the growth of this short-lived isotope. On the other hand, the activity from $^{114\text{m}}\text{In}$ should be measured after the decay of the co-separated $^{115\text{m}}\text{In}$ activity, if the highest sensitivity is to be attained. Interferences caused by possible threshold reactions can be neglected.

RADIOCHEMICAL SEPARATIONS

Ion-exchange separation

Irradiation of the zinc sulphate solutions gives rise to important activities from $^{69\text{m}}\text{Zn}$, ^{24}Na , ^{56}Mn , ^{64}Cu and ^{67}Cu . To separate the large matrix activities from the minor activities from cobalt, iron, indium and cadmium, clean separations with high decontamination factors are necessary. In the present investigation, the ^{24}Na , ^{56}Mn ,

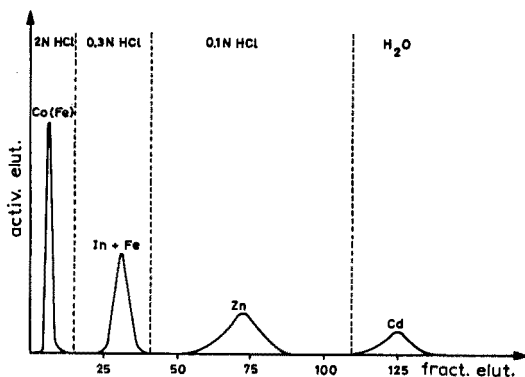


Fig. 1. Elution curve of cobalt, indium, zinc and cadmium from Dowex I-X8 column ($1.3 \text{ cm}^2 \times 26 \text{ cm}$).

^{64}Cu and ^{67}Cu were eluted together with the ^{60}Co with 2 N hydrochloric acid. The other important active elements were retained on the column. It appeared, however, that a small fraction ($\pm 10\%$) of the iron was eluted together with the cobalt fraction, probably because of the presence of an important amount of sulphate ions in the sample. The indium could be removed from the column together with the bulk of the iron activity with 0.3 N hydrochloric acid. The matrix activity ($^{69\text{m}}\text{Zn}$ and ^{65}Zn) was eluted with 0.1

N hydrochloric acid. Finally, the cadmium activity was collected with water. The separation was checked with tracers as shown in Fig. 1.

Iron extraction

The iron which was eluted partly with the cobalt fraction and partly together with the indium fraction, was separated by extractions with isopropyl ether from 8 *N* hydrochloric acid solution and collected. The co-extraction of cobalt or indium was less than 0.5%. It appeared that the organic phase was still slightly contaminated with ²⁴Na and ⁴⁶Sc. Therefore, the iron was back-extracted into water and precipitated as hydroxide. Because scandium forms a soluble amine complex in an excess of ammonia, a separation became possible. γ -Spectrometric purity control with a high-resolution germanium-lithium spectrometer showed no sodium or scandium contamination.

Cobalt extraction

In the first fraction the cobalt activity could be measured after the decay of the isotopes ²⁴Na, ⁶⁴Cu, ⁶⁷Cu and ⁵⁶Mn. It was however preferred to separate cobalt by an extraction with α -nitroso- β -naphthol into chloroform. More than 99% of the cobalt activity could be separated in a radiochemically pure state.

Indium extraction

From hydrobromic acid medium indium was extracted into isopropyl ether, and then back-extracted into a 5 *N* hydrochloric acid solution. Tracer experiments showed that the yield of the indium separation was 99.5% and the interferences of cobalt and zinc in the extraction were less than 0.2% and 0.3% respectively.

Cadmium extraction

A separation of cadmium from zinc is possible by extraction of the iodide complex into cyclohexanone, as the stability constants of ZnI₄²⁻ (log *K* = -5.4) and CdI₄²⁻ (log *K* = 6.2) are sufficiently different¹¹. The extraction is performed from a medium containing 0.1 *N* iodide and 0.25 *N* ammonia. Tracer experiments showed that 99% of the cadmium could be extracted, while only 0.7% of the zinc was co-extracted. As the previous separation on ion-exchange column had already insured a decontamination factor of more than 10⁵, radiochemically pure cadmium fractions could be separated from the irradiated zinc sulphate.

EXPERIMENTAL METHOD

Evaporate samples of 1 ml of zinc sulphate solution, seal in quartz vials and irradiate for 2 days in the BR-2 reactor at a thermal neutron flux of $8 \cdot 10^{12}$ n/cm².sec. Simultaneously irradiate identical zinc sulphate samples to which have been added 100 μ l of solutions containing known amounts of cobalt, iron, indium and cadmium. Two days after the end of irradiation, break the silica tubes. Make the sample solution 2 *N* in hydrochloric acid and add 200 μ g of carrier of each of the elements to be determined. Place the solution on the top of a Dowex 1-X8 column (100-200 mesh; 1.3 cm² \times 26 cm) previously converted to the chloride form. Elute cobalt with 5 column volumes of 2 *N* hydrochloric acid. Collect indium together with the bulk of the iron activity with

8 volumes of 0.3 *N* hydrochloric acid. Collect the zinc matrix activity with 20 volumes of 0.1 *N* hydrochloric acid. Collect cadmium with 9 volumes of water.

Evaporate the cobalt and indium fractions each to 2 ml. Add hydrochloric acid in order to obtain 20 ml of an 8 *N* solution. Extract the iron with two 10-ml portions and one 5-ml portion of isopropyl ether. Back-extract the iron with four 10-ml portions of water. After the addition of 2 mg of iron carrier and 0.5 mg of scandium carrier, neutralize the solution carefully with 0.25 *N* ammonia and add 10 ml of 6 *N* ammonia in excess. Filter the iron hydroxide, wash and dry. Measure the ^{59}Fe activity by γ -spectrometry and sum the counts under the photopeaks at 1099 and 1291 keV.

Evaporate the 8 *N* hydrochloric acid solution containing the cobalt to a few milliliter and dilute to 50 ml with 2 *N* hydrochloric acid. After the addition of 1 ml of 20% sodium nitrate solution and 1 ml of 1% α -nitroso- β -naphthol in acetic acid, adjust the pH to 3-4, and after 30 min extract the cobalt complex with 10 ml of chloroform; add another 1 ml of reagent solution and extract again with one 10-ml portion and one 5-ml portion of chloroform. Wash the organic phases with 2 *N* hydrochloric acid and dilute to 25 ml in a volumetric flask. Measure the activities under the peaks at 1173 and 1332 keV.

Evaporate the solution containing the indium to just dry, add 8 ml 1 *M* hydrobromic acid and extract twice with 10-ml portions of isopropyl ether. To the aqueous phase, add 48% hydrobromic acid to obtain a 4.5 *N* hydrobromic acid medium. Extract the indium with four 10-ml portions of isopropyl ether. Wash the collected organic phases with 4.5 *N* hydrobromic acid and back-extract the indium by equilibration with four 10-ml portions of 5 *N* hydrobromic acid. Collect the solutions containing the indium and count by γ -spectrometry. Measure the count rate under the dominant photopeak at 191 keV.

Concentrate the cadmium fraction to 25 ml and add 25 ml of a 0.2 *N* potassium iodide-0.5 *N* ammonia solution. Extract the cadmium with two 10-ml portions and one 5-ml portion of cyclohexanone. Measure the cadmium activity by means of the energy peaks at 336 and 527 keV.

RESULTS AND CONCLUSION

The amounts of cobalt, iron, indium and cadmium were determined in two zinc sulphate solutions (Table II). Radiochemically pure fractions were separated. Calculations from the counts under two different photopeaks resulted in values which were in agreement within the standard deviations. The reproducibility as reflected in the standard deviations was quite adequate. The results for cadmium were in good agreement with those obtained by other methods. Although activation analysis of indium is very sensitive, no indium could be detected in the zinc sulphate samples.

To establish if relative errors were introduced, a systematic addition method was also examined for each of the elements. Several samples were prepared and spiked with varying amounts of standards. The results of the addition method for cobalt are shown in Fig. 2.

Solution III on electrolysis, gave only a low yield of zinc whereas solution V appeared to give satisfactory yields. The two samples were found to contain almost equal amounts of each element, hence it is unlikely that the deposition of zinc is inhibited by one of these elements in these samples.

TABLE II

DETERMINATION OF COBALT, IRON, INDIUM AND CADMIUM

Element determined	Analysis	γ -Ray used (keV)	Concentrations found ($\mu\text{g/ml}$)	
			Sample III	Sample V
Co	1	1173	0.38	0.35
		1332	0.33	0.34
	2	1173	0.38	0.33
		1332	0.39	0.32
	Mean value		0.37 ± 0.01	0.34 ± 0.01
Fe	1	1099	25.2	—
		1291	24.0	—
	2	1099	26.5	—
		1291	26.8	—
	Mean value		25.7 ± 1.0	—
In	1	191	<0.011	<0.010
Cd	1	336	0.40	0.45
		527	0.39	0.47
		336	0.45	0.45
	2	336	0.46	0.45
		527	0.43 \pm 0.01	0.45 \pm 0.01
	Mean value		0.50	0.38
	Industrial analysis			
Polarographic analysis				

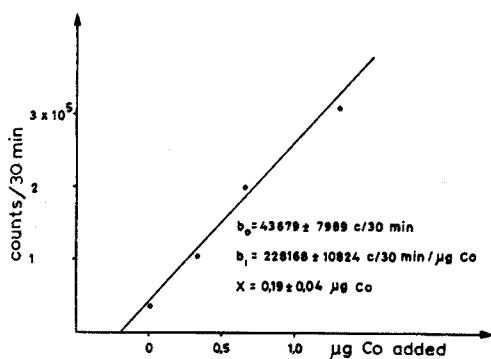


Fig. 2. Addition method of analysis for cobalt.

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SUMMARY

A neutron activation analysis for the simultaneous determination of cobalt, iron, indium and cadmium in electrolytic zinc sulphate solutions is described. The chemical separation, in hydrochloric acid medium, involved anion exchange followed by solvent extraction. Concentrations of $0.3 \mu\text{g Co/ml}$, $25 \mu\text{g Fe/ml}$ and $0.4 \mu\text{g Cd/ml}$ were found. The concentration of indium was below the detection limit ($0.01 \mu\text{g/ml}$).

RÉSUMÉ

On décrit une analyse par activation aux neutrons pour le dosage simultané du cobalt, du fer, de l'indium et du cadmium dans le sulfate de zinc électrolytique. La séparation chimique en milieu acide chlorhydrique comprend échange d'anions et extraction dans un solvant. On a trouvé des concentrations de 0.3 μg Co/ml, 25 μg Fe/ml et 0.4 μg Cd/ml. La concentration en indium est en dessous de la limite de détection (0.01 μg /ml).

ZUSAMMENFASSUNG

Es wird die gleichzeitige Bestimmung von Kobalt, Eisen, Indium und Cadmium in elektrolytischen Zinksulfatlösungen mit Hilfe der Neutronenaktivierungsanalyse beschrieben. Die chemische Abtrennung geschieht aus salzsaurem Medium mit einem Anionenaustauscher und anschließender Flüssigextraktion. Konzentrationen von 0.3 μg Co/ml, 25 μg Fe/ml und 0.4 μg Cd/ml wurden gefunden. Die Konzentration von Indium lag unterhalb der Nachweisgrenze von 0.01 μg /ml.

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THE DETERMINATION OF CALCIUM AND MAGNESIUM IN STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Traces of calcium and magnesium in inclusions have a significant effect on the properties of steel; investigations by PRIDANTSEV AND KONDRAT'EV¹ and ZHALYBIN AND ERSHOV², showed a relationship between improved steel quality and reduced magnesium contents.

Electron microprobe analyser studies in these laboratories have shown the presence of calcium as *ca.* 8% (w/w) CaO·Al₂O₃ and magnesium as *ca.* 20% (w/w) MgO·Al₂O₃, in inclusions in steel specimens. Initial investigations established that the respective calcium and magnesium contents of most steels were less than 20 µg/g, although certain products contained 20–200 µg/g. Calcium and magnesium distribution was found to be heterogeneous throughout ingots and a research programme required the development of suitable procedures for the range 1–200 µg/g with particular reference to the range 1–20 µg/g.

Adequate procedures are available for the determination of 20–200 µg/g of calcium^{3–9} and magnesium^{8, 10–14} in iron and steel, but are not suitable for extension to the range 1–20 µg/g. The majority of the above methods rely upon solvent extraction to remove the bulk of the iron; however, nickel and chromium ions generally remain in the aqueous phase. Mercury cathode separations are more effective and remove iron, nickel and chromium, although contamination problems are increased. An exception was the method of ADACHI *et al.*¹⁵, who reported an emission spectrographic procedure with a lower detection limit of 1 µg/g calcium; lanthanum carrier was used to concentrate the calcium as a fluoride precipitate.

Investigation of a point-to-plane optical emission spectrometric technique showed that a range of calcium and magnesium was present in several standard samples maintained in these laboratories, although the appropriate agencies have not standardized these elements. The objective of the present investigations was to obtain absolute values for the calcium and magnesium content of standard samples so that, ultimately, a direct reading, optical emission spectrometric analysis could be developed for the rapid quality-control of steel.

A consideration of sensitivities indicated that an atomic absorption spectrophotometric technique, without prior separation and with a detection limit of 1 µg/g calcium and magnesium, could be developed for steel, provided that matrix interferences could be overcome. A technique without separations is preferred for reasons of speed, minimum handling, complete avoidance of glassware and minimum problems from air-borne contamination.

EXPERIMENTAL

Apparatus

Varian-Techtron atomic absorption spectrophotometer AA4 with digital readout, AB50 burner (titanium head; slot, 5 cm × 0.055 cm) and standard magnesium and calcium hollow-cathode lamps.

Sampling

The lathe area must be clean, the atmosphere free from dust, and the turnings collected on polyethylene film and stored in polystyrene bottles. Direct contact between hands and sample should be avoided.

Reagents

Calcium carbonate, iron, nickel, chromium and magnesium: Johnson and Matthey, spectrographically standardised.

Strontium chloride and sodium carbonate anhydrous: AnalaR.

Magnesium solution. Weigh 0.500 g of magnesium crystals into a 600-ml polytetrafluorethylene beaker. Add 10 ml of water, 10 ml of hydrochloric acid (s.g. 1.18) and dissolve, using a PTFE cover. Dilute to 500 ml and store in a polyethylene bottle. One ml of solution contains 1.00 mg of magnesium.

Calcium solution. Dry calcium carbonate at 285° for 2 h and weigh 1.249 g into a 600-ml PTFE beaker. Add 20 ml of water and 10 ml of hydrochloric acid (s.g. 1.18). When reaction has ceased, stir to remove carbon dioxide, dilute to 500 ml and store in a polyethylene bottle. One ml of solution contains 1.00 mg of calcium.

Prepare a calibration solution which contains 20 µg calcium and 20 µg magnesium per ml.

Recommended procedure

Use platinum and plastic apparatus throughout and pre-rinse with hydrochloric acid and distilled water. Weigh a 1-g sample into a 100-ml PTFE beaker and prepare a calibration series of appropriate matrix for the range 0–200 µg/g calcium and magnesium. Add 450 ± 5 mg of strontium chloride and dissolve by heating under a PTFE cover, with 15 ml of hydrofluoric acid (s.g. 1.18) and by oxidising with 10 ml 50% (v/v) nitric acid. Add 10 ml of perchloric acid (s.g. 1.66), evaporate to fumes and fume for 5 min. Dissolve in 15 ml of water and filter through a Whatman No. 540 filter paper into a tared polyethylene bottle. Wash with hot water. If tungstic oxide is present, wash the precipitate with ammonia solution (s.g. 0.88), discarding the washings. Transfer the filter paper to a platinum crucible, cover, char and ignite at 600° until free from carbonaceous material. Add 5 ml of hydrofluoric acid (s.g. 1.18) and 1 ml of perchloric acid (s.g. 1.66). Evaporate to dryness and bake for 5 min. Remove from the heat, add 345 ± 5 mg of anhydrous sodium carbonate and fuse at 1100° for 15 min. Cool, extract with 10 ml of water and 7 ml of 10% (v/v) perchloric acid, and boil for 5 min. Filter through a Whatman No. 540 filter paper into the appropriate tared polyethylene bottle and dilute with water to 107.0 g nett. Measure the absorbance at Ca 422.7 nm (expansion × 2) and Mg 285.2 nm (expansion × 1.5), using a Varian-Techtron AB 50 burner and a nitrous oxide-acetylene flame.

RESULTS AND DISCUSSION

Preliminary experiments indicated that a sample concentration of 1 g/100 ml would give the required detection limit with a nitrous oxide-acetylene flame and a suitable cation to suppress the ionization of calcium and magnesium atoms.

The initial experiments used a Varian Techtron AB40 stainless-steel slot-burner (5 cm \times 0.050 cm). Occasionally this burner developed carbon build-up or solids-bridging across the burner slot, thus affecting the precision of the results and necessitating an interruption of the reading process; during the investigation an improved AB50 burner became available and these difficulties were eliminated. The new burner also showed improved reliability in operation and increased sensitivity; the contributing factors being a larger slot width, better heat dissipation through the larger heat sink, and a grooved valley on either side of the slot which reduced the turbulence caused by secondary air and increased the favourable absorption zone in the flame.

An assessment of the likely solubility of inclusions of the type *ca.* 8% (w/w) $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and *ca.* 20% (w/w) $\text{MgO} \cdot \text{Al}_2\text{O}_3$ indicated that complete solubility of calcium and magnesium would not be achieved with hydrofluoric acid. Several workers¹⁶⁻¹⁸ have indicated the beneficial effect of sodium ions in preventing excessive ionization, particularly of calcium atoms at the high temperature of the nitrous oxide-acetylene flame. Thus the necessity to fuse the insoluble residues with a sodium salt would supply also the required sodium concentration to suppress ionization effects. Strontium ions, although unsuitable as a fusion agent, were investigated for the suppression of the interferences and for the inhibition of excessive ionization of calcium and magnesium atoms; strontium had been shown previously to be a suitable cation to suppress interferences in the determination of minor amounts of magnesium in steel with an air-acetylene flame¹¹. The ionization potentials for sodium, strontium, calcium and magnesium¹⁹ respectively are 5.1; 5.7; 6.1 and 7.6 eV.

FLEMING²⁰ has indicated that the maximum sensitivity for calcium occurs in a mixed air/nitrous oxide-acetylene flame. Therefore mixed air/nitrous oxide-

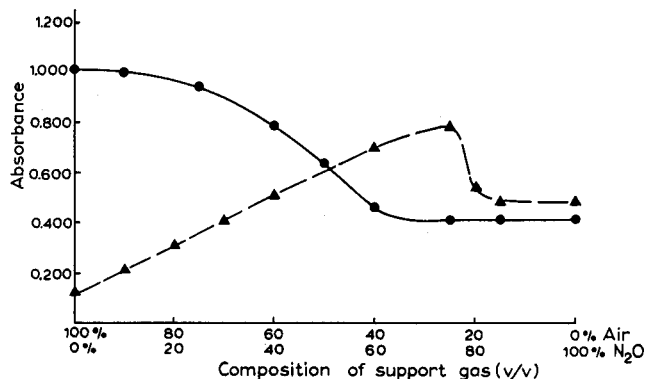


Fig. 1. The influence of support gas composition on the sensitivity for magnesium and calcium. (▲) Absorbance ($\times 2$) 10,000 p.p.m. Fe, 1,500 p.p.m. Na, 2 p.p.m. Ca. (●) Absorbance ($\times 1$) 10,000 p.p.m. Fe, 1,500 p.p.m. Na, 2 p.p.m. Mg.

TABLE I
A STUDY OF THE SUPPORT GAS COMPOSITION AND POTENTIAL INTERFERENCES IN THE DETERMINATION OF CALCIUM

Sample composition	$\mu\text{g/g Ca}$	Nett absorbance ($\times 10^3$) (sensitivity $\times 2$)					
		Support gas composition (v/v)					
		100% air	80% air 20% N ₂ O	40% air 60% N ₂ O	25% air 75% N ₂ O	20% air 80% N ₂ O	100% N ₂ O
100 Fe	40	33	63	140	163	110	101
100 Fe	100	83	158	349	407	272	254
100 Fe	200	167	317	698	816	545	506
50 Fe	200	188	294	702	815	544	510
80 Fe, 20 Ni	200	171	299	698	827	552	508
50 Fe, 30 Cr, 20 Ni	200	113	320	703	833	548	506
50 Fe, 30 Cr, 20 Ni, 2 Al, 0.5 P	200	43	194	688	702	553	506

TABLE II

A STUDY OF SUPPORT GAS COMPOSITION AND POTENTIAL INTERFERENCES IN THE DETERMINATION OF MAGNESIUM

Sample composition		Nett absorbance ($\times 10^3$) (sensitivity $\times 1$)				
		Support gas composition (v/v)				
Matrix elements (%)	$\mu\text{g/g Mg}$	100% air	75% air 25% N ₂ O	60% air 40% N ₂ O	40% air 60% N ₂ O	100% N ₂ O
100 Fe	40	206	188	160	92	86
100 Fe	100	510	472	400	229	214
100 Fe	200	1,022	947	799	460	429
50 Fe	200	1,031	948	808	462	430
80 Fe, 20 Ni	200	1,029	967	813	459	429
50 Fe, 30 Cr, 20 Ni	200	1,009	955	805	458	429
50 Fe, 30 Cr, 20 Ni, 2 Al, 0.5 P	200	786	939	800	460	428

acetylene flame types were studied for solutions containing 10,000 p.p.m. iron, 1,500 p.p.m. sodium and respectively 2 p.p.m. of calcium and magnesium. The total flow rate of nitrous oxide and air was 7.5 l/min at 172 kN/m² and of acetylene was 2.3 l/min at 69 kN/m². The results are shown in Fig. 1 and confirm the general observations of FLEMING²⁰, the maximum sensitivity for calcium occurring with a 25% (v/v) air/75% (v/v) nitrous oxide-acetylene mixture.

Consequently, test solutions were prepared on the basis of a sample concentration of 1 g/100 ml in order to study potential interferences as a function of support gas composition; variations in steel composition were simulated, and separate or combined additions of 500, 1000, 1500, 2000 and 3000 p.p.m. of sodium and strontium were made.

Initial studies showed that interferences occurred in the mixed air/nitrous oxide-acetylene flames which previously had given maximum sensitivity. Therefore several air/nitrous oxide-acetylene flames were studied. Pertinent results for solutions containing 1500 p.p.m. of sodium plus strontium are shown for calcium (Table I) and magnesium (Table II). The absorbances shown are nett; the appropriate absorbances for the zero concentration test solutions have been deducted.

The results for calcium show that interferences are observed until the support gas contains at least 80% (v/v) nitrous oxide. It was noted further that the reproducibility of absorbance readings is poorer when the support gas contains 75% (v/v) or less of nitrous oxide, *i.e.* when sensitivity is changing rapidly as a function of the nitrous oxide content of the support gas. The results for magnesium show that interferences are observed until the support gas contains at least 40% (v/v) nitrous oxide. Therefore it was decided to use 100% (v/v) nitrous oxide as the support gas for both the magnesium and the calcium determinations.

When 100% (v/v) nitrous oxide was the support gas, a study of varying strontium or sodium concentration showed that the plateau of maximum effectiveness had been achieved when 1500 p.p.m. of either cation was present; for a wide range of matrix compositions, the spread of absorbances for test solutions containing strontium was smaller than the spread obtained for test solutions containing sodium. Since a minimum amount of sodium carbonate is required for the fusion of insolubles, a concentration of 1500 p.p.m. of both sodium and strontium was selected to buffer ionization effects and control potential interferences.

TABLE III

A STUDY OF POTENTIAL INTERFERENCES IN SOLUTIONS WITH AND WITHOUT ADDITIONS OF SODIUM PLUS STRONTIUM

Sample composition	Matrix elements (%)		Nett calcium absorbance ($\times 10^3$) (sensitivity $\times 2$)		Nett magnesium absorbance ($\times 10^3$) (sensitivity $\times 1.5$)	
	$\mu\text{g/g}$ Ca	$\mu\text{g/g}$ Mg	0 p.p.m. Na +	1500 p.p.m. Na +	0 p.p.m. Na +	1500 p.p.m. Na +
			0 p.p.m. Sr	1500 p.p.m. Sr	0 p.p.m. Sr	1500 p.p.m. Sr
Aqueous	200	200	266	492	574	645
20 Ni	200	200	320	500	622	657
30 Cr	200	200	418	506	621	645
50 Fe	200	200	340	510	622	645
70 Fe, 30 Cr	200	200	432	510	639	651
75 Fe, 15 Cr, 10 Ni	200	200	422	514	648	636
80 Fe, 20 Ni	200	200	354	508	640	644
50 Fe, 30 Cr, 20 Ni	40	40	86	101	129	129
50 Fe, 30 Cr, 20 Ni	100	100	216	254	322	323
50 Fe, 30 Cr, 20 Ni	200	200	432	506	644	644
50 Fe, 30 Cr, 20 Ni, 2 Al, 0.5 P	200	200	444	506	644	642
100 Fe	40	40	72	101	128	129
100 Fe	100	100	180	254	320	321
100 Fe	200	200	360	506	640	644
100 Fe, 2 Al, 0.5 P	200	200	390	508	644	640
100 Fe, 0.5 P	200	200	354	508	632	644
100 Fe, 2 Al	200	200	396	510	652	642

Pertinent results are shown in Table III. The absorbances shown are nett; the appropriate absorbances for the zero concentration test solutions have been deducted. The results confirm the effectiveness of the addition agents in suppressing

TABLE IV

CALCIUM AND MAGNESIUM CONTENT OF STANDARD STEELS

Sample no.	Nominal composition (%)	Calcium found		Magnesium found	
		$\mu\text{g/g}$	1σ ($n=5$)	$\mu\text{g/g}$	1σ ($n=5$)
NBS 55d (M)	0.01 C, 0.03 Mn	5	2	<0.5	0.5
NBS 101d (M)	19 Cr, 9 Ni	4	1	1.0	1.0
NBS 160a (M)	19 Cr, 14 Ni	5	1	10.0	1.5
NBS 1167 (R)	0.1 C, 0.3 Mn	1	1	<0.5	0.5
BCS SS31 (R)	0.5 C, 0.5 Si	14	2	0.5	0.5
BCS SS32 (R)	0.1 C, 1.1 Mn	7	1	1.0	0.5
BCS SS35 (R)	0.3 C, 0.7 Mn	20	2	2.0	1.0
BHP SS67 (S)	0.04 C, 0.3 Mn	<1	1	<0.5	0.5
BHP SS69 (S)	3.8 Si, 1.1 Nb	47	2	4.0	1.0
BHP SS78 (R)	13 Cr, 0.5 Si	18	1	5.0	0.5
BHP SS112 (R)	24 Cr, 21 Ni	36	2	1.0	0.5
BHP SS113 (R)	26 Cr, 5 Ni	18	2	1.5	1.0
BHP SS128 (R)	19 Cr, 10 Ni	3	1	0.5	0.5

BHP = Broken Hill Proprietary Co. Ltd.

M = Millings

BCS = British Chemical Standard

R = Round

NBS = National Bureau of Standards (U.S.A.)

S = Square

the potential interferences. The results also indicate that it is not mandatory to match closely the matrix of the calibration series with those of the actual assays. Thus a proposed procedure which should be applicable to all steels is available.

Suitable standard samples are not available for calcium and magnesium concentrations at the levels covered by this investigation. The proposed procedure was applied to a series of reference standard samples and secondary standards which would give a suitable range of results for the preparation of emission spectrographic curves. The standards were selected for analysis by screening numerous reference samples by means of point-to-plane optical emission spectrometry. The validity of the results and the impurity levels of the reference metals and chemicals were confirmed by using half weight blank techniques.

The results (Table IV) indicate that the required detection limits for calcium and magnesium in steel can be obtained by the proposed procedure. A suitable set of standards is available to study the application of point-to-plane optical emission spectrographic analyses directly to solid samples.

Appreciation is expressed to The Broken Hill Proprietary Company Limited, for permission to publish this work.

SUMMARY

A study was made of the determination of 1–200 $\mu\text{g/g}$ of total calcium and magnesium in steel by atomic absorption spectrophotometry. A direct procedure which avoided the use of glass apparatus was selected in order to avoid contamination problems which can occur with dissolution, separation and concentration techniques. Sodium and strontium ions are used to eliminate interferences and control the ionization of calcium and magnesium atoms in the nitrous oxide–acetylene flame. Investigations showed that although maximum sensitivity occurred in mixed air/nitrous oxide–acetylene flames, the higher temperature nitrous oxide–acetylene flame is required to overcome interferences. Results are presented for selected standard samples.

RÉSUMÉ

Une étude est effectuée pour le dosage total du calcium et du magnésium (1–200 $\mu\text{g/l}$) dans l'acier par spectrophotométrie par absorption atomique. Un procédé direct est choisi pour éviter l'utilisation d'appareil de verre afin de supprimer les problèmes de contamination lors des techniques de dissolution, séparation et concentration. On utilise le sodium et le strontium pour éliminer les interférences et contrôler l'ionisation des atomes de calcium et de magnésium dans la flamme oxyde nitreux–acétylène. La température plus élevée des flammes oxyde nitreux–acétylène est nécessaire pour supprimer des interférences. Des résultats sont présentés pour des échantillons standards choisis.

ZUSAMMENFASSUNG

Die Bestimmung von 1–200 μg Calcium und Magnesium pro Gramm Stahl mit

der Atomabsorptionsspektroskopie wurde untersucht. Es wurde ein Verfahren, welches die Verwendung von Glassapparaturen vermeidet ausgewählt um Verunreinigungen, welche durch Auflösung, Abtrennung und Konzentration der Elemente hervorgerufen werden können, zu verhindern. Natrium- und Strontiumionen werden zur Eliminierung von Störungen verwendet und zur Kontrolle der Ionisation von Calcium und Magnesiumatomen in der Stickstoffoxyd-Acetylen-Flamme. Die Untersuchungen zeigten, dass, obwohl die maximum Empfindlichkeit mit einer Luft-Stickstoffoxyd-Acetylen-Flamme erreicht wird, die höhere Temperatur der Stickstoffoxyd-Acetylen-Flamme erforderlich ist, damit keine Störungen auftreten. Es werden die Ergebnisse für ausgewählte Standardproben angegeben.

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CATHODE-RAY-EXCITED EMISSION SPECTROSCOPIC ANALYSIS OF TRACE RARE EARTHS

PART III. DETERMINATION OF TERBIUM

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Cathode-ray-excited emission (CREE) spectroscopy of trace rare earths in a matrix has been discussed previously for the cases of qualitative detection¹ (Part I of this series), and for the quantitative determination of europium² (Part II). As was pointed out in Part I, CREE spectroscopy provides a rapid, non-destructive analytical procedure. This procedure takes advantage of the fact that trace amounts of rare earths can be excited efficiently by cathode rays to emit characteristic *f-f* luminescence, which can be isolated optically and measured photoelectronically.

The hauptlinien spectrum for analysis of rare earths in a matrix of yttrium oxide, and a table of relative sensitivities was given in Part I, where it was shown that the 544-nm line is most useful for terbium. This emission line [⁵D₄-⁷F₅] therefore was selected as the primary detection line for the quantitative determination of trace amounts of terbium.

EXPERIMENTAL TECHNIQUES

Sample preparation

The yttrium oxide used as the matrix material was of "ultrapure" grade, *i.e.* 99.9999% pure with respect to rare earths. Preliminary analyses of the yttrium oxide as "blank" material showed no lines attributable to terbium, and a faint trace of dysprosium*. Series of yttrium oxides containing terbium, as the sulfate, in amounts from 5·10⁻⁶% to 10⁻³%, were prepared by firing at 1100° in silica crucibles, for the same time. The crucibles were purified by firing charges of the pure yttrium oxide, preliminary to the series firings.

Firing temperature

It is apparent that the firing conditions in which samples are prepared for analysis must be constant for all samples. In particular, it is essential that the firing temperature be carefully controlled. The effect of firing temperature on the intensity of the 544-nm emission is shown in Fig. 1, for temperatures of 400-1100°. It is seen that diffusion and incorporation of the terbium is complete at about 1000°. For this reason, 1100° was selected.

* High resolution CREE analysis, as discussed later in this paper, showed the presence of about 16 p.p.b. of terbium in the "blank" oxide.

Measurements

A demountable cathode-ray equipment² was used in conjunction with a grating spectroradiometer and RCA 1P21 multiplier phototube. Samples were placed in order of increasing terbium concentration on the metal sample disk, and were measured successively. Accelerating potentials of 16 kV were used primarily, with beam currents of the order of 1 μ A.

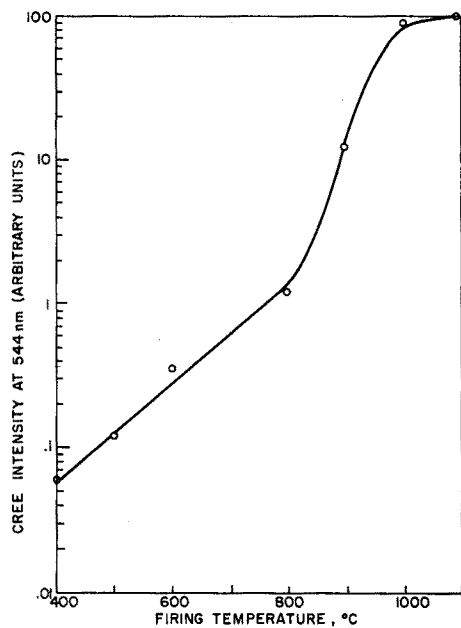


Fig. 1. Intensity at 544 nm as a function of firing temperature.

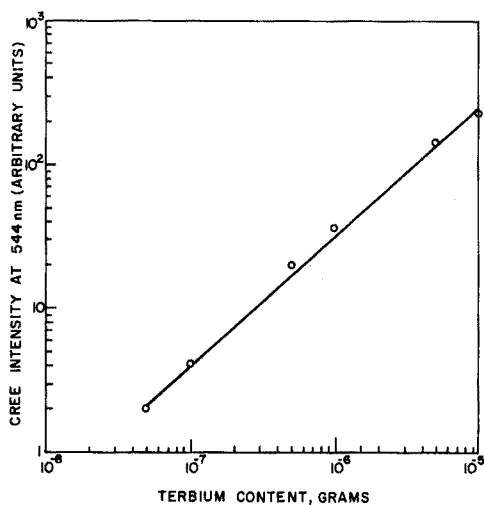


Fig. 2. Intensity at 544 nm as a function of terbium concentration in Y_2O_3 matrix (16 kV, 1 μ A).

RESULTS AND DISCUSSION

The cathodoluminescence emission intensity of the 544-nm line as a function of terbium in yttrium oxide is shown in Fig. 2, for an accelerating potential of 16 kV. A series in which the 551-nm line from terbium was measured, gave lower intensities, in agreement with the sensitivity data given previously¹.

With this type of measurement, the detection limit is about 20 p.p.b., which is about the same as that obtained by WALTERS *et al.*³ by X-ray fluorescence, and by LINARES *et al.*⁴ who utilized X-ray tubes operated at 50 kV. The normal CREE analyses reported in Part II and in Fig. 2 of the present paper were performed with a spectrometer which had a band-pass of about 5 nm. By going to higher resolution (a band-pass of less than 1 nm), and thus rejecting background (broad-band-luminescence), the signal-to-noise aspect can be improved. Figure 3 shows the actual traces from the high-resolution spectrometer for three samples of terbium, 0, 10 and 50 p.p.b., added to yttrium oxide. A semi-quantitative analysis of these curves yields an estimate of about 16 p.p.b. of terbium in the "blank" yttrium oxide.

As operated, the total noise level was about 1 p.p.b. Thus, for a signal-to-noise detection limit of 2, 2 p.p.b. of terbium would be detectable. With signal-to-noise retrieval systems, such as signal averaging devices, the detection limit could probably be less than 1 p.p.b. No attempt was made to determine this, because of the unavailability of starting material which is completely free of terbium.

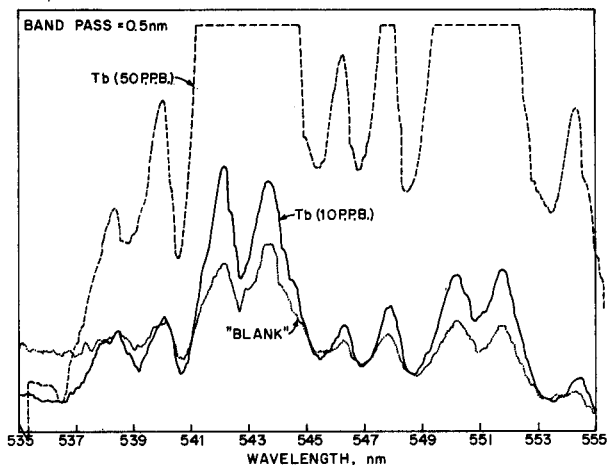


Fig. 3. High-resolution spectrometer traces for Y_2O_3 with added 50 p.p.b. and 10 p.p.b. of terbium. Trace for "blank" Y_2O_3 shows an estimated 16 p.p.b. of terbium to be present in the raw material.

TABLE I

ANALYSIS OF TERBIUM IN YTTRIUM OXIDE MATRIX

<i>Tb added (p.p.m.)</i>	<i>Tb found (p.p.m.)</i>
0.07	0.06
0.40	0.43
6.0	5.2

"Added-found" data were obtained by preparing samples of terbium in yttrium oxalate, and analyzing by means of the standard curve of Fig. 2. The results are given in Table I.

Interferences

As was pointed out previously², other rare earth ions in the same matrix may interact, and by doing so, may affect the terbium luminescence emission intensity. These interactions depend on concentration, ion-type, and type of matrix. In the present work, concentration quenching from terbium itself can be taken as minimal in the trace range of terbium under investigation. However, if other species of rare earths are present simultaneously with terbium, such rare earths may interfere with the radiative process which results in the emission of the terbium detection line. Where an interfering ion emits in a spectral region which overlaps that from the desired ion, thereby yielding a positive error, such spectral reinforcement may be avoided by making use of a secondary line².

The effect of ten of the rare earths, in 100-p.p.m. amounts, used as interfering ions of the analysis of 5 p.p.m. of terbium in yttrium oxide is shown in Fig. 4, with the unpoisoned material normalized to 100. It is seen that the poisoning efficiency differs with the different rare earths, being worst for the lighter rare earths. It is of interest that the worst interfering ions (Pr, Nd and Dy) are those that exhibit maximum

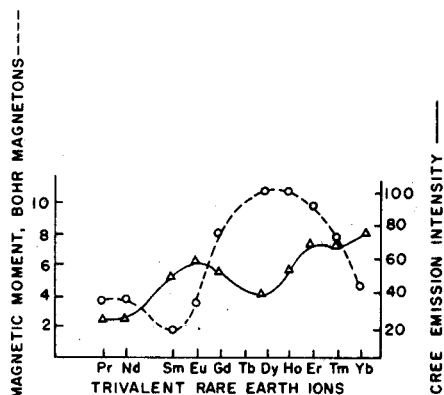


Fig. 4. Intensity at 544 nm as a function of rare earth interference for $Y_2O_3:Tb$ (5 p.p.m.):RE (100 p.p.m.).

magnetic moments in the well-known double-peak figure of a plot of Bohr magnetons *versus* rare earths ions⁵. Thus, praseodymium(III) and neodymium(III) with moments of 3.61 and 3.66 Bohr magnetons occur at the maximum of the first peak; and dysprosium(III) and holmium(III) with moments of about 10.5 Bohr magnetons occur at the maximum of the second peak. Further work is planned to investigate the effects of these ions on the emission from rare earths.

The possibility of ions of the first transition group interfering with the rare earths, possibly via *f-d* coupling has been discussed in Part II and was found to occur with europium in yttrium oxide. Results of tests of such poisoning for terbium are shown in Table II, for 0.5 p.p.m. of terbium in yttrium oxide, prepared with 100 p.p.m. of each of iron, manganese and nickel.

TABLE II

CREE EMISSION INTENSITIES AT 544 nm FOR $Y_2O_3:Tb$, DOPED WITH IRON, MANGANESE AND NICKEL

Material	Intensity
$Y_2O_3:Tb$ (0.5 p.p.m.)	100
$Y_2O_3:Tb$ (0.5 p.p.m.):Fe (100 p.p.m.)	42
$Y_2O_3:Tb$ (0.5 p.p.m.):Mn (100 p.p.m.)	76
$Y_2O_3:Tb$ (0.5 p.p.m.):Ni (100 p.p.m.)	100

Again, a roughly qualitative correlation can be seen between degree of poisoning and the magnetic moment of the first transition group ion, with observed moments⁶ in aqueous solution for manganese(II) and iron(III) of about 5.9 Bohr magnetons; about 5.3 Bohr magnetons for iron(II); and about 3.2 Bohr magnetons for nickel(II),

with somewhat lower values for these ions in solids. The case of the iron interference was investigated in greater detail; the results for $Y_2O_3 : Tb$ (5 p.p.m.): Fe are summarized in Fig. 5, for iron concentrations of 1–100 p.p.m. A monotonic decrease in CREE intensity *versus* iron concentration is indicated; over this range.

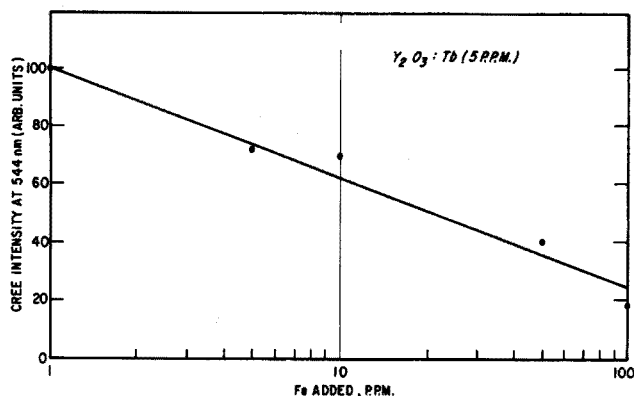


Fig. 5. Intensity at 544 nm as a function of iron addition.

DISCUSSION

The feasibility of cathode-ray-excited emission analysis for trace amounts of terbium quantitatively has been shown. The detection limit in an yttrium oxide matrix is of the order of 2 p.p.b., and higher sensitivity can probably be achieved by instrumental improvements in signal-to-noise ratios.

The differences between interference effects for europium in yttrium oxide, as described in Part II, and the present work on terbium in the same matrix, indicate the need for exploring individually the CREE analyses of the various rare earth ions, which is planned in subsequent papers.

The aid of R. A. KAUFFUNGER in materials preparation, and of Dr. W. H. FONGER and Mr. J. GERBER in the measurements aspects is gratefully acknowledged.

SUMMARY

The technique of trace analysis of rare earths by cathode-ray-excited emission spectroscopy has been applied to the determination of terbium in an yttrium oxide matrix. With the 544-nm emission from terbium as the detection wavelength, and with high-resolution spectrometry, a detection limit of about 2 p.p.b. can be attained. The effect of sample firing temperature during diffusion and crystallization is treated in detail. Effects of other rare earth and first transition group interferences are discussed.

RÉSUMÉ

La méthode de dosage de traces de terres rares par spectroscopie d'émission à rayons cathodiques a été appliquée à l'analyse du terbium dans une matrice d'oxyde

d'yttrium. Une limite de détection de 2 p.p.b. peut être atteinte avec l'émission 544 nm du terbium. On examine en détail l'influence de la température au cours de la diffusion et de la cristallisation. Discussion sur l'influence d'autres terres rares et du premier groupe de transition.

ZUSAMMENFASSUNG

Eine Technik zur Spurenanalyse Seltener Erden durch Anregung der Emissionsspektren mit Kathodenstrahlen wurde für die Bestimmung von Terbium in Yttriumoxid-Matrix angewendet. Mit einem hoch-auflösenden Spektrometer ergab sich für die 544 nm-Linie eine Nachweisgrenze von 2 p.p.b. Der Einfluss der Glühtemperatur während der Diffusion und Kristallisation wird im einzelnen behandelt. Störungen durch andere Seltene Erden und Elemente der 1. Übergangsgruppe werden diskutiert.

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THE POTENTIOMETRIC DETERMINATION OF FLUORINE IN NUCLEAR FUEL REPROCESSING SOLUTIONS

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The dissolution of irradiated reactor fuel elements at Eurochemic proceeds in two steps, namely, the dissolution of the fuel element cladding, followed by the dissolution of the uranium fuel core. Fuel elements clad in zircaloy-2 (a zirconium alloy containing 1.5% tin) are de-clad by means of an ammonium fluoride-ammonium nitrate solution. The final solution is about 0.8 *M* in ammonium fluoride and 0.8 *M* in ammonium fluorozirconates, and is about 5.6 *M* in fluorine.

Fluorine-containing precipitates left in the dissolver are dissolved in nitric acid in the subsequent dissolution step. Aluminium nitrate is added to the fuel core solution to complex the fluoride before the fuel solution is fed to the first extraction cycle. The uranium feed solution is about 1 *M* in uranyl nitrate, up to 2 *N* in nitric acid, up to 0.1 *M* in aluminium and usually more than 10^{-2} *M* in fluorine. For process control reasons, the fluorine concentrations in the de-cladding solution and the uranium feed solution have to be determined on a routine basis. These solutions contain a high concentration of γ -emitting nuclides, hence the analyses must be carried out by remote control in lead-shielded air-tight boxes to cope with the radiation exposure hazard.

The final product of the reprocessing process is at present a uranyl nitrate solution, which contains about 400 g of uranium per l and is 0.5–1.0 *N* in nitric acid, and which may contain a maximum amount of 25 p.p.m. of fluorine. Analyses are required to prove that this specification has been met. Methods of determining the fluorine concentrations with a fluoride-sensitive electrode after a relatively simple pre-treatment, to ensure that the fluorine is available as fluoride, are described in this paper.

EXPERIMENTAL

Apparatus

An Orion fluoride-sensitive electrode, model 94-09, and a saturated calomel electrode as reference electrode were used for the fluoride-ion activity measurements^{1,2}. The electrodes were inserted into the solution which was to be measured in a 50-ml polyethylene beaker. The cell potential difference was measured under magnetic stirring by means of a recording millivolt-meter (Metrohm Potentiograph, Models E 436 and 336). To approach conditions prevailing in lead-shielded boxes, no special precautions were taken to keep the temperature (*ca.* 21–24°) constant for most of the measurements. A constant response was indicated by the mV-meter

within 5 min for fluoride concentrations above 10^{-4} M and after 15 min for lower fluoride concentrations. Polyethylene vessels were used throughout the experiments.

A cation-exchange column was employed for the separation of fluoride from uranium; 5 g of Dowex 50W-X4, H⁺-form, 100–200 mesh (moisture content $68 \pm 3\%$) were suspended in water and placed in a glass column of 13 mm internal diameter giving a resin bed height of ca. 40 mm.

Standard solutions and reagents

Standard fluoride solutions were made by dissolving exactly weighed amounts of purified sodium fluoride in double distilled water. Reagent-grade sodium fluoride was purified by preparing a saturated solution in water, filtering off the excess salt, precipitating with ethanol and drying at 150° .

A standard ammonium fluoride–ammonium fluorozirconate solution was prepared by dissolving zircaloy in a known amount of standard hydrofluoric acid in the presence of ammonium nitrate and adjusting the solution to pH 5 with ammonia. The hydrofluoric acid was standardized against standard sodium fluoride solution by means of the fluoride-sensitive electrode as described below.

A triethanolamine–hydrochloric acid buffer was prepared by adding 14.9 g of triethanolamine to about 500 ml of water, adjusting the pH to 7 with the acid and diluting to 1 l with water.

RECOMMENDED PROCEDURES FOR THE DETERMINATION OF FLUORINE

Zirconium decladding solutions (F concentration (C) = 0.5–5 M)

Dilute 0.5 ml of the sample solution to 50 ml with water adjusted to pH 9 with ammonia. Prepare a second dilution by pipetting 1 ml of the first dilution into a 10-ml volumetric flask and fill up to the mark with the pH 7 buffer solution. Measure the potential difference E and repeat the measurement. Calculate $\log C$ and C by introducing the average E value and the coefficients P and B of the calibration equation in the expression: $\log C = 10^3 (P - \bar{E})/B$.

Concentrated uranyl nitrate solutions

(a) *Standard addition method (F concentration (C) > $1.5 \cdot 10^{-3}$ M)*. Pipette into each of three 10-ml volumetric flasks 1 ml of the sample solution. Add to the second flask, 0.250 ml of the standard fluoride solution I ($8 \cdot 10^{-3}$ M) and to the third flask 0.250 ml of the standard fluoride solution II ($1.6 \cdot 10^{-2}$ M). Fill all three flasks to the mark with 3 M ammonium acetate solution. Measure the potential difference of the electrode pair inserted into the three solutions (E_0 , E_1 and E_2) and repeat the measurements. Calculate $p = (E_1 - E_2)/(E_0 - E_1)$ from the average E values and calculate r by interpolation from the following table:

$p = 0.622$	0.585	0.549	0.513	0.477
$r = 0.45$	0.50	0.55	0.60	0.65

Calculate C from the equation: $C = 2 \cdot 10^{-3}(1 - r)/r$ moles/l.

(b) *Comparison with standards (F concentration (C) > $1.5 \cdot 10^{-4}$ M)*. Prepare two fluoride standard solutions, having fluoride concentrations S and $2S$ and the same uranium and acid concentrations as the sample solution. The fluoride concen-

tration C of the sample solution must be in the interval S and $2S$. Pipette 1 ml of the three solutions into 10-ml volumetric flasks. Fill all three flasks to the mark with 3 M ammonium acetate solution. Measure the potential difference of the electrode pair inserted in the three solutions (E_c , E_1 and E_2) and repeat the measurements. Calculate from the average E values $\log C$ and C by introducing $q = (\bar{E}_1 - \bar{E}_c) / (\bar{E}_1 - \bar{E}_2)$ into the equation: $\log C = q \cdot \log 2 + \log S$.

(c) *Determination after ion-exchange separation (F concentration (C) > $1.5 \cdot 10^{-4} M$).* Prepare two identical ion-exchange columns as described above. Pipette 1 ml of the sample solution onto the top of one column and 1 ml of a fluoride standard of approximately identical composition onto the top of the other column (fluoride concentrations C and S respectively). Elute fluoride from both columns with 5 ml of 0.1 N nitric acid, followed by 10 ml of distilled water. Neutralize the two eluted solutions with the same amount of sodium hydroxide solution. Evaporate the two solutions to incipient dryness. Take the two residues up in 3 M ammonium acetate and dilute to 10 ml in volumetric flasks. Measure the potential difference of the electrode pair inserted into the two solutions (E_c and E_s) and repeat the measurements. Calculate $\log C$ and C by introducing the average E values, the coefficient B of the calibration equation, and S into the expression: $\log C = (\bar{E}_c - \bar{E}_s) / B + \log S$.

Uranium feed solutions (F concentration (C) > $10^{-2} M$)

Dilute 0.5 ml of the sample solution to 50 ml with 3 M ammonium acetate. Measure the potential difference E of the electrode pair inserted into the solution and repeat the measurements. Calculate $\log C$ and C by introducing the average E value and the coefficients P and B of the calibration equation into the expression: $\log C = 10^2 (P - \bar{E}) / B$.

RESULTS AND DISCUSSION

The potential (E) between the electrodes inserted into solutions differing only in fluoride ion activity obeys a Nernst-type relation¹:

$$E = E_0 - \frac{RT}{F} \ln A_{F^-}$$

in which A_{F^-} is the fluoride ion activity in the diluted solution. The fluoride ion activity is equal to the product of the fluoride ion concentration and the fluoride ion activity coefficient. For a solution of constant ionic strength and temperature, E_0 , RT/F and the activity coefficient are constant. The measured potential difference (in mV) can therefore be related to the fluoride concentration C (in moles/l) by an equation of the type:

$$E = P - B \log C$$

in which the constants P and B are established by measurements on standard fluoride solutions. This equation can be used for the determination of unknown fluoride concentrations if measured under identical conditions.

Zirconium decladding solutions

The total amount of fluorine in decladding solutions has to be made available

in the form of free fluoride ions for its electrometric determination. An experiment was designed to show that the soluble zirconium fluorine complexes can be hydrolyzed by sufficient dilution. Water made alkaline by ammonia to pH 9 was used to achieve nearly complete hydrolysis. The final dilution was accomplished by 0.1 *M* triethanolamine-hydrochloric acid buffer to guarantee an almost constant ionic strength and to obtain a constant pH of 7, as, at this pH, the complexing of fluoride by hydrogen ions and the electrode response caused by hydroxyl ions can be neglected. The use of alkali salts was avoided to prevent precipitates of alkali-zirconium-fluoride compounds.

Four standard sodium fluoride solutions, the standard hydrofluoric acid and four ammonium fluorozirconate solutions were used. The fluorine concentrations of the last four solutions, which were made by mixing aliquots of the standard hydrofluoric acid and the standard ammonium fluorozirconate solution, were only known in relation to the concentration of the hydrofluoric acid solution. The composition of the solutions is shown in Table I. Aliquots of the nine solutions were diluted and

TABLE I
EXPERIMENTAL SOLUTIONS

Solutions	Estimated F or Zr concn. (<i>M</i>)	Known fluoride concn. (<i>M</i>)	Measured fluoride concn. (<i>M</i>)
Sodium fluoride		7.50 · 10 ⁻⁴ 1.50 · 10 ⁻³ 3.00 · 10 ⁻³ 6.00 · 10 ⁻³	
Hydrofluoric acid	F = 6 · 10 ⁻³	<i>a</i>	<i>a</i> = 5.80 · 10 ⁻³
Fluorozirconate	F = 6 · 10 ⁻³ Zr = 8 · 10 ⁻⁴ F = 6 · 10 ⁻³ Zr = 4 · 10 ⁻⁴ F = 6 · 10 ⁻⁴ Zr = 8 · 10 ⁻⁵ F = 6 · 10 ⁻⁴ Zr = 4 · 10 ⁻⁵	<i>a</i> <i>a</i> 0.9 <i>a</i> 0.1 <i>a</i> 0.09 <i>a</i>	<i>a</i> = 5.55 · 10 ⁻³ <i>a</i> = 5.63 · 10 ⁻³ <i>a</i> = 5.57 · 10 ⁻³ <i>a</i> = 5.78 · 10 ⁻³

measured, according to the recommended procedure, on ten different days in random sequence. The potential differences measured on the four sodium fluoride solutions were analysed statistically⁴. The fluoride concentrations were chosen so that they differed by a factor of 2 to simplify the analysis. The evaluation gave an estimate of the measurement error which was constant on the different days, showed that the equation is linear in log *C* over the range investigated, indicated that the day-to-day variation had not caused a significant displacement of the mean response but had a significant influence on the coefficient *B* of the equation, and resulted in 10 equations to be applied for interpretation of the measurements on the different days. The day-to-day variation of the coefficient *B* over the relatively large concentration range is most probably a temperature effect. The equations are of the type:

$$E = \bar{E} - B (\log C - \overline{\log C_s})$$

in which \bar{E} is the average of the potential difference measurements and $\overline{\log C_s}$ is the average log fluoride concentration of the standards. The equations were in our case:

$$E = -0.81 - B (\log C + 2.974)$$

in which the coefficient B for each day had values of about 57. The error in a calculated fluoride concentration, found after insertion of the potential difference measured on an unknown solution in the equation, is determined by the measurement error which is $s(E) = 1.1$, $DF = 20$ in our case, and the errors in \bar{E} and B , which are related to the measurement error. By disregarding the day-to-day variation $s(E)$ increases to 1.5, $DF = 38$. It can be shown that the standard deviation of a $\log C$ determination is maximally $2.4 \cdot 10^{-2}$ (at the end of the concentration range). The relative standard deviation of a calculated fluoride concentration, based on a single measurement, can be estimated to be $s(\log C)/\log e$ or between 4.5 and 5%. This error is decreased by a factor $k^{-0.5}$ in the case of k repeated measurements.

The calculation of the five unknown fluoride concentrations resulted, after conversion, in five values for the hydrofluoric acid concentration (a); these are listed in the Table. The standard deviation of the listed values, which are averages of 10 determinations, is about 1.7% or $0.1 \cdot 10^{-3} M$. As the five values show no significant difference, this means there is a nearly complete hydrolysis of the zirconium-fluorine complexes for the zirconium concentrations and dilution factors investigated.

Concentrated uranyl nitrate solutions

General considerations. The aim of this part of the investigation was to measure fluoride directly in nitric acid-uranyl nitrate solutions, after the uranium had been complexed and the acid buffered, but with a minimum of dilution. Preliminary experiments indicated that the differences in the concentrations of highly charged ions such as uranyl and citrate in the complexed sample solutions compared with their concentrations in the standard solution caused intolerable changes in the background potential P , which invalidated a calibration equation.

Concentrated ammonium acetate solution was used for complexing and buffering in these experiments. A sample solution, 1.7 M in uranyl nitrate and 0.5 N in nitric acid, was prepared. To 1-ml aliquots of this solution, 0.25 ml of six standard fluoride solutions, differing by a factor of 2 in concentration, and 3 M ammonium acetate were added to make a volume of 10 ml. Another six solutions were made starting from a 1.7 M uranyl nitrate solution which was 1 N in nitric acid. The 12 solutions were measured on five different days in random sequence. The average measurements E , their differences ΔE and the variances $s^2(E)$ are collected in Table II. The results prove that even small differences in the acid content of the solution influence the E value, that the difference ΔE is constant if the fluoride concentration is more than $1.5 \cdot 10^{-4} M$, and that the measurement error is not significantly different for the different E levels. A day-to-day variation could not be detected over the relatively small concentration range. The coefficient B is equal to $\Delta E/\log 2$ and is thus 65 for fluoride concentrations more than $1.5 \cdot 10^{-4} M$. This value is higher than the value predicted by the Nernst equation for diluted solutions.

Standard addition method. These results suggested the use of the standard addition method, in which known amounts of fluoride are added to the sample solution to ensure the same background potential⁵. A requirement is that the fluoride measurements are carried out in a fluoride concentration range in which the coefficient B in the calibration equation is constant.

TABLE II
POTENTIAL DIFFERENCE MEASUREMENTS (mV)^a

Fluoride concn. (M)	$1.53 \cdot 10^{-5}$	$3.07 \cdot 10^{-5}$	$6.14 \cdot 10^{-5}$	$1.53 \cdot 10^{-4}$	$3.07 \cdot 10^{-4}$	$6.14 \cdot 10^{-4}$
1.7 M U 0.5 N H	$E = 161.4$ $\Delta E = 8.2$	153.2 13.1	140.1	131.1 20.0	111.1 19.0	92.1
1.7 M U 1.0 N H	$E = 165.0$ $\Delta E = 11.3$	153.8 12.4	141.3	131.4	112.9 19.8	93.1
	$\Delta E = 9.75$ $s^2(E) = 0.27$ $s(E) = 0.88, DF = 48,$	12.75 0.66 $s(E) = 0.94$	2.13	0.30	19.6 1.30	0.64

^a With no fluoride present, $E = 170$.

The method is based on the measurements of the three potential differences E_c , E_1 and E_2 on the sample solution, sample solution plus a known amount and sample solution plus twice the same amount, having the fluoride concentrations C , $C+S$ and $C+2S$. The ratio p , defined as $(E_1 - E_2)/(E_c - E_1)$ is related to the concentrations C and S by:

$$p = \frac{-\log \{1+S/(C+S)\}}{\log \{1-S/(C+S)\}} = \frac{-\log (1+r)}{\log (1-r)}$$

in which $r=S/(C+S)$. The value of r corresponding to an experimental p value can be found from a constructed table or graph relating p and r . The concentration C can then be calculated from the equation: $C=S(1-r)/r$.

An error study can be based on the approximate equation:

$$C = \frac{S(3p-1)}{2(1-p)}$$

which is obtained by approximating the logarithms by series. It shows that the error of C is a minimum for $p=0.55$. The optimum conditions for measurement are thus obtained for $S=1.4C$. The value of $S=2 \cdot 10^{-3} M$ used in the recommended procedure is adequate for $C=1.5 \cdot 10^{-3} M$. The relative standard deviation of C for $p=0.55$ is approximately:

$$\text{rel. } s(C) = 7.2 \frac{s(E)}{E_1 - E_2}$$

Introduction of the values $s(E)=0.94$ and $E_1 - E_2=19.6$ from Table II into the expression, results in the estimate of $\text{rel. } s(C) = 35\%$ in the case of single measurements of the potential differences. This error is decreased by a factor $k^{-0.5}$ in the case of k repeated measurements. The detection limit of $1.5 \cdot 10^{-3} M$ fluoride in a $1.7 M$ uranium solution corresponds to a fluoride concentration of 70 p.p.m.

Comparison with standards. The uranium and acid concentrations in the pure final product are established with high precision. This makes it possible to lower the detection limit and the error of the fluoride determination by interpretation of the potential difference measurement E_c by means of the measurements E_1 and E_2 on two standard fluoride solutions, having the same uranium and acid concentrations as the sample solution. The recommended procedure describes the choice of two standard concentrations S and $2S$, so that the concentration C is in the interval, and assumes a constant coefficient B over the interval. The derivation results in the equation:

$$\log C = q \log 2 + \log S$$

in which q is defined as $(E_1 - E_c)/(E_1 - E_2)$.

An error study shows that:

$$\text{rel. } s(C) = \frac{\log 2 \{2(q^2 - q + 1)\}^{0.5}}{\log e(E_1 - E_2)} \cdot s(E)$$

This relative error is a maximum for a C value near the standard concentration ($q=1$), and, for $E_1 - E_2=9.75$ (see Table II), is a minimum for a C value in the middle of the interval and for $E_1 - E_2=19.6$; it is therefore between 4 and 10% in

the case of single measurements of the potential differences. This error is decreased by a factor $k^{-0.5}$ in the case of k repeated measurements. The detection limit of $1.5 \cdot 10^{-4} M$ fluoride in $1.7 M$ uranium solution corresponds to a fluoride concentration of 7 p.p.m.

Determination after ion-exchange separation. An alternative method for the determination of fluoride in concentrated uranyl nitrate solution is the measurement of the fluoride after removal of cations by means of a strongly acidic cation-exchange resin (Dowex 50W). A procedure is recommended in which the unknown concentration is determined relative to a standard, assuming that the same fraction of the fluoride is recovered in the two separations. The two concentrations should be close enough to enable the use of the same coefficient B for the interpretation of the measurements of the two potential differences. The magnitude of the fraction recovered was measured at three fluoride levels differing by a factor of 2. According to the recommended procedure, 1 ml of a solution containing 400 mg of uranium, 1 meq of nitric acid and $3.75 \cdot 10^{-2}$, $7.5 \cdot 10^{-2}$ or $1.5 \cdot 10^{-1}$ mmol of fluoride, was pipetted on a column and eluted. The fluoride was measured in the final solutions, which should have the concentrations C , $2C$ and $4C$ or briefly $f_i C$. As a control, the same amounts of fluoride were diluted directly to the final solutions. The measured fluoride concentrations should be S , $2S$ and $4S$ or briefly $f_i S$. The corresponding potential difference measurements can be represented as:

$$E_i^c = P - B (\log f_i + \log C) \text{ and}$$

$$E_i^s = P - B (\log f_i + \log S)$$

indicating that the responses E_i^c and E_i^s versus $\log f_i$ are two parallel straight lines. It can be shown⁶ that the logarithm of the fraction recovered and its variance is:

$$F = \log C/S = \frac{\bar{E}^c - \bar{E}^s}{B} \text{ and } s^2(F) = \frac{s^2(E)}{B^2} \frac{2}{3k}$$

in which \bar{E} is the average of the E measurements on the three fluoride levels and k is the number of repeated measurements of the potential differences. The experiment gave 88 and 101% as the 95% confidence limits of the fraction recovered.

If the recommended procedure is followed, the fluoride concentration of the sample solution C , and its relative error can be found from:

$$\log C = (E_c - E_s)/B + \log S \text{ and rel. } s(C) = \frac{s(E) \cdot 2^{0.5}}{B \log e}$$

For $s(E) = 0.94$ and $B = 60$, this relative error in case of a single measurement of the potential differences is estimated to be 5%.

Fluoride determination in uranium feed solutions

The fluoride concentration to be measured in these solutions is relatively high (higher than $10^{-2} M$). Dilution of an aliquot with a 3 M ammonium acetate may mask differences in the electrode response, caused by the difference in composition of the sample solution, and may complex interfering cations. The influence of differences in composition was investigated on four solutions containing 0.1 M aluminium and the same amount of fluoride, and differing in uranium (0.84 M and 1.7 M) and acidity levels (1 N and 2 N nitric acid). The fluoride concentration was

measured by the recommended procedure. Only the combination of high uranium and high acid content gave a significantly higher response than in the three other cases. The method can be applied in practice because the uranium concentration is about 1 M. The relative error in the case of a single measurement of the potential differences is *ca.* 5%.

The first dilution required for the fluorine determination in zirconium de-cladding solution and the direct measurement of fluoride in uranium feed solution can be carried out easily by remote control. Equipment adapted for these purposes⁷ has been used routinely. The fluoride-sensitive electrode has been applied during several months for routine measurements in the highly γ -active feed solutions without a noticeable effect on its performance.

SUMMARY

The determination of fluoride in zirconium decladding (Zirflex) solutions, uranium feed solutions and uranium final product solutions is described. The procedures are based on potential measurements of a fluoride-sensitive electrode *versus* a saturated calomel electrode after a relatively pre-treatment of the sample, *e.g.* dilution, complexing of metal constituents or separation by a cation-exchange column.

RÉSUMÉ

On décrit des procédés pour la détermination de la concentration en fluor dans les solutions de dégainage de zirconium (Zirflex), les solutions d'alimentation d'uranium, et les solutions finales d'uranium. Les déterminations sont basées sur des mesures de potentiel d'une électrode sensible aux fluorures par rapport à une électrode au calomel saturé, après un prétraitement de l'échantillon relativement simple tel que: dilution, formation de complexes avec les constituants métalliques ou séparation à l'aide d'une colonne d'échange cationique.

ZUSAMMENFASSUNG

Die Bestimmung von Fluorid in Zirkonium- und Uraniumlösungen wird beschrieben. Das Verfahren beruht auf Potentialmessungen einer fluoridempfindlichen Elektrode gegen eine gesättigte Kalomelektrode, nachdem relativ einfache Vorbehandlungen der Probe wie z.B. Verdünnung, Komplexbildung oder Abtrennung durch einen Kationenaustauscher vorgenommen sind.

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STUDIES WITH DITHIZONE. PART XIII¹. THE EXTRACTION OF METHYL-, BENZYL-, AND *p*-BROMOPHENYLMERCURY(II) DITHIZONATES

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The effect of pH on the extraction into carbon tetrachloride of a number of organomercury(II) dithizonates from mixed anion buffers (acetate-chloride, phosphate-citrate, chloride-glycinate) covering a range of pH values from 0-12 was studied by Cox^{2,3}. The statement that *p*-fluorophenylmercury(II) acetate and *p*-iodophenylmercury(II) chloride react with a solution of dithizone to give mercury(II) dithizonate has been shown to be incorrect⁴ and it seemed advisable to re-investigate also the behaviour of methylmercury-, benzylmercury-, and *p*-bromophenylmercury(II) dithizonates which were stated to decompose at high pH to give mercury dithizonate and for which very anomalous extraction curves were reported. Thus, while phenylmercury(II) dithizonate behaved normally (Fig. 1, curve 1), the percentage extracted in the case of methylmercury(II) chloride increased with acidity at first and then remained fairly constant to pH 4.5; with increasingly alkaline buffers the absorbancy of the organic phase rose again to reach a maximum between pH 8.4 and 8.7 and then fell off again (Fig. 1, curve 2). At no stage did the percentage extraction found remain constant to better than 1.5% and the values reported for the highest alkalinities, *viz.* 92.5%*, 108.7%, 55.1% and 82.8% for pH 9.69, 9.93, 9.95 and 10.20, respectively, follow no regular pattern and throw grave doubts on the validity of all the results for this system. The pH-extraction curves for benzylmercury(II) and *p*-bromophenylmercury(II) dithizonates (Fig. 1, curves 3 and 4) were said to show the same anomalous behaviour.

However, in the present work, when freshly purified laboratory samples of these organomercurials were used, the earlier results of Cox could not be reproduced and the pH-extraction curves showed no unusual features (Table I and Fig. 1, curves 5, 6 and 7).

An essential difference between the conditions used in the present experiments and those reported by Cox was in the time of phase-equilibration. Cox contacted the aqueous and organic phases by mechanical shaking for 30 min³. In the present work, it was found that partition equilibrium was achieved within 1-3 min and that in the case of methylmercury, benzylmercury, and *p*-bromophenylmercury dithizonate, the extraction from mixed buffers was effectively quantitative in the pH ranges 2.0-9.0,

* This value is incorrectly given as 29.5 in Table V, p. 469 of ref. 3. There is a further arithmetical error on p. 470, lines 10 and 11, where the last two entries under pH 8.33 should read 0.408 and 122.0% respectively.

1.3–8.5, and 0.95–9.0, respectively. When the extractions were carried out from an aqueous phase which was 1.0 *M* with respect to sodium perchlorate, and in the absence of anions that form complexes with mercury(II), the ranges were considerably greater, *viz.* 1.1–9.0, 0.0–9.8, 0.0–9.9.

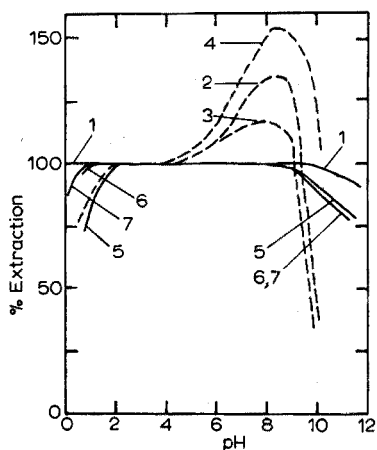


Fig. 1. The effect of pH on the extraction of organomercury(II) cations, RHg^+ , from aqueous buffers into solutions of dithizone, H_2Dz , in carbon tetrachloride. Curve 1: $\text{R}=\text{C}_6\text{H}_5$; Curves 2 and 5: $\text{R}=\text{CH}_3$; Curves 3 and 6: $\text{R}=\text{C}_6\text{H}_5\text{CH}_2$; Curves 4 and 7: $\text{R}=\textit{p}\text{-Br}\cdot\text{C}_6\text{H}_4$. Curves 2, 3 and 4 from Cox, ref. 3. Curves 5, 6 and 7, present work.

When, however, extractions were carried out from a phosphate–citrate buffer at pH 8.24 with times of shaking extended to 30, 90 and 240 min, the optical density, A_{620} , at 620 nm (where the absorption of dithizone is maximal and that of organomercury complexes very small) decreased progressively. Since the absorbancy attributable to the organomercury dithizonate at $\lambda_{\text{max}}=478$ nm is calculated by subtracting from the observed value of A_{478} , the contribution arising from any excess of dithizone remaining in the organic phase (which can be calculated from the observed value of A_{620} and the known ratio $\epsilon_{478}/\epsilon_{620}$ for pure dithizone), any such decrease in the amount of free dithizone would lead to an over-estimate of the amount of organomercurial that had been extracted. A progressive loss of total dithizone was also confirmed by “reverting” the organic phase with an acidified solution of potassium iodide⁵. Not only did the absorbancy at 620 nm decrease with time but the peak ratio (A_{620}/A_{450}) also decreased. This suggested that oxidation was taking place, and after dithizone had been completely extracted into dilute (1:100) isopiestic ammonia, the organic phase showed the characteristic absorption spectrum of the “yellow oxidation product”. Since this absorbs strongly over the range 400–450 nm, it would contribute spurious absorption that could also lead to an over-estimate of the concentration of methylmercury(II) dithizonate extracted. The presence of adventitious metal impurities (*e.g.* zinc) in one of the buffers could also have contributed to the anomalous results presented by Cox.

It was confirmed that each of the dithizonates named in the title were 1:1 complexes by using the method of continuous variations modified for 2-phase systems³. The characteristic features of their spectra are listed in Table I with Cox’s values for comparison.

TABLE I
THE ABSORPTION SPECTRA OF ORGANOMERCURY DITHIZONATES

	λ_{max}	ϵ_{max}	λ_{min}	ϵ_{min}	λ_{max}	ϵ_{max}	Source ^a
CH ₃ Hg(HDz)	478	33,000	275	2,400	372	15,600	A
	477	23,800	—	—	—	—	B
C ₆ H ₅ ·CH ₂ Hg(HDz)	478	35,300	265	2,300	372	24,400	A
	478	33,300	—	—	—	—	B
<i>p</i> -Br·C ₆ H ₄ ·Hg(HDz)	478	37,400	263	2,300	373	20,200	A
	478	39,400	—	—	—	—	B

^a A: present work. B: refs. 2 and 3.

EXPERIMENTAL

Preparation of compounds

Methylmercury(II) iodide was synthesised by a Grignard reaction between methylmagnesium iodide and mercury(II) chloride in dry ether. Recrystallization from methanol gave colourless crystals (m.p. 143°; lit. 145°⁶). (Found: Hg, 58.5%; calcd. for CH₃HgI, 58.6%).

Benzylmercury(II) chloride prepared analogously⁶ formed needles (m.p. 104°) on recrystallization from ethanol. (Found: Hg, 61.2%; calcd. for C₇H₇ClHg, 61.3%).

p-*Bromophenylmercury(II) chloride*. Mercury(II) chloride (3 g) was heated under reflux for 3 h with bromobenzene (17 g) and a few drops of glacial acetic acid. Hot aqueous ethanol (50 ml of 50% v/v) was then added and the mixture filtered while hot. Excess of an alcoholic solution of calcium chloride was then added and the *p*-bromophenylmercury(II) chloride which separated on cooling was collected and recrystallized from hot ethanol (yield 25%, m.p. 261°; lit. 249.5°⁷, 250°⁸). (Found: Hg, 51.0%; calcd. for C₆H₄BrHgCl, 51.2%).

For analysis the organic moiety was destroyed by wet oxidation with 70% perchloric acid. Mercury was then determined absorptiometrically with dithizone.

Reagents

Dithizone was purified by extracting it from carbon tetrachloride into metal-free ammonium hydroxide⁹, washing this aqueous solution with pure carbon tetrachloride; and back-extracting the dithizone into fresh carbon tetrachloride by adding an excess of isopiestic hydrochloric acid⁹. The cycle was repeated several times until the peak ratio (A_{620}/A_{450}) reached the value of 1.7. De-ionised water was used throughout. Carbon tetrachloride was purified by GEIGER AND SANDELL'S method¹⁰.

Buffers were purified of trace metals by extractions with dithizone, but so far as possible these were prepared from materials obtained by isopiestic distillation⁹. The customary precautions were observed in cleansing all glassware for use with dithizone. Absorptiometric measurements were carried out in matched 1-cm cells with a Unicam SP 500 spectrophotometer.

Extraction of organomercury(II) dithizonates

Aqueous buffer (5 ml) and 5 ml of an aqueous solution of the organomercury(II) halide ($1.616 \cdot 10^{-5}$ M) were equilibrated with 10 ml (excess) of a solution of dithizone

in carbon tetrachloride ($2.757 \cdot 10^{-5} M$) by shaking for 2–3 min. The phases were separated and the optical density of the organic phase was measured at 478 and 620 nm. The ratio A_{478}/A_{620} for pure dithizone was found to be 0.45. The percentage extracted was calculated from the absorbancy of the extracted complex at 478 nm and the value of ϵ_{478} (Table I) determined experimentally²

RESULTS

The percentage extractions obtained at different pH values for methylmercury(II) dithizonate are shown in Table II, and the values for the other two organomercurials are given in Table III.

TABLE II

VARIATION OF EXTRACTION OF METHYLMERCURY(II) DITHIZONATE WITH pH FOR BUFFERED SOLUTIONS

pH	O.D. observed		O. D. calculated		% Extraced
	Mixed complexes at 478 nm	620 nm	Dithizone alone at 478 nm	Complex alone at 478 nm	
0.85	0.615	0.530	0.238	0.377	73.6
1.44	0.666	0.442	0.199	0.467	91.4
2.22	0.690	0.395	0.178	0.512	100
3.77	0.690	0.396	0.178	0.512	100
4.68	0.690	0.396	0.178	0.512	100
6.38	0.690	0.395	0.178	0.512	100
7.38	0.685	0.381	0.172	0.513	100
8.03	0.671	0.258	0.161	0.510	99.6
9.18	0.561	0.142	0.064	0.497	97.1
10.31	0.464	0.026	0.012	0.452	88.2
11.85	0.400	0.033	0.015	0.385	75.2

TABLE III

VARIATION OF EXTRACTION OF BENZYL MERCURY(II) AND *p*-BROMOPHENYLMERCURY DITHIZONATES WITH pH FOR BUFFERED SOLUTIONS

<i>Benzylmercury(II) dithizonate</i>				<i>p-Bromophenylmercury(II) dithizonate</i>			
pH	% Extr.	pH	% Extr.	pH	% Extr.	pH	% Extr.
0.68	97.3	4.68	100.0	0.20	84.8	3.77	100.0
0.89	98.4	5.72	100.0	0.26	89.4	5.72	100.0
1.21	99.8	8.08	99.4	0.53	97.7	6.68	100.0
1.44	99.8	9.18	98.5	0.95	100.0	8.15	100.0
2.22	100.0	10.31	87.6	1.44	100.0	9.74	95.0
3.77	100.0			2.22	100.0	10.33	87.7

Extractions into carbon tetrachloride were also carried out from an aqueous phase 0.1 *M* with respect to sodium perchlorate, the pH being adjusted by small additions of isopiestic hydrochloric or acetic acid or ammonia. The results are given in Table IV. It will be noted that the ranges for quantitative extraction are greater than those previously found from buffers containing complexing anions. The effect is found for a much wider variety of organomercury compounds and will be discussed in a later paper¹¹.

TABLE IV

VARIATION OF EXTRACTION WITH pH FOR UNBUFFERED SOLUTIONS

<i>Methylmercury dithizonate</i>		<i>Benzylmercury dithizonate</i>		<i>p-Bromophenylmercury dithizonate</i>	
pH	% Extr.	pH	% Extr.	pH	% Extr.
0.43	74.2	0.00	100.0	0.0	99.8
1.01	98.1	0.51	97.7	0.52	99.8
1.31	99.8	1.10	100.2	1.11	100.0
2.34	100.1	1.29	100.4	1.37	100.2
4.21	100.3	2.30	99.8	2.33	99.9
5.62	100.0	3.49	100.1	3.55	100.2
6.68	99.5	5.80	100.2	5.72	100.0
8.31	99.8	6.71	100.0	6.79	99.8
9.58	97.2	8.38	99.5	8.44	100.0
10.36	89.9	9.42	100.2	9.70	99.7
		9.95	98.5	10.42	97.3
		10.25	96.8	11.23	95.4

SUMMARY

1:1 Complexes are formed between dithizonate ions, HDz⁻, and certain organomercury cations, RHg⁺ (R = methyl, benzyl, and *p*-bromophenyl). Their absorption spectra in carbon tetrachloride and the effects of pH on the percentage extracted from aqueous buffers containing, or free from, auxiliary complexing agents have been studied. The anomalous behaviour previously reported could not be confirmed.

RÉSUMÉ

Des complexes 1:1 sont formés entre des ions dithizonates, HDz⁻ et certains cations organomercuriels RHg⁺ (R = méthyl, benzyl et *p*-bromophényl). On examine leurs spectres d'absorption dans le tétrachlorure de carbone et l'influence du pH sur le pourcentage extrait de tampons aqueux en présence ou en l'absence d'agents complexants auxiliaires. L'anomalie de comportement décrite précédemment ne pourrait pas être confirmée.

ZUSAMMENFASSUNG

1:1-Komplexe werden zwischen Dithizonationen, HDz⁻, und gewissen organischen Quecksilberkationen, RHg⁺ (R = Methyl, Benzyl und *p*-Bromophenyl) gebildet. Ihre Absorptionsspektren in Tetrachlorkohlenstoff, der Einfluss des pH-Werts auf die prozentuale Extraktion aus wässrigen Puffern oder in Anwesenheit von Hilfskomplexbildnern wurde untersucht. Das früher erwähnte anormale Verhalten konnte nicht bestätigt werden.

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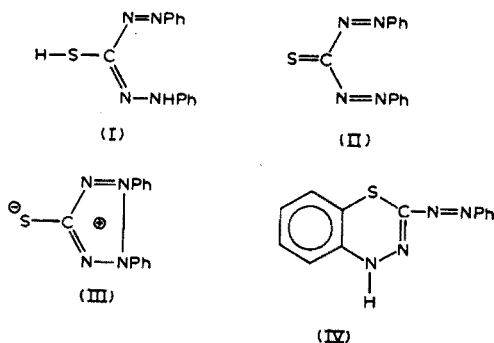
STUDIES WITH DITHIZONE. PART XIV. A NEW OXIDATION PRODUCT OF DITHIZONE

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The deterioration of solutions of the reagent dithizone (1,5-diphenyl-3-mercaptoformazan; (I), H₂Dz) is a matter of some consequence in analytical practice and it has commonly been attributed to oxidation. Deliberate attempts to oxidise dithizone with amyl nitrite led BAMBERGER *et al.*¹ to isolate a reddish orange compound which he formulated as the thiocarbodiazone (II). The same compound can be obtained with a variety of oxidising agents (*e.g.* hydrogen peroxide, iodine, manganese dioxide, potassium permanganate) and one of us² has shown the product to be identical with that isolated by OGILVIE AND CORWIN³ by oxidising dithizone with alkaline hexacyanoferrate (III), and formulated by him as the sydnone (III). Another isomeric oxidation product of dithizone is the purple compound first reported by OGILVIE AND CORWIN³ and investigated in greater detail by MAHNOT⁴. It appears from its chemical reactions and X-ray crystallography⁵ to possess the unexpected structure (IV).



If the oxidation of dithizone is carried out by treating its solution in chloroform with a weakly alkaline solution of hydrogen peroxide, the sydnone (III) is the main product. If, however, the oxidation is carried out with 30% hydrogen peroxide in a strongly alkaline medium, the main product is a violet-purple compound C₁₃H₁₂O₃N₄S that is not identical with (IV) and which proves to be 1,5-diphenylformazan-3-sulphonic acid (V). The presence of a sulphonic group is indicated by two strong absorption bands in the infrared spectra (KBr disc) at 13.28 and 13.50 μ indicative of an —SO₃H group⁶. The intense absorption band at 9.66 μ is characteristic of an S=O stretching vibration⁷. The new compound formed a characteristic derivative with S-benzylthiuronium hydrochloride, *viz.* the crystalline red benzylthiuronium-1,5-diphenylformazan-3-sulphonate.

1,5-Diphenylformazan-3-sulphonic acid dissolves readily in most organic sol-

vents to give solutions whose characteristics are shown in Table I. The differences in colour are quite striking, and when the spectra are compared (Fig. 1), it is obvious that the two absorption bands in acetone (curve 2) correspond closely with the separate long-wave peaks in chloroform (curve 1) and ethanol (curve 3) and that the three curves intersect at a common point (460 nm). This resemblance to an isosbestic point suggested that an acid-base equilibrium might be involved. This was confirmed by the spectra in chloroform saturated with hydrogen chloride (curve 4) and ammonia gas (curve 5) respectively. The acidic solutions of the sulphonic acid are reddish-violet in colour and absorb at λ_{max} 523 nm (ϵ_{max} $3.62 \cdot 10^4$); whereas the basic solution contain-

TABLE I

ABSORPTION SPECTRA OF 1,5-DIPHENYLFORMAZAN-3-SULPHONIC ACID

(Molecular extinction coefficients in parentheses given as $10^8 \epsilon$)

Chloroform	Acetone	Ethanol
λ_{max} 523 (31.17) (shoulder at 548 nm)	512 (18.52) (shoulder at 542 nm) λ_{min} 448 (12.43)	—
λ_{max} λ_{min} 375 (3.52)	410 (14.19)	423 (15.47) 350 (4.96)
λ_{max} 289 (10.08) (shoulder at 335 nm)		(broad shoulder \sim 300 nm)
λ_{min} 270 (9.35)		
λ_{max} 265 (10.01)		250 (14.30)

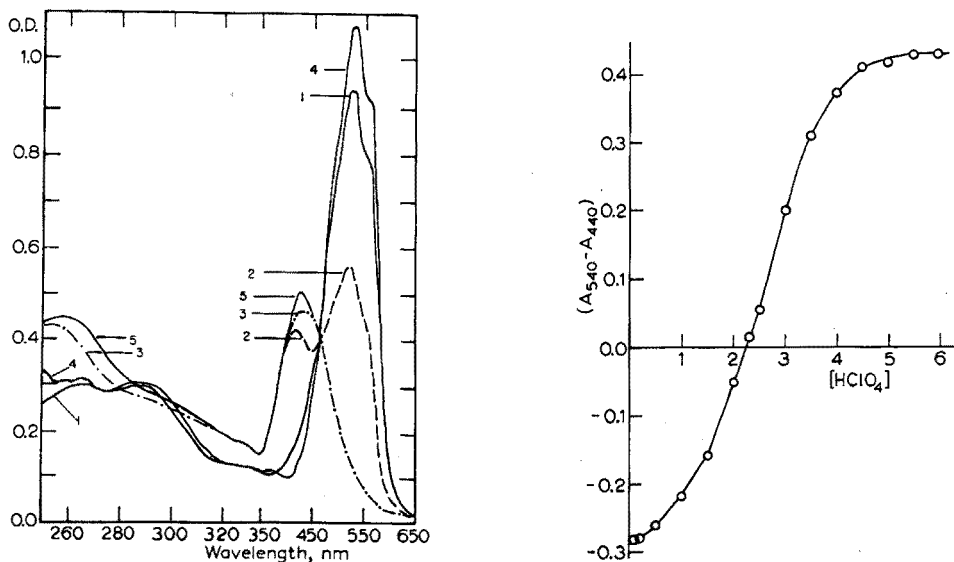


Fig. 1. The absorption spectra of $3.0 \cdot 10^{-5} M$ solutions of 1,5-diphenylformazan-3-sulphonic acid in chloroform (curve 1), acetone (curve 2), ethanol (curve 3), chloroform saturated with HCl gas (curve 4), chloroform saturated with ammonia gas (curve 5).

Fig. 2. The optical density of $1.850 \cdot 10^{-5} M$ solutions of 1,5-diphenylformazan-3-sulphonic acid in perchloric acid at 540 nm minus the optical density at 440 nm.

ing the sulphonate ion absorbs at λ_{\max} 425 nm (ϵ_{\max} $2.34 \cdot 10^4$). In aqueous solution the sulphonic acid absorbs at 540 nm (ϵ_{\max} 28,540) and the sulphonate ion at 440 nm (ϵ_{\max} 18,780). By measurements (Table II) on a $1.850 \cdot 10^{-5}$ M solution in perchloric acid of concentrations ranging from 0.1 to 6 M, it was possible to determine spectrophotometrically the position of equilibrium in the dissociation $V \rightleftharpoons VI$:

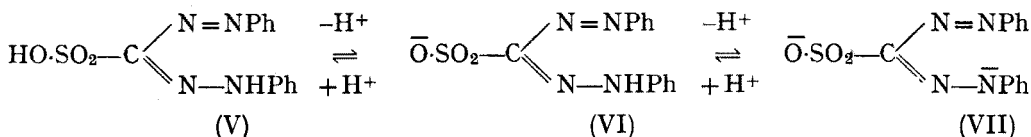


TABLE II

THE ABSORPTION SPECTRUM OF 1,5-DIPHENYLFORMAZAN-3-SULPHONIC ACID IN PERCHLORIC ACID. DETERMINATION OF pK_1

[HClO ₄]	<i>H</i> ₀ value	Absorbancy (1-cm cell) at	
		440 nm	540 nm
0.1		0.347	0.265 ^a
0.2		0.350	0.283 ^a
0.5		0.341	0.323 ^a
1.0	-0.22	0.326	0.430 ^a
1.5	-0.53	0.312	0.152
2.0	-0.78	0.278	0.227
2.5	-1.01	0.236	0.291
3.0	-1.23	0.192	0.393
3.5	-1.47	0.152	0.462
4.0	-1.72	0.134	0.508
4.5	-1.97	0.121	0.517
5.0	-2.23	0.105	0.520
5.5	-2.52	0.100	0.531
6.0	-2.84	0.099	0.530

^a Measurements in 4-cm cell.

The isosbestic point at 475 nm is clearly defined and from the position of the point of inflection in the plot of the difference in absorbancy at 540 and 440 nm against the concentration of perchloric acid (Fig. 2), the acid dissociation constant pK_1 defined by the equation

$$H_0 = \log [B]/[BH^+] + pK_1$$

was calculated, as described by DAVIS AND GEISSMAN⁸, as -0.92 ± 0.1 .

When aqueous solutions of 1,5-diphenylformazan-3-sulphonic acid are made alkaline, the yellow colour changes to reddish violet as the equilibrium $VI \rightleftharpoons VII$ is displaced to the right. The absorption spectra (Fig. 3) show a well defined isosbestic point at 472 nm and by plotting the difference between the optical densities at 520 and 440 nm against the pH the value $pK_2 = 12.9$ ($\mu = 1$ M sodium nitrate) was derived by the method previously used⁸.

Whereas the sydnone (III) is the main product when the oxidation of dithizone (I) is carried out in neutral or slightly alkaline solution, the proportion of the sydnone

diminishes and that of the sulphonic acid (V) increases as the alkalinity is raised. It would appear that kinetic factors favour the formation of (V) from the anion derived by loss of a proton from the acidic thiol group in (I) for which the value $pK = 4.5$ has been reported⁹. It is noteworthy that conditions that favour the formation of the purple isomer (IV) of the sydnone (III), *viz.* heating under reflux with glacial acetic acid³ or

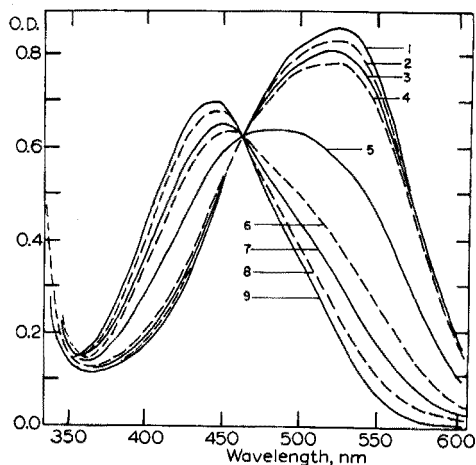


Fig. 3. The absorption spectra of $1.85 \cdot 10^{-5} M$ solutions of 1,5-diphenylformazan-3-sulphonic acid in aqueous sodium hydroxide containing sodium nitrate ($\mu = 1 M$). Curves 1-9 for pH 13.73, 13.63, 13.54, 13.42, 13.12, 12.73, 12.12, 11.42, and 7.73 respectively.

prolonged contact with concentrated solutions of mineral acids in aqueous dioxan^{4,10} are those in which the thiol function of (I) is suppressed and the dithizone reacts predominantly in the tautomeric thione form $\text{Ph.N}=\text{N.CS.NH.NH.Ph}$ or even as its conjugate acid.

EXPERIMENTAL

Preparation of 1,5-diphenylformazan-3-sulphonic acid

Dithizone (B.D.H. laboratory grade) was first purified by taking up in iso-pestically distilled dilute ammonia solution, filtering and reprecipitation by hydrochloric acid. The purified dithizone (2.0 g) was dissolved in sodium hydroxide solution (250 ml of 0.5 M) and treated dropwise with 30% hydrogen peroxide (40 ml; excess) in a 500-ml flask fitted with a mechanical stirrer (20 min). Stirring was continued for a further 40 min and the reaction mixture was filtered through a sintered glass funnel. The filtrate was cooled to 0° and acidified with the minimum amount of sulphuric acid (10 M) when 1,5-diphenylformazan-3-sulphonic acid separated as a brownish-black precipitate. It was taken up in the minimum amount of 0.1 M sodium hydroxide and after cooling to 0°, the sulphonic acid was reprecipitated with hydrochloric acid, dried, and finally recrystallized from chloroform as very fine brown-black needles (m.p. 181° decomp.; yield, 56%). (Found: C, 51.10, 51.15; H, 3.95, 3.85; N, 18.45, 18.25; S, 10.87, 10.45%. $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_3\text{S}$ requires, C, 51.28; H, 3.97; N, 18.41; S, 10.54%).

Preparation of thiuronium derivative

When cold aqueous solutions of 1,5-diphenylformazan-3-sulphonic acid (0.2 g) and S-benzylisothiuronium chloride (0.2 g) were mixed, *S-benzylthiuronium-1,5-diphenylformazan-3-sulphonate* separated in quantitative yield and formed bright orange needles (m.p. 179°) on crystallization from 50% aqueous ethanol. (Found: C, 53.58, 53.51; H, 4.80, 4.79%. $C_{21}H_{22}N_6O_3S_2$ requires C, 53.65; H, 4.71%).

Determination of pK_1

Aliquot portions (2 ml) of a stock solution of $2.3125 \cdot 10^{-4}$ M sulphonic acid (V) in deionised water were mixed in various proportions with a concentrated solution of AnalaR perchloric acid and made up to 25 ml. The optical density of each sample was measured at 540 and 440 nm with a Unicam S.P. 500 spectrophotometer instrument in matched silica cells. All measurements were controlled thermostatically at 25°. The results are given in Table II and shown graphically in Fig. 2.

The absorption spectra of all the samples were recorded with a Unicam S.P. 700 spectrophotometer. All the curves intersected at an isosbestic point at 475 nm.

Determination of pK_2

Aliquot portions (2 ml) of $2.3125 \cdot 10^{-4}$ M sulphonic acid (V) in deionised water were mixed with x ml of standard carbonate-free 2.5 M sodium hydroxide and $(10-x)$ ml of 2.5 M sodium nitrate and made up to 25 ml. All solutions were made up in CO₂-free water and transferred by nitrogen pressure into vessels flushed with nitrogen. Spectra were recorded in cells thermostatted at 25° immediately after the solutions

TABLE III

THE ABSORPTION SPECTRA OF 1,5-DIPHENYLFORMAZAN-3-SULPHONIC ACID IN SODIUM HYDROXIDE AT $\mu = 1.0$ (NaNO₃) AND 25°

[NaOH]	pH	Absorbancy (2-cm cell) at	
		440 nm	520 nm
$1.0 \cdot 10^{-6}$	7.725	0.688	0.238
$1.0 \cdot 10^{-5}$	8.725	0.690	0.240
$1.0 \cdot 10^{-4}$	9.725	0.687	0.245
$1.0 \cdot 10^{-3}$	10.725	0.687	0.250
$2.5 \cdot 10^{-3}$	11.123	0.687	0.260
$5.0 \cdot 10^{-3}$	11.424	0.678	0.270
$1.0 \cdot 10^{-2}$	11.725	0.667	0.300
$2.5 \cdot 10^{-2}$	12.123	0.638	0.333
$5 \cdot 10^{-2}$	12.424	0.615	0.410
$1.0 \cdot 10^{-1}$	12.725	0.580	0.520
$1.5 \cdot 10^{-1}$	12.901	0.550	0.586
$2.5 \cdot 10^{-1}$	13.123	0.515	0.672
$3.5 \cdot 10^{-1}$	13.269	0.487	0.727
$5.0 \cdot 10^{-1}$	13.424	0.471	0.780
$6.5 \cdot 10^{-1}$	13.538	0.455	0.803
$7.5 \cdot 10^{-1}$	13.601	0.448	0.818
$8.0 \cdot 10^{-1}$	13.628	0.443	0.826
$8.5 \cdot 10^{-1}$	13.654	0.440	0.842
$9.5 \cdot 10^{-1}$	13.703	0.440	0.845
$10.0 \cdot 10^{-1}$	13.725	0.440	0.850

had been made up. The various spectra intersected at a well-defined isosbestic point at 472 nm (Fig. 3), confirming the acid-base equilibrium $\text{VI} \rightleftharpoons \text{VII}$. The optical densities at 440 nm (yellow ion; VI) and 520 nm (reddish-violet anion; VII) were measured with a Unicam S.P. 500 spectrophotometer and are given in Table III.

In calculating the pH corresponding to calculated $[\text{OH}^-]$, the value $K_w = 1.884 \cdot 10^{-14}$ for 25° and $\mu = 1.0$ was used¹¹. The optical density at 520 nm minus the optical density at 440 nm was plotted against pH to give a sigmoid curve (not reproduced, but resembling Fig. 2), from which the value $\text{p}K_2 = 12.90$ was calculated as previously described⁸.

SUMMARY

The oxidation of dithizone with hydrogen peroxide in strongly alkaline solutions yields 1,5-diphenylformazan-3-sulphonic acid as a violet compound which loses a proton to give yellow solutions of the corresponding sulphonate ion and reddish-violet solutions on removal of a second proton from an imino-group. The acid dissociation constants $\text{p}K_1 = -0.92$ and $\text{p}K_2 = 12.9$ ($\mu = 1 \text{ M NaNO}_3$) were determined spectrophotometrically.

RÉSUMÉ

L'oxydation de la dithizone par le peroxyde d'hydrogène en solutions fortement alcalines conduit à la formation de l'acide 1,5-diphénylformazane-3-sulfonique violet qui par perte d'un proton donne des solutions jaunes de l'ion sulfonate correspondant et des solutions violet rouge par départ d'un second proton du groupe imino. Les constantes de dissociation acides $\text{p}K_1 = -0.92$ et $\text{p}K_2 = 12.9$ ($\mu = 1 \text{ M NaNO}_3$) ont été déterminées par spectrophotométrie.

ZUSAMMENFASSUNG

Die Oxydation von Dithizon mit Wasserstoffperoxyd in stark alkalischer Lösung führt zu 1,5-Diphenylformazan-3-sulfonsäure. Diese violette Verbindung führt bei Angabe eines Protons zu gelben Lösungen des korrespondierenden Sulfonats und zu rötlich-violetten Lösungen bei Angabe eines zweiten Protons von der Imino-Gruppe. Die Säuredissoziationskonstanten $\text{p}K_1 = -0.92$ und $\text{p}K_2 = 12.9$ ($\mu = 1 \text{ M NaNO}_3$) wurden spektralphotometrisch bestimmt.

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STUDIES WITH DITHIZONE. PART XV¹. FURTHER REACTIONS WITH ORGANOMERCURY COMPOUNDS

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Dithizone (diphenylthiocarbazone, 3-mercapto-1,5-diphenylformazan; H₂Dz) is widely used in trace-metal analysis and since its sensitivity often exceeds that of spectrographic procedures, it has been employed by a number of authors²⁻⁷ for the detection and absorptiometric determination of organomercury compounds. Miller *et al.*² reported that ethylmercury(II) chloride and phenylmercury(II) chloride react with solutions of dithizone in carbon tetrachloride to give yellow 1:1 complexes which can be extracted into the organic phase. Their absorption spectra were stated to be similar to, though not identical with that of mercury dithizonate, Hg(HDz)₂, and that of *o*-HOOC·CH₂·C₆H₄·CO·NHCH₂·CH(OCH₃)·CH₂Hg(HDz).

IRVING AND COX⁵ investigated the reactions between dithizone and a number of other organomercury compounds and showed that strongly coloured 1:1 complexes of the general formula RHg(HDz) were formed when R = CH₃, C₂H₅, C₆H₅·CH₂, C₆H₅, *p*-CH₃·C₆H₄, *p*-Cl·C₆H₄ and *p*-Br·C₆H₄. The statement that *p*-fluorophenylmercury(II) acetate and *p*-iodophenylmercury(II) chloride were anomalous in reacting to form Hg(HDz)₂ instead of the expected 1:1 complexes⁵ was later shown to be in error⁶. The improbable report that solutions of methyl-, benzyl-, and *p*-bromophenylmercury dithizonates in chloroform decompose rapidly in contact with both neutral and alkaline aqueous solutions to form Hg(HDz)₂ was reinvestigated in a previous paper⁸ but the original observations could not be repeated and no anomalous behaviour could be confirmed. The interaction of dithizone with a much wider variety of organomercurials is reported in the present paper.

With the exception of trichloromethylmercury(II), which did not give a complex stable enough to be fully investigated, all the organomercurials were found to yield strongly coloured yellow complexes with dithizone which could be extracted into carbon tetrachloride from aqueous solutions covering a wide range of pH values (*cf.* Table I). When the optimum pH range over which extraction is complete had been established, the stoichiometry of each complex could be investigated. In some cases the method of continuous variations was used, modified as previously described⁹ for two-phase systems*. The results for pentafluorophenylmercury(II) dithizonate, shown in Fig. 1, are typical of this method which was also used¹⁰ for compounds numbered 16, 17 and 18. In each case the location of the extrema at 50 moles % of each component establishes the general formula R Hg(HDz).

* There is a typographical error in the simplified equation (11a) which should read

$$A_j = \alpha C p c (e c - n p_R \epsilon_R) / \{ p_R + (K_R / [H^+]) \}.$$

TABLE I
EXTRACTION OF ORGANOMERCURY (II) DITHIZONATES INTO CARBON TETRACHLORIDE AND THE ABSORPTION CHARACTERISTICS OF THE EXTRACTS
(Values of molar extinction coefficients are given ($\times 10^{-3}$) in parentheses)

No.	Cation	pH range for complete extraction		λ_{max}	λ_{min}	λ_{max}	Ref. ^a
		From 1.0 M sodium perchlorate	From mixed anion buffers				
1	$C_6F_5 \cdot Hg^+$	0.0-10.4	0.0-9.8	~ 262 (~ 17.4)	374 (2.2)	482 (38.2)	A
2	2,3-(HO)(NO ₂) $\cdot C_6H_3 \cdot Hg^+$	0.0-10.3	0.6-10.0	273 (20.0)	376 (5.4)	477 (37.5)	A
3	<i>p</i> -F $\cdot C_6H_4 \cdot Hg^+$	0.0-10.1	0.95-9.4	265 (18.6)	373 (2.1)	478 (36.0)	A
4	<i>p</i> -Cl $\cdot C_6H_4 \cdot Hg^+$	0.0-9.8	0.90-9.4	263 (20.0)	375 (2.2)	480 (34.9)	A
5	<i>p</i> -Br $\cdot C_6H_4 \cdot Hg^+$	0.0-9.9	0.95-9.0	~ 263 (~ 20.2)	373 (2.3)	481 (34.8)	B
6	<i>p</i> -I $\cdot C_6H_4 \cdot Hg^+$	0.0-11.7	1.6-11.7	268 (~ 21.4)	375 (2.5)	478 (37.4)	A
7	$C_6H_5 \cdot Hg^+$	0.0-10.0	1.1-8.9	263 (18.7)	375 (2.1)	477 (34.8)	A
				266	477 (33.4)	477 (40.1)	B
8	<i>o</i> -CH ₃ O $\cdot C_6H_4 \cdot Hg^+$	0.0-9.9	1.2-8.3	279 (20.0)	376 (2.3)	497	E
9	$C_6H_5 \cdot CH_2 \cdot Hg^+$	0.0-9.8	1.3-8.5	265 (24.4)	372 (2.3)	477 (35.9)	A
10	<i>o</i> -HO $\cdot C_6H_4 \cdot Hg^+$	0.0-10.2	1.5-9.9	272 (19.4)	372 (2.3)	478 (33.3)	B
11	<i>p</i> -HO $\cdot C_6H_4 \cdot Hg^+$	0.0-9.8	1.6-9.7	263 (17.5)	375 (2.2)	480 (34.7)	A
12	<i>o</i> -HO $\cdot CH_2 \cdot C_6H_4 \cdot Hg^+$	0.0-9.7	1.75-9.8	262 (18.1)	373 (2.0)	480 (31.5)	A
13	<i>p</i> -HOOC $\cdot C_6H_4 \cdot Hg^+$	0.0-7.0	1.8-7.0	261 (18.8)	373 (2.2)	480 (35.4)	A
14	<i>o</i> -HOOC $\cdot C_6H_4 \cdot Hg^+$	0.0-7.0	1.9-7.0	263 (18.0)	376 (2.2)	480 (31.6)	A
15	<i>p</i> -CH ₃ CONH $\cdot C_6H_4 \cdot Hg^+$	0.0-9.5	2.2-9.5	263 (29.0)	374 (2.3)	481 (32.5)	A
16	<i>p</i> -(CH ₃) ₂ N $\cdot C_6H_4 \cdot Hg^+$	0.0-9.4	2.75-9.5	272 (33.5)	374 (2.6)	476 (33.1)	A
17	2,5-(HOOC)(NH ₂) $\cdot C_6H_3 \cdot Hg^+$	2.4-6.9 ^b	3.0-6.8 ^b	278 (29.4)	374 (4.0)	480 (34.1)	A
18	<i>p</i> -NH ₂ $\cdot C_6H_4 \cdot Hg^+$	2.5-9.2	3.45-8.3	262 (30.0)	375 (3.2)	480 (32.3)	A
19	<i>p</i> -CH ₃ $\cdot C_6H_4 \cdot Hg^+$	—	2.1-7.5	—	—	483 (34.1)	A
20	$C_6H_5 \cdot Hg^+$	0.0-9.4	1.8-9.2	276 (15.0)	375 (2.2)	478 (34.2)	B
				—	—	476 (35.1)	A
				—	—	475 (31.7)	B
21	CH ₃ $\cdot Hg^+$	1.1-9.0	2.0-9.0	275 (15.6)	372 (2.4)	475	C
				—	—	480	D
				—	—	478 (33.0)	A
				—	—	477 (33.8)	B

^a A: present work; B: J. J. Cox, *D. Phil. Thesis*, Oxford, 1960; C: in chloroform, ref. 2; D: in 95% ethanol-water, ref. 3; E: in chloroform, ref. 4.
^b In chloroform.

An alternative method, a form of extractive titration, was used with other mercurials. Here a constant known amount of dithizone in carbon tetrachloride of concentration C_R and a variable amount of organomercurial of concentration C_M were shaken with a constant volume of aqueous buffer to maintain the pH within the range over which preliminary measurements had shown the extraction to be

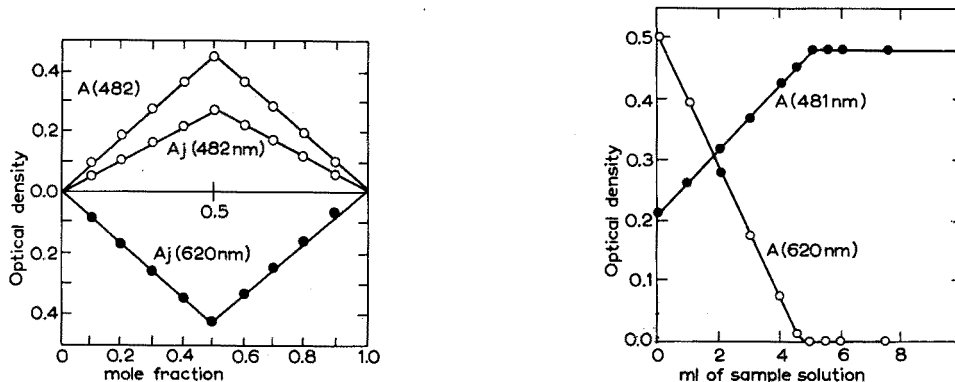


Fig. 1. The method of continuous variations applied to a two-phase system (carbon tetrachloride–aqueous buffer of pH 2.1 and $\mu = 1.0 M NaClO_4$) for determining the stoichiometry of pentafluorophenylmercury(II) dithizonate.

Fig. 2. Extractive titration of a $1.47 \cdot 10^{-5} M$ solution of dithizone in carbon tetrachloride by a $2.996 \cdot 10^{-5} M$ aqueous solution of *o*-carboxyphenylmercury(II) chloride of pH 2.95.

quantitative (*cf.* Table I). After equilibration, the organic phase was removed and its optical density measured at the wavelength of maximum absorption of the complex, and also at 620 nm where the absorption of dithizonate itself is maximal. The total absorbancy is given by

$$A = [H_2Dz]_{org} \epsilon_R + [M(HDz)_n]_{org} \epsilon_C = C_R \epsilon_R + C_M (\epsilon_C - n \epsilon_R) \quad (I)$$

where ϵ_C and ϵ_R are the molecular extinction coefficients of the complex and dithizone respectively. At 620 nm, $n \epsilon_R > \epsilon_C$ and a plot of A against C_M will be a straight line of negative slope intersecting a horizontal line at the point where $n C_M = C_R$ and the whole of the reagent has been transformed into its metal complex. For measurements at the wavelength of maximum absorption for the complex, $\epsilon_C > n \epsilon_R$, and the situation is reversed. The application of this method to the complex formed by *o*-carboxyphenylmercury(II) chloride is described in the experimental section and the data are shown in Fig. 2. The equivalence point where 5.0 ml of $2.996 \cdot 10^{-5} M$ organomercurial has reacted with 10 ml of $1.47 \cdot 10^{-5} M$ dithizone establishes the ratio $[R \cdot Hg^+] : [H_2Dz] = 1.02 : 1$. Similar proofs of the general formula $RHg(HDz)$ were obtained experimentally¹⁰ for the compounds numbered 2, 3, 6, 8, 10, 11, 12, 13, 14, and 15. The stoichiometry of the remaining compounds had been established previously⁵. The sharpness of the intersection of the straight lines in Fig. 2 indicates that the organomercury dithizonates are very stable complexes.

The stoichiometry of all the complexes having been established, it was possible to determine their molecular extinction coefficients by either (a) a total conversion or (b) a graphical method. Both methods were used to obtain values of ϵ in the visible region while method (a) alone was used for measurements in the ultra-

TABLE II

PERCENTAGE EXTRACTION OF VARIOUS ORGANOMERCURIALS AT DIFFERENT PH VALUES IN BUFFERED MEDIA

<i>Pentafluorophenylmercury(II) dithizonate</i>												
pH	0.0	0.36	0.78	1.46	1.67	2.24	4.69	6.07	7.28	8.26	9.32	10.21
% extr.	99.6	99.8	100.0	100.0	99.8	100.2	100.0	99.0	100.8	100.1	99.8	96.5
<i>2-Hydroxy-3-nitrophenylmercury(II) dithizonate</i>												
pH	0.38	0.73	1.43	2.82	3.92	5.75	6.55	7.57	9.08	9.90	11.40	
% extr.	93.5	99.8	99.7	100.2	99.4	100.5	99.8	99.1	100.2	99.6	89.9	
<i>p-Chlorophenylmercury(II) dithizonate</i>												
pH	0.40	0.78	1.31	2.22	3.71	4.69	5.68	7.68	9.63	10.59		
% extr.	93.8	98.1	99.9	100.3	100.0	100.2	99.7	99.5	98.2	95.1		
<i>o-Methoxyphenylmercury(II) dithizonate</i>												
pH	0.29	0.55	1.01	2.22	3.77	4.68	5.68	5.71	6.69	8.25	9.25	10.33
% extr.	77.9	93.6	98.2	99.9	100.0	100.0	100.0	100.0	100.0	100.0	73.6	58.1
<i>Phenylmercury(II) dithizonate</i>												
pH	0.31	0.54	1.10	2.31	3.76	4.71	5.66	6.71	8.24	9.23	10.32	
% extr.	81.1	94.1	99.8	99.6	100.1	100.0	99.9	99.6	99.4	96.2	93.4	
<i>2-Hydroxyphenylmercury(II) dithizonate</i>												
pH	0.52	1.12	1.61	1.93	2.17	3.91	4.10	4.75	6.52	8.42	9.23	10.25
% extr.	88.1	96.2	99.6	100.2	100.1	99.8	99.6	99.2	100.5	99.6	99.8	95.2
<i>2-Hydroxymethylphenylmercury(II) dithizonate</i>												
pH	0.52	1.18	1.63	2.01	3.91	4.18	4.75	6.52	8.46	9.28	10.29	
% extr.	87.1	96.8	99.8	100.2	100.0	99.6	99.5	98.9	100.2	99.8	97.2	
<i>4-Hydroxymethylphenylmercury(II) dithizonate</i>												
pH	0.51	1.16	1.59	1.96	2.19	3.86	4.20	4.80	6.53	8.38	9.28	10.26
% extr.	88.5	95.2	99.6	99.8	100.2	100.0	99.5	99.8	100.2	100.0	99.8	95.6
<i>2-Carboxyphenylmercury(II) dithizonate</i>												
pH	1.17	1.63	2.17	3.92	4.27	4.69	6.89	8.32	9.26	10.39		
% extr.	95.2	96.5	100.1	99.8	99.6	100.0	100.0	41.2	5.2	0.0		
<i>4-Carboxyphenylmercury(II) dithizonate</i>												
pH	1.18	1.65	2.07	3.86	4.28	4.78	6.52	6.89	8.34	9.27	10.38	
% extr.	95.2	97.7	99.6	99.5	100.0	100.2	99.8	100.0	39.2	6.2	0.0	
<i>2-Carboxy-5-aminophenylmercury(II) dithizonate</i>												
pH	1.62	2.19	3.86	4.37	4.69	5.41	6.72	8.29	9.36	10.41		
% extr.	78.9	91.1	100.0	99.8	100.1	99.5	100.0	33.8	2.1	0.0		
<i>2-Aminophenylmercury(II) dithizonate</i>												
pH	1.63	2.22	3.82	4.39	4.71	6.81	8.71	8.23	9.32	10.43		
% extr.	71.2	82.3	100.2	100.0	99.6	99.5	100.1	100.1	98.2	89.4		
<i>2-Acetylamino-phenylmercury(II) dithizonate</i>												
pH	1.19	1.65	2.19	3.86	4.31	4.71	6.73	8.36	9.31	10.41		
% extr.	91.1	94.2	99.8	100.2	100.0	100.0	99.8	99.2	99.8	95.1		
<i>4-Dimethylamino-phenylmercury(II) dithizonate</i>												
pH	1.65	2.18	3.86	4.31	4.71	5.39	6.71	8.29	9.36	10.38		
% extr.	81.8	92.6	100.0	99.8	100.1	100.0	100.0	99.8	100.0	96.4		

violet. Representative examples of each method are described in the experimental section and the characteristics of the various optical spectra are collected in Table I which includes some earlier data on other relevant dithizone complexes of mercury(II) and its derivatives.

When the molecular extinction coefficients are known, it becomes possible to calculate the actual percentages of complexes extracted under various conditions (Table I).

EXPERIMENTAL

Materials

Samples of the organomercury(II) compounds were purchased or prepared by published methods and recrystallised several times before use. For analysis the organic moiety was destroyed by wet-ashing and boiling the sample under reflux with 70% perchloric acid: mercury was then determined absorptiometrically with dithizone. Halogens were determined after fusion with sodium peroxide in a Parr bomb. The following compounds were prepared.

o-Hydroxyphenylmercury(II) chloride¹¹, m.p. 152° from hot water. (Found: Hg, 60.7%. Calcd. for C₆H₅OHgCl, Hg, 60.9%). *p*-Aminophenylmercury(II) chloride¹², m.p. 188° from ethanol. (Found: Hg, 61.0%. Calcd. for C₆H₅ClNHg, Hg, 61.1%). *p*-Acetylaminophenylmercury(II) acetate¹², m.p. 221° from hot water. (Found: Hg, 50.7%. Calcd. for C₁₀H₁₁NO₃Hg, Hg, 50.75%). *p*-Dimethylaminophenylmercury(II) chloride¹², m.p. 225° from chloroform. (Found: Hg, 56.2%. Calcd. for C₈H₁₀ClNHg, 56.3%). *o*-Anhydromercuri-*p*-aminobenzoic acid¹³, was taken up in sodium hydroxide (3.4 ml of 2 N sodium hydroxide per g of acid) and filtered: acidification of the filtrate gave the pure anhydro-compound. (Found: Hg, 59.8%. Calcd. for C₇H₅O₂NHg, Hg, 59.8%). *o*-Carboxylphenylmercury(II) chloride was prepared similarly and finally recrystallised from large volumes of hot water (Found: Hg, 55.8%. Calcd. for C₇H₅ClO₂Hg, Hg, 56.1%). *o*-Hydroxymethylphenylmercury(II) chloride¹⁴, m.p. 120° from hot water. (Found: Hg, 58.35%. Calcd. for C₇H₇OClHg, 58.45%). *p*-Hydroxymethylphenylmercury(II) chloride¹⁴, m.p. 250° from hot ethanol. (Found: Hg, 58.3%. Calcd. for C₇H₇OClHg, 58.45%). *p*-Carboxyphenylmercury(II) chloride was prepared by oxidation of the above *p*-hydroxymethyl compound with alkaline permanganate at 100°. After being cooled, the solution was acidified with hydrochloric acid and the *p*-carboxyphenylmercury(II) chloride which separated was recrystallised from hot ethanol. (Found: Hg, 55.9%. Calcd. for C₇H₅O₂ClHg, 56.1%). Ethylmercury(II) chloride. A commercial sample (L. Light Ltd.) was recrystallised twice from hot ethanol, m.p. 192° (lit. 192.5¹⁵). (Found: Hg, 75.56%. Calcd. for C₂H₅ClHg, 75.7%). 2-Hydroxy-3-nitrophenylmercury(II) chloride was prepared by ÅKERFELDT's procedure¹⁶ and gave yellow crystals, m.p. 189° from ethanol. (Found: Hg, 53.5%. Calcd. for C₆H₄ClO₂NHg, 53.6%). *p*-Fluorophenylmercury(II) chloride was prepared by heating mercury(II) acetate (3.0 g), fluorobenzene (10 g) and a few drops of glacial acetic acid under reflux for 2 h. After the addition of 50 ml of hot aqueous ethanol (50% v/v) the mixture was filtered hot and treated with an excess of alcoholic calcium chloride. The precipitated *p*-fluorophenylmercury(II) chloride was recrystallised from hot benzene, m.p. 277° (yield 50%). (Found: Hg, 60.7%, F, 6.0%. C₆H₄ClFHg requires Hg, 60.6%; F, 5.7%). *p*-Chlorophenylmercury(II) chloride,

TABLE III
PERCENTAGE EXTRACTION OF VARIOUS ORGANOMERCURIALS AT DIFFERENT pH VALUES IN UNBUFFERED MEDIA

<i>Pentafluorophenylmercury(II) dithizonate</i>														
pH	0.0	0.52	1.12	1.34	2.20	3.72	4.69	5.82	6.81	8.41	9.62	10.51	11.12	11.91
% extr.	99.9	100.1	100.0	100.0	99.8	100.0	99.8	100.2	100.0	99.9	100.0	99.7	98.1	97.72
<i>2-Hydroxy-3-nitrophenylmercury(II) dithizonate</i>														
pH	0.0	0.54	1.13	1.68	2.29	4.71	6.21	8.52	9.74	10.52	10.98	11.28		
% extr.	100.0	100.0	99.8	99.9	100.1	99.7	99.9	100.0	99.8	98.7	97.2	95.6		
<i>p-Fluorophenylmercury(II) dithizonate</i>														
pH	0.0	0.53	1.11	1.36	2.25	3.65	5.92	6.82	8.51	9.71	10.48	11.22		
% extr.	99.8	100.0	99.8	99.8	100.0	100.0	100.0	99.8	99.9	100.0	98.7	96.4		
<i>p-Chlorophenylmercury(II) dithizonate</i>														
pH	0.0	0.52	1.12	2.27	3.59	3.72	5.89	6.84	8.54	9.68	10.50	11.21	11.92	
% extr.	99.9	100.0	100.1	99.8	100.1	99.8	99.7	98.9	100.2	100.1	98.2	96.5	95.2	
<i>p-Iodophenylmercury(II) dithizonate</i>														
pH	0.0	0.52	1.10	2.32	3.60	5.62	6.75	8.39	9.69	10.47	11.23	11.92		
% extr.	100.0	99.9	100.3	99.7	100.0	100.0	99.7	100.4	99.7	100.0	99.8	97.4		
<i>o-Hydroxyphenylmercury(II) dithizonate</i>														
pH	0.0	0.52	1.19	1.35	2.32	3.54	4.45	5.65	6.79	8.35	9.43	10.49	11.08	
% extr.	99.7	99.8	100.3	100.5	98.9	100.2	99.7	100.7	98.8	99.8	100.2	98.2	95.8	
<i>p-Hydroxymethylphenylmercury(II) dithizonate</i>														
pH	0.0	0.51	1.25	3.69	5.73	6.69	8.31	9.58	10.48	10.96				
% extr.	100.1	99.9	100.5	99.8	100.8	99.7	98.9	99.6	97.2	95.6				
<i>o-Hydroxymethylphenylmercury(II) dithizonate</i>														
pH	0.0	0.49	1.32	5.65	6.54	8.27	9.50	10.39	10.82					
% extr.	100.1	99.7	100.2	99.7	99.4	99.6	99.5	96.2	94.3					
<i>p-Carboxyphenylmercury(II) dithizonate</i>														
pH	0.0	0.51	1.14	2.39	5.81	6.82	8.29	9.53	10.98					
% extr.	100.0	99.8	100.2	99.9	100.4	100.0	41.0	4.8	0.0					

<i>o</i> -Carboxyphenylmercury(II) dithizonate										
pH	0.0	0.51	1.13	3.64	5.57	6.70	8.30	9.60	11.10	
% extr.	100.0	99.7	100.2	99.8	100.6	99.8	42.2	3.9	0.0	
<i>o</i> -Hydroxyphenylmercury(II) dithizonate										
pH	0.0	0.52	1.19	1.35	2.32	3.54	4.45	5.65	6.79	8.35
% extr.	99.7	99.8	100.3	100.5	98.9	100.2	99.7	100.7	98.8	99.8
										10.49
										98.2
										95.8
<i>p</i> -Aminophenylmercury(II) dithizonate										
pH	1.18	1.62	2.48	4.31	5.66	6.76	8.32	9.41	10.45	
% extr.	58.7	83.6	98.9	99.8	100.1	99.8	100.0	96.4	87.8	
<i>2</i> -Carboxy-4-aminophenylmercury(II) dithizonate										
pH	0.96	1.61	2.46	4.21	5.72	6.68	8.41	9.33	10.39	10.81
% extr.	53.2	81.1	99.8	99.9	100.1	100.0	37.2	6.4	0.0	93.2
<i>p</i> -Acetylaminophenylmercury(II) dithizonate										
pH	0.0	0.53	1.14	3.52	5.62	6.54	8.28	9.54	10.39	10.81
% extr.	99.8	100.2	99.3	100.2	99.7	100.2	100.2	99.1	95.3	93.2
<i>p</i> -Dimethylaminophenylmercury(II) dithizonate										
pH	0.0	0.63	1.13	2.31	5.76	6.74	8.39	9.57	10.46	
% extr.	100.0	99.8	99.6	100.5	100.3	99.6	98.9	97.6	95.1	
<i>o</i> -Methoxyphenylmercury(II) dithizonate										
pH	0.0	0.54	1.13	1.36	2.25	3.61	5.68	6.76	8.43	9.51
% extr.	100.1	99.8	99.7	100.5	100.0	100.0	99.8	100.1	100.0	98.8
										10.31
										97.2
										91.5
<i>Methylmercury(II) dithizonate</i>										
pH	0.43	1.01	1.31	2.34	4.21	5.62	6.68	8.31	9.58	10.36
% extr.	74.2	98.1	99.8	100.1	100.3	100.0	99.5	99.8	97.2	89.9
<i>Ethylmercury(II) dithizonate</i>										
pH	0.0	0.42	1.17	2.28	5.65	6.72	8.42	9.62	10.39	
% extr.	99.8	99.8	100.1	100.2	99.8	100.1	99.8	98.6	95.2	

prepared similarly in 40% yield, was recrystallised from hot ethanol, m.p. 225° (lit. 225°¹⁷, 228°¹⁸, 240°¹⁹). (Found: Hg, 57.6%. Calcd. for C₆H₄Cl₂Hg, 57.7%). *p*-Iodophenylmercury(II) chloride was only obtained in poor yield (4%) by direct mercuriation of iodobenzene. It formed microcrystals, m.p. 287°, from hot benzene. (Found: Hg, 45.4%. Calcd. for C₆H₄ClIHg, 45.7%). Phenylmercury(II) chloride²⁰, m.p. 261° from hot ethanol. (Found: Hg, 64.9. Calcd. for C₆H₅ClHg, 65.1%). *o*-Methoxyphenylmercury(II) chloride. The corresponding acetate was first prepared²¹ and converted to the less soluble chloride by treating with aqueous sodium chloride. After recrystallisation from hot alcohol, it had m.p. 172–173°. (Found: Hg, 58.35%. Calcd. for C₇H₇ClOHg, 58.45%). Trichloromethylmercury(II) chloride. (Found: Hg, 58.0%. Calcd. for CCl₄Hg, 58.1%). Bis-trichloromethylmercury. (Found: Hg, 45.75%. Calcd. for C₂Cl₆Hg, 45.87%). Pentafluorophenylmercury(II) bromide. (Found: Hg, 44.6%. Calcd. for C₆F₅BrHg, 44.8%). The last three substances were kindly donated by Professor C. G. COATES of Durham University.

Reagents

Dithizone, carbon tetrachloride and aqueous buffers were purified as described previously¹. The customary precautions were observed in cleaning all glassware for use with dithizone. Absorptiometric measurements were carried out in matched 1-cm silica cells with a Unicam SP 500 spectrophotometer and spectra were also recorded with the SP 700.

The influence of pH on the extractability of organomercury dithizonates

In a typical experiment 10 ml of a solution of dithizone in carbon tetrachloride ($2.88 \cdot 10^{-5}$ M) was equilibrated with 5 ml of an aqueous solution of *p*-aminophenylmercury(II) chloride ($3.01 \cdot 10^{-5}$ M) and 5 ml of an aqueous buffer by shaking for 2–3 min in a stoppered Pyrex test-tube. After separating the phases, the organic phase was removed and its absorbancy measured at 483 nm, the wavelength found to give the maximum absorption for *p*-aminophenylmercury(II) dithizonate in a preliminary measurement, and also at 620 nm where the optical density caused by dithizone is maximal and that arising from the mercury complex is very small. From the reading at 620 nm, the absorbancy of the unreacted dithizone at 483 nm was calculated (from data from the absorption spectrum of pure dithizone) and subtracted from the experimental value at 483 nm to give the optical density arising from the organomercury dithizonate alone. The percentage extraction was then calculated from the molecular extinction coefficient obtained in independent measurements (q.v.). The pH of the aqueous phase was measured after equilibration. Partition measurements were made with chloride–acetate, phosphate–citrate, and glycine–chloride buffers with the results shown in Table II.

In view of the possibility that the anions present in the aqueous buffers (chloride, acetate, citrate, phosphate and glycinate) could complex the organomercury cation and so reduce the percentage of extraction, a series of parallel partition measurements were carried out in which the aqueous phase consisted of 1.0 M sodium perchlorate containing various small amounts of hydrochloric acid or sodium hydroxide. The results obtained are given in Table III.

Data for methyl-, benzyl-, and *p*-bromophenylmercury(II) dithizonates are given in Part XIII. Stable complexes of trichloromethylmercury(II) could not be prepared.

Determination of the stoichiometry of pentafluorophenylmercury(II) dithizonate

A series of mixtures was prepared from x ml of a solution of purified dithizone in carbon tetrachloride ($2.25 \cdot 10^{-5} M$) and $(10-x)$ ml of pentafluorophenylmercury(II) bromide ($2.25 \cdot 10^{-5} M$) in the same solvent. Each mixture was equilibrated with 10 ml of an aqueous acetate buffer of pH 2.1 for 2–3 min. After the phases had separated, the optical density of the organic phase was measured in a 1-cm cell at 482 nm (maximum for the complex) and 620 nm (maximum for dithizone). The results shown in Table IV were obtained. The value $A_{450} = 0.461$ for the dithizone and the "peak ratio" $A_{620}/A_{450} = 1.69$ confirmed its purity. A_j is the Job ordinate, *i.e.* the difference between the measured optical density and that calculated on the assumption that no reaction has taken place⁹. The results shown graphically in Fig. 1 where the extrema appear at 50 moles percent of each component establishes the 1:1 stoichiometry and the formula $C_6F_5Hg(HDz)$. The same method was used for compounds 16, 17 and 18¹⁰.

TABLE IV

DETERMINATION OF STOICHEIOMETRY OF PENTAFLUOROPHENYLMERCURY(II) DITHIZONATE

Dithizone (moles %)	10	20	30	40	50
A_{482} , expt.	0.084	0.170	0.257	0.343	0.431
A_{620} , expt.	0.002	0.002	0.002	0.002	0.003
A_j , 482 nm	0.050	0.101	0.154	0.205	0.259
A_j , 620 nm	-0.084	-0.170	-0.257	-0.343	-0.430
Dithizone (moles %)	60	70	80	90	100
A_{482} , expt.	0.412	0.405	0.373	0.353	0.344
A_{620} , expt.	0.136	0.278	0.438	0.595	0.778
A_j , 482 nm	0.206	0.164	0.098	0.043	—
A_j , 620 nm	-0.331	-0.267	-0.184	-0.105	—

Determination of the stoichiometry of o-carboxyphenylmercury(II) dithizonate

A series of mixtures comprising 10 ml of a $1.47 \cdot 10^{-5} M$ solution of dithizone in carbon tetrachloride, 2.5 ml of an acetate buffer of pH 2.95, x ml of an aqueous $2.996 \cdot 10^{-5} M$ solution of *o*-carboxyphenylmercury(II) chloride and $(10-x)$ ml of water were prepared and shaken for 2–3 min. The phases were then allowed to separate and the optical density of each organic phase was measured in 1-cm silica cells at 481 and 620 nm respectively.

The results are shown graphically in Fig. 2 and lead to the molar ratio $[RHg^+] : [H_2Dz] = 1.02:1$. Similar measurements were made for compounds 2, 3, 6, 8, and 10–15¹⁰.

Determination of the molecular extinction coefficient of o-hydroxyphenylmercury(II) dithizonate by method (a)

A highly purified solution of dithizone in carbon tetrachloride was completely converted to the corresponding complex by equilibration with very slightly more than the equivalent amount of an aqueous solution of *o*-hydroxyphenylmercury(II) chloride in a buffer of pH 2.4 based on 0.1 *M* sodium perchlorate. After phase separation the optical density of the organic phase was measured at 480, 272 and 372 nm,

the previously determined maxima and minimum for the organomercury dithizonate. The process was repeated with four different concentrations of dithizone. Results are shown below.

(i) Initial absorbancies of dithizone solution

	(1)	(2)	(3)	(4)
A, 620 nm	0.976	0.758	0.477	0.379
A, 450 nm	0.578	0.450	0.283	0.226
Peak ratio	1.69	1.69	1.69	1.68

(ii) Optical absorbancy of resulting complex.

	(1)	(2)	(3)	(4)
A, 480 nm	0.958	0.754	0.480	0.380
A, 372 nm	0.061	0.053	0.030	0.025
A, 272 nm	0.539	0.425	0.271	0.212

whence

$10^{-3} \epsilon_{\max}$ at 480 nm	34.3	34.4	34.8	34.6
$10^{-3} \epsilon_{\max}$ at 372 nm	2.2	2.4	2.2	2.3
$10^{-3} \epsilon_{\max}$ at 272 nm	19.3	19.4	19.5	19.4

This method was used for compounds 1-20 inclusive.

Determination of the molecular extinction coefficient of o-methoxyphenylmercury(II) dithizonate by the graphical method (b)

Six portions (10 ml) of a solution of purified dithizone in carbon tetrachloride were equilibrated with increasing amounts (but none exceeding a 1:1 molar ratio) of o-methoxyphenylmercury(II) chloride in an acetate buffer (10 ml) of pH 2.5. After

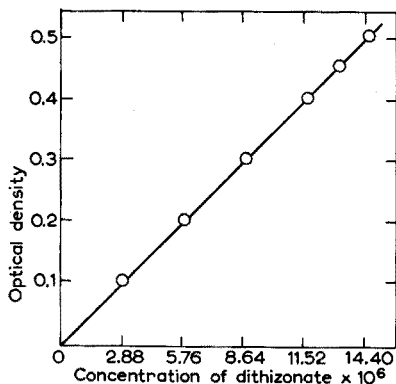


Fig. 3. Determination of the molecular extinction coefficient of a solution of $o\text{-CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$ in carbon tetrachloride at 477 nm by the graphical method.

phase separation the optical density of the organic phase was measured at 477 nm (maximum for the complex) and also at 620 nm (maximum for dithizone). From the experimentally determined ratio $\epsilon_{477}/\epsilon_{620} = 0.450$ for pure dithizone the value of the absorbancy at 620 nm was used to calculate the contribution of residual dithizone to

the absorbancy at 477 nm. The absorbancy due to the complex alone when plotted against the concentration of mercurial (C) gave a straight line (Fig. 3) whose slope gave the desired molecular extinction coefficient as $\epsilon_{477} = (35.9 \pm 0.4) \cdot 10^3$.

DISCUSSION

The effect of pH on the extractability of alkyl- and aryl-mercury(II) dithizonates of general formula $\text{RHg}(\text{HDz})$ depends not only on the nature of the radical R, but also on the composition of the buffer mixture. This is illustrated by Figs. 4 and 5.

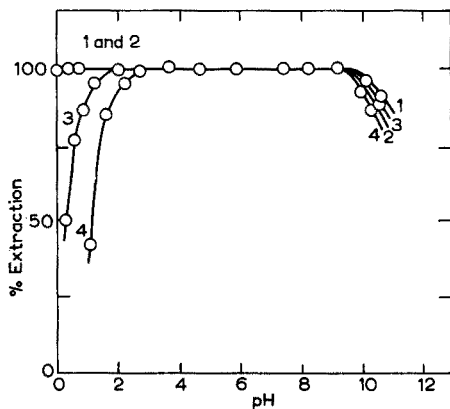


Fig. 4. Comparison between the percentages of various organomercurials extracted by dithizone from a 1.0 M solution of sodium perchlorate (curves 1 and 2) and from mixed anion buffers (curves 3 and 4). Curves 1 and 3 refer to $p\text{-HO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$ and curves 2 and 4 to $p\text{-(CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$.

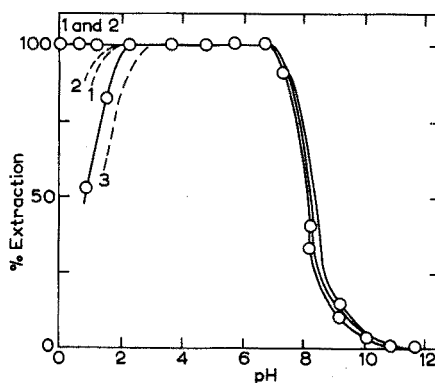
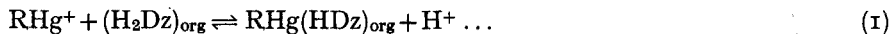


Fig. 5. The effect of pH on the percentage of organomercurial extracted by solutions of dithizone. Curve 1, $o\text{-HOOC}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$; curve 2, $p\text{-HOOC}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$; curve 3, $2,5\text{-(HOOC)(NH}_2)_2\cdot\text{C}_6\text{H}_3\cdot\text{Hg}(\text{HDz})$. Curves 1 and 2, carbon tetrachloride. Curve 3, chloroform. Solid curves refer to extraction from 1.0 M sodium perchlorate. Broken curves refer to extraction from mixed-anion buffers.

Consider first the more acidic regions. The partition equilibrium can be represented by eqn. (1) with equilibrium constant K_{ex}



where the subscript org distinguishes species in the organic phase. The total concentration of mercury, C_{Hg} , is given by

$$C_{\text{Hg}} = [\text{RHg}^+] + [\text{RHg}(\text{HDz})]_{\text{org}} + \sum_1 [\text{RHgX}_j] + \sum_1 [\text{RHgY}_j] + \dots \quad (2)$$

where X and Y represent complexing ligands. The term $[\text{RHg}(\text{HDz})]$ for the concentration of dithizonate in the aqueous phase will obviously be negligible in view of the magnitude of the partition coefficient.

The total concentration of organomercurial in the aqueous phase can, therefore, be represented as $\alpha_{\text{X,Y}}[\text{RHg}^+]$ where $\alpha_{\text{X,Y}}$ is a numerical coefficient (greater than unity) whose magnitude depends upon the concentration of the auxiliary

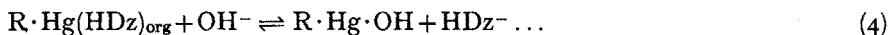
complexing agents X, Y ... and the magnitude of the corresponding formation constants for the species RHgX , RHgX_2^- , RHgX_3^{2-} , RHgY , RHgY_2^- , RHgY_3^{2-} etc.²². It follows from eqns. (1) and (2) that the percentage extracted, E , is given by:

$$E = 100 [\text{RHg}(\text{HDz})]_{\text{org}} / C_{\text{Hg}} = 100 / \{1 + (\alpha[\text{H}^+] / K_{\text{ex}}[\text{H}_2\text{Dz}]_{\text{org}})\} \dots \quad (3)$$

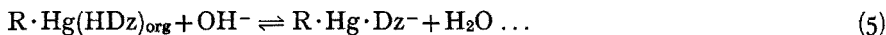
As predicted, the effect of increasing the hydrogen ion concentration is to tend to reduce the percentage extracted, although this effect is minimised by a high value of K_{ex} . Where anionic components of the buffers are able to form complexes with the cation RHg^+ , the value of α rises above unity and this likewise effects a decrease in E .

Where the organomercurial contains an amino group, as in compounds 17 ($\text{R} = 2,5\text{-(HOOC)(NH}_2\text{)C}_6\text{H}_3^-$) and 18 ($\text{R} = p\text{-NH}_2 \cdot \text{C}_6\text{H}_4^-$), the formation of the conjugate acid at low pH values will reduce the effective concentration for extraction by eqn. (1) as shown by the data in Table I. Over the pH range studied, the effect is not detectable with p -dimethylaminophenylmercury(II) doubtless because the corresponding value of K_{ex} is much larger for this cation.

The small but definite decrease in the percentage extracted at high pH values is a feature common to all the compounds studied (*cf.* Fig. 4). Three explanations are possible. Competition with hydroxide ions could produce a water-soluble hydroxy-complex



Ionisation of the remaining hydrogen atom in the metal dithizonate could give rise to an anionic species



This process is analogous to what must be regarded as a preliminary stage in the formation of secondary dithizonates from the primary dithizonates of such metals as silver, mercury and copper: we shall discuss these reactions in detail elsewhere.

Finally, it must be remembered that with increasing pH the ionisation of dithizone itself diminishes the magnitude of the term $[\text{H}_2\text{Dz}]_{\text{org}}$ in consequence of the equilibrium



which has been fully investigated in earlier papers²³.

When aliquot portions of a solution of phenylmercury(II) dithizonate in carbon tetrachloride were equilibrated with equal volumes of solutions of sodium hydroxide for 5 min, no changes were observed in the position or intensity of the absorption bands over the pH range 7 to 14 and the aqueous phases showed no bands arising from absorption by the ion HDz^- ($\epsilon_{\text{max}} = 23,000$ at 470 nm) or to a phenylmercury dithizonate ion, $\text{C}_6\text{H}_5 \cdot \text{HgDz}^-$. It thus appears that the observed decreases in the percentage extraction in strongly alkaline solution can best be interpreted in terms of eqn. (6), *i.e.* as being due to the decrease in the term $[\text{H}_2\text{Dz}]_{\text{org}}$ caused by the excess of dithizone. At the same time it must be recorded that secondary dithizonates, $(\text{R} \cdot \text{Hg})_2\text{Dz}$, can be obtained under the appropriate conditions and even the ionisation stage (eqn. (5)) can be studied quantitatively²⁴.

When the organomercurial contains a carboxy group, as in p -carboxy-

o-carboxy-, and 2-carboxy-5-amino-phenylmercury(II) (compounds 13, 14 and 17), the percentage extraction decreases dramatically when the pH of the aqueous phase exceeds 7 (Fig. 5). For instance, with *o*-carboxyphenylmercury dithizonate the value drops from 100% at pH 7 to 41% at pH 8.3 and to zero at pH 11.0. This effect is due in the first instance to the formation of the water-soluble yellow anion $^{-}\text{OOC}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$, but in still more alkaline solutions a magenta coloured complex $^{-}\text{OOC}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}\cdot\text{Dz}^{-}$ appears. The quantitative treatment of these equilibria will form the subject of a later paper²⁴.

The high intensity of absorption in the visible region ($\log \sim 4.5$) of the various primary organomercury(II) dithizonates so far studied (Table I) confirms the value of this property for their determination. On the other hand, the remarkable similarities between the spectra of different arylmercury dithizonates, $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$, despite changes in the nature of the substituent X do not lend themselves to any simple procedures for the analysis of mixtures. That λ_{max} always lies within the range 465–483 nm and ϵ_{max} within the range 31,500–39,400, and that no correlation can be drawn between individual values and the nature of the substituent X suggests that its inductive and/or mesomeric effect is only weakly transmitted through the mercury atom. A similar explanation has been put forward²⁵ to account for the similarity between the spectra of phenylmercury(II) chloride, bromide, and acetate²⁶. However, the conclusion of significance to analysts is that the visible spectra of a primary dithizonate derived from any organomercurial not listed in Table I can be predicted within narrow limits.

The ultraviolet spectra of the organomercury dithizonates (Table I) show greater variations than the visible spectra (λ_{max} 261–279 nm; ϵ_{max} 15,000–33,500) and some of the differences could clearly be exploited analytically. It is, however, difficult to derive any quantitative relationship with the nature of the substituent X that could be used predictively. This is because absorption spectra in the region 206–210 nm are common to all mercury compounds²⁷, and in arylmercury compounds this absorption will be associated with that caused by the primary absorption of the phenyl ring system ($\epsilon_{\text{max}} \sim 47,000$ at 180 nm and $\sim 7,000$ at 200 nm for benzene itself), while absorption at 260 nm will be due to the secondary band of benzene. In the arylmercury(II) dithizonates both bands at ~ 205 and 260 nm caused by the arylmercury residue will be further associated with the bands arising from the phenyl groups in dithizone itself. Since dithizone absorbs strongly at 200 nm ($\epsilon_{\text{max}} \sim 34,000$) and at 275 nm ($\epsilon_{\text{max}} \sim 14,500$) it is not surprising that the ultraviolet spectra of the complexes $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$ cannot be correlated in simple terms with the nature of the substituent X.

The effect of the substituent X in arylmercury(II) chlorides, $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$, has been shown to shift the bands to higher wavelengths and to increase their intensity^{28–28}, to an extent that can be explained in terms of its tendency to release or withdraw electrons. Similar effects can be seen in the complexes $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}(\text{HDz})$ and a comparison of the available data is given in Table V.

Although the ultraviolet spectra of compounds 1, 3, 4, 5, 6, 11, 12, 13 and 14 differ little from that of phenylmercury dithizonate (compound 7), the introduction of as strongly electron-releasing group in the ortho- or para-position (HO, MeO, HO, NMe₂ in compounds 2, 8, 10, 16) produces a definite bathochromic shift. The hypsochromic effect of the basic amino groups in compounds 15, 16, 17 and 18 is very

TABLE V

COMPARISONS BETWEEN THE ULTRAVIOLET SPECTRA OF $X \cdot C_6H_4 \cdot HgCl$ and $X \cdot C_6H_4 \cdot Hg(HDz)$

X	$X \cdot C_6H_4 \cdot HgCl$		Ref.	$X \cdot C_6H_4 \cdot Hg(HDz)^a$	
	λ (nm)	log ϵ		λ (nm)	log ϵ
<i>p</i> -NH ₂	253	4.13	27	262	4.27
	254	4.14	28		
H	258	2.46	27, 28	263	4.27
	259	2.57	26		
<i>p</i> -Cl	264.5	2.43	27	263	4.30
	264	2.46	26		
<i>o</i> -OH	225 ^b	3.80	28	272	4.29
	282	3.52	28		
	283	3.52	28		
<i>o</i> -CH ₃ O	227	3.73	28	279	4.30
	280	3.43	28		
<i>p</i> -N(CH ₃) ₂	272	4.30	28	272	4.53

^a Present work.^b Inflection. Spectra of dithizonates were measured in carbon tetrachloride, those of the chlorides in ethanol.

striking. The replacement of chlorine in CH_3HgCl (λ_{max} 206 nm, log ϵ 3.17) by a dithizone residue to give $CH_3Hg(HDz)$ (λ_{max} 275 nm, log ϵ 4.19) causes a large bathochromic shift.

We wish to express our gratitude to the Royal Society for the loan of a recording spectrophotometer and one of us (A.M.K.) thanks the National Research Centre of the United Arab Republic for study leave and financial assistance.

SUMMARY

The reactions between dithizone and a wide variety of organomercurials of general formula $R \cdot Hg^+ X^-$ have been investigated. The intensely coloured complexes of formula $R \cdot Hg(HDz)$ that are formed in acid solution can be extracted quantitatively in an organic phase and used for the absorptiometric determination of the parent mercurial. Extractabilities, absorption spectra and molar extinction coefficients are reported and discussed in relation to the nature of the organic radical R attached to the mercury(II) ion.

RÉSUMÉ

Les réactions entre dithizone et une grande variété de composés organo-mercuriels de formule générale $R \cdot Hg^+ X^-$ ont été examinées. Les complexes très colorés, de formule $R \cdot Hg(HDz)$, formés en milieu acide peuvent être extraits quantitativement en phase organique et utilisés pour le dosage absorptiométrique du dérivé mercuriel. Les extractibilités, les spectres d'absorption et les coefficients d'extinction molaire sont donnés et examinés en relation avec la nature du radical organique R lié à l'ion mercure(II).

ZUSAMMENFASSUNG

Die Reaktionen zwischen Dithizon und einem grossen Zahl von organischen Quecksilberverbindungen der allgemeinen Formel $R \cdot Hg^{+}X^{-}$ wurden untersucht. Die intensiv gefärbten Komplexe mit der Formel $R \cdot Hg(HDz)$, die in saurer Lösung gebildet werden, können quantitativ mit einer organischen Phase extrahiert werden und zur absorptiometrischen Bestimmung des Quecksilbers verwendet werden. Die Extrahierbarkeit, die Absorptionsspektren und die molaren Extinktionskoeffizienten werden angegeben und die Beziehung zu der Natur des organischen Radikals R, welches an das Quecksilber(II)-Ion gebunden ist, diskutiert.

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STUDIES WITH DITHIZONE. PART XVI. WATER-SOLUBLE ARYLMERCURY(II) DITHIZONATES AND SECONDARY ARYLMERCURY(II) DITHIZONATES

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In a previous paper¹ it was shown that a wide variety of organomercury(II) cations formed stable yellow complexes with dithizone (3-mercapto-1,5-diphenylformazan; H₂Dz) that could be extracted into carbon tetrachloride. The extraction of these 1:1 complexes, R·Hg(HDz), was shown to be quantitative over a wide pH range that usually extended to pH 8.5 and often as high as 9.5. When, however, the aryl

TABLE I

THE EFFECT OF pH ON THE EXTRACTION OF CERTAIN ORGANOMERCURY(II) DITHIZONATES, R₂Hg(HDz), INTO CARBON TETRACHLORIDE FROM 1.0 M SODIUM PERCHLORATE

Compound R=	pH and % extr.				
o-HOOC·C ₆ H ₄ -	pH	6.70	8.30	9.60	11.10
	%	99.8	42.2	3.9	0.0
p-HOOC·C ₆ H ₄ -	pH	6.82	8.29	9.53	10.98
	%	100.0	41.0	4.8	0.0
2,5-(HOOC)(NH ₂)·C ₆ H ₃ -	pH	6.68	8.41	9.33	10.39
	%	100.0	37.2	6.4	0.0

TABLE II

OPTICAL CHARACTERISTICS OF AQUEOUS AND CARBON TETRACHLORIDE PHASES DURING THE PARTITION OF o-CARBOXYPHENYLMERCURY(II) DITHIZONATE AT VARIOUS pH VALUES

pH	Aqueous phase			Organic phase		
	λ_{max}	(10 ³ ϵ_{max})	Colour	λ_{max}	(10 ³ ϵ_{max})	Colour
6.98	—	—	colourless	481	(34.1)	orange-yellow
7.43	—	—	colourless	481	(34.1)	orange-yellow
8.39	471	(—) ^a	faint yellow	481	(—) ^a	orange-yellow
9.22	470	(17.2)	yellow	—	—	colourless
10.23	470	(18.2)	yellow	—	—	colourless
11.25	475	(19.4)	orange-yellow	—	—	colourless
11.54	508	(20.5)	orange-red	—	—	colourless
11.68	516	(22.7)	orange-red	—	—	colourless
12.28	526	(32.5)	magenta	—	—	colourless
12.59	526	(32.5)	magenta	—	—	colourless

^a Not determined. There were no further changes in spectra above pH 12.28.

group attached to mercury contained a carboxy group, there was a dramatic reduction in the percentage extracted above pH 7 (Table I), and there were concomitant changes in the colours of the two phases (Table II).

The water-soluble species formed from *o*-anhydromercuribenzoic acid in the pH range 9.0 to 10.5 is certainly the anion $-\text{OOC} \cdot \text{C}_6\text{H}_4 \cdot \text{Hg}(\text{HDz})$, and it is noteworthy that its spectrum is quite similar to that of the dithizonate ion itself ($\lambda_{\text{max}} = 470 \text{ nm}$; $\epsilon_{\text{max}} = 23,000$) and the same sort of hypsochromic shift and reduction in intensity is experienced when dithizone ($\lambda_{\text{max}} = 620 \text{ nm}$; $\epsilon_{\text{max}} = 34,000$) ionises in aqueous alkali.

In more strongly alkaline solutions ($\text{pH} \geq 12$), a magenta-coloured complex is formed but this can be reconverted to the yellow water-soluble complex, or re-extracted as the yellow primary dithizonate $\text{RHg}(\text{HDz})$ by adjusting the pH to about 10 or below 7, respectively. Its composition was shown by extractive titration (*cf.* Fig. 1) to involve equimolecular amounts of *o*-carboxyphenylmercury(II) chloride and dithizone (experimental ratio 1:1.06), and it is very probably formed from the yellow anion $-\text{OOC} \cdot \text{C}_6\text{H}_4 \cdot \text{Hg}(\text{HDz})$ by loss of a proton from the imino group of the dithizone residue. It should thus be formulated as $-\text{OOC} \cdot \text{C}_6\text{H}_4 \cdot \text{Hg} \cdot \text{Dz}^-$. The behaviour of the other two organomercurials that contain carboxy groups (Table I) was found to be qualitatively similar and a corresponding explanation seems probable.

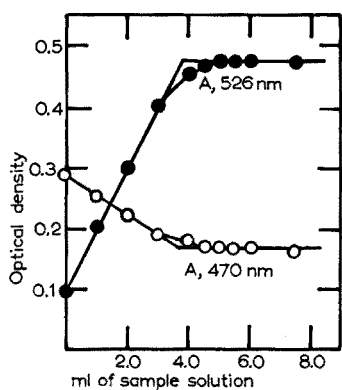


Fig. 1. Determination of the stoichiometry of the complex formed between dithizone and the cation *o*- $\text{HOOC} \cdot \text{C}_6\text{H}_4 \cdot \text{Hg}^+$ by extractive titration into carbon tetrachloride. The sample solution used was $2.99 \cdot 10^{-5} \text{ M}$.

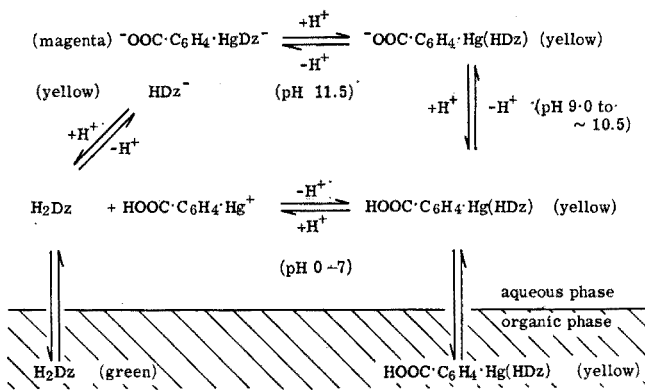
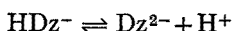


Fig. 2. Equilibria in the two-phase system water-carbon tetrachloride involving dithizone, the *o*-carboxyphenylmercury(II) cation and the several complexes formed over different pH ranges.

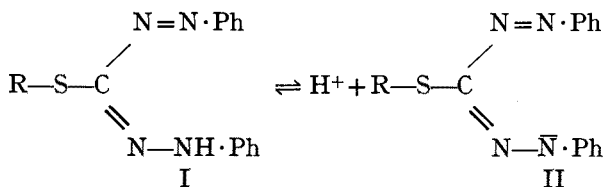
The reaction between dithizone and *o*-carboxyphenylmercury(II) (usually in the form of *o*-anhydromercuribenzoic acid) has been used analytically by WROŃSKI for the determination of sulphides², but no explanation of the reaction had hitherto been offered. The method consists in dissolving the sulphide in aqueous alkali and titrating with a standard solution of *o*-carboxyphenylmercury(II) hydroxide with dithizone as indicator; at the end-point the excess of organomercurial reacts with the yellow dithizonate ion, HDz^- , to give the magenta complex described above. The various equilibria in the two-phase system are summarised in Fig. 2.

The dissociation of a hydrogen atom from the imino group of the yellow primary dithizonate ion, $-\text{OOC} \cdot \text{C}_6\text{H}_4 \cdot \text{Hg}(\text{HDz})$, to form a magenta-coloured anion provides a

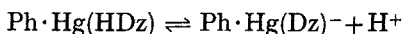
visible demonstration of what would be expected from the dithizonate ion, HDz^- , itself and which has been postulated (without any supporting evidence) as occurring in the formation of secondary (keto) dithizonates³. BUCH AND KOROLEFF⁴ accepted that dithizone could behave as a dibasic acid but they thought that the dissociation of the second stage would proceed without any change in spectra. On the other hand, GEIGER AND SANDELL⁵ attributed the red-violet colour produced when dithizone dissolves in strong potassium hydroxide ($> 10 N$) to the formation of the ion Dz^{2-} . They were aware that their alkali contained appreciable quantities of silver which could have produced just such a colour but they had added cyanide to inhibit the formation of a silver complex. They inferred that the extent of ionisation in the process



implied an acid dissociation constant of less than 10^{-15} and in view of the ease with which dithizone decomposes in very alkaline media⁶, no better estimate is available. On the other hand, the dissociation of a proton from the imino group of the uncharged species S-methyldithizone (I; $\text{R} = \text{CH}_3$) has been studied quantitatively⁷ since it takes place in a more accessible pH range.



It is noteworthy that such an ionisation of an imino-hydrogen is implicit in all the formulae put forward to account for the formation of secondary (keto) dithizonates from primary dithizonates and excess of metal—usually under strongly alkaline conditions³. Indeed, it proved possible to study the acid dissociation constant of primary phenylmercury(II) dithizonate (I and II; $\text{R} = \text{C}_6\text{H}_5\text{-Hg}$) spectrophotometrically by measurements in an aqueous monophasic containing sufficient ethanol to keep it in solution. The relative proportions of the magenta-coloured anion, $\text{Ph}\cdot\text{Hg}\cdot\text{Dz}^-$, and its yellow conjugate acid, $\text{Ph}\cdot\text{Hg}(\text{HDz})$, were obtained from measurements of optical densities at 526 and 676 nm, their respective absorption maxima (Fig. 3, curves 3 and 2). For the process



defining the acid dissociation constant K , we can write

$$\begin{aligned}
 \text{p}K &= \text{pH} + \log\left\{\frac{[\text{Ph}\cdot\text{Hg}(\text{DHZ})]}{[\text{Ph}\cdot\text{Hg}(\text{Dz})^-]}\right\} \\
 &= \text{pH} + \log\left\{\frac{(A - A_L)}{(A_{HL} - A)}\right\}
 \end{aligned}$$

where A_{HL} , A_L are the optical densities of solutions containing the same total amount of metal complex present entirely as the species $\text{Ph}\cdot\text{Hg}(\text{HDz})$ and $\text{Ph}\cdot\text{Hg}(\text{Dz})^-$, respectively, and A is the optical density at some specified intermediate pH value. The results of measurements in a 52.75% (v/v) ethanol-water mixture are shown in Fig. 4 and lead to the value $\text{p}K = 11.46 \pm 0.01$. Similar measurements in 46, 42 and 36% (v/v) ethanol-water mixtures gave the values 11.48, 11.57 and 11.52, respectively.

The magenta-coloured anion, $\text{Ph} \cdot \text{Hg} \cdot \text{Dz}^-$, is readily reconverted to the yellow conjugate acid $\text{Ph} \cdot \text{Hg}(\text{HDz})$ by acidifying the solution. However, the addition of excess organomercurial, with the object of preparing the secondary dithizonate, $(\text{Ph} \cdot \text{Hg})_2\text{Dz}$, did not affect the visible absorption spectra to any great extent (Fig. 3,

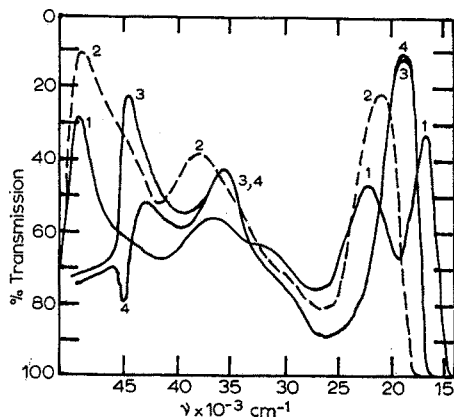


Fig. 3. Absorption spectra in 75% (v/v) ethanol-water mixtures. Curve 1. Dithizone alone ($\lambda_{1,\text{max}}=598$ nm, $\epsilon_{1,\text{max}}=29,300$; $\lambda_{2,\text{max}}=445$ nm, $\epsilon_{2,\text{max}}=17,800$). Curve 2. Primary phenylmercury(II) dithizonate at pH ~ 6 ($\lambda_{\text{max}}=476$ nm, $\epsilon_{\text{max}}=32,500$). Curve 3. The anion $\text{C}_6\text{H}_5\text{HgDz}^-$ produced at pH ~ 13 ($\lambda_{\text{max}}=526$ nm, $\epsilon_{\text{max}}=49,500$). Curve 4. Effect of adding excess $\text{C}_6\text{H}_5\text{Hg}^+$ at pH ~ 13 .

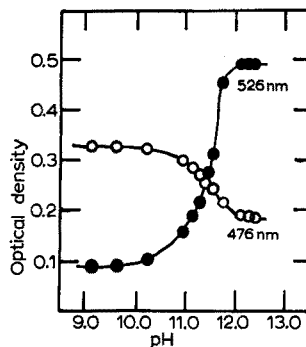


Fig. 4. Determination of the acid dissociation constant of primary phenylmercury(II) dithizonate in 52.7% (v/v) ethanol.

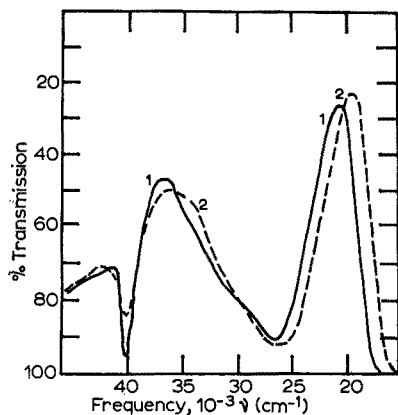
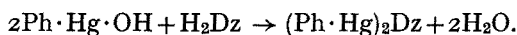


Fig. 5. Absorption spectra in chloroform of complexes of phenylmercury(II) with dithizone. Curve 1. Primary dithizonate ($\lambda_{1,\text{max}}=476$ nm, $\epsilon_{\text{max}}=32,300$; $\lambda_{2,\text{max}}=270$ nm, $\epsilon_{\text{max}}=18,200$). Curve 2. Secondary dithizonate ($\lambda_{1,\text{max}}=510$ nm, $\epsilon_{1,\text{max}}=40,000$; $\lambda_{2,\text{max}}=272$ nm, $\epsilon_{2,\text{max}}=17,200$).

curve 4). This may well be due to the instability of the secondary complex in aqueous alcoholic solution, for spectral evidence of the formation of a secondary complex was obtained in a chloroform solution (Fig. 5, curve 2). It proved impossible to determine its composition by the method of continuous variations or by extractive titration¹ but this can be inferred indirectly from the number of protons (2) liberated per molecule of

dithizone (see Experimental section) during its formation by the reaction



Several other organomercurials were found to behave like phenylmercury(II) in forming both primary and secondary dithizonates. The latter were invariably less stable than the primary dithizonates¹, and less soluble in chloroform or carbon tetrachloride, and they absorbed at longer wavelengths (Table III).

TABLE III

OPTICAL CHARACTERISTICS OF SECONDARY ORGANOMERCURY(II) DITHIZONATES IN CCl₄ OR CHCl₃

Cation	λ_{max} (nm)	$10^{-3} \epsilon_{max}$	Solvent ^a
C ₆ H ₅ ·Hg ⁺	502	35.0	A
<i>p</i> -F·C ₆ H ₄ ·Hg ⁺	512	41.0	B
	510	40.0	A
<i>p</i> -Cl·C ₆ H ₄ ·Hg ⁺	510	43.0	B
	510	41.0	A
<i>p</i> -Br·C ₆ H ₄ ·Hg ⁺	515	42.5	B
	510	42.0	A
<i>p</i> -I·C ₆ H ₄ ·Hg ⁺	514	41.5	A
C ₆ H ₅ ·Hg ⁺	510	38.5	A
	510	40.0	B
<i>o</i> -CH ₃ O·C ₆ H ₄ ·Hg ⁺	510	40.5	B
C ₆ H ₅ ·CH ₂ ·Hg ⁺	515	38.0	B
<i>p</i> -(CH ₃) ₂ N·C ₆ H ₄ ·Hg ⁺	514	39.0	A
C ₂ H ₅ ·Hg ⁺	514	42.0	B

^a A: in chloroform; B: in carbon tetrachloride.

The insensitivity of the spectra of both primary¹ and secondary organomercury dithizonates, R·Hg(HDz) and (R·Hg)₂Dz, to variations in the nature of the residue R has shown that this property, though valuable for the determination of individual organomercurials or for the assessment of the total content of admixtures, does not lend itself to the analysis of the separate components of even a binary mixture unless one of these contains a carboxy group (*cf.* Tables I and II). In this case, separation by liquid-liquid extraction can be effected at an appropriate pH and the yellow or magenta-coloured anionic species produced in the aqueous phase and the yellow species remaining in the organic phase can be used for the determination of the two organomercurials. In a number of cases a "reversion method"⁸ can be used to advantage. Thus, the primary dithizonates from the cations R = *p*-HO·CH₂·C₆H₄- and R = *p*-HOOC·C₆H₄- can be extracted into carbon tetrachloride and their total concentration determined by measuring the optical density at 480 nm where both have the same molecular extinction coefficients, $\epsilon_{max} = 31,500^1$; by equilibrating the organic phase with an aqueous buffer of pH above 11, the whole of the mercurial containing the carboxy group is transferred to the aqueous phase and the optical density of the residual organic phase gives the concentration of the cation *p*-HO·CH₂·C₆H₄·Hg⁺ directly and that of *p*-HOOC·C₆H₄·Hg⁺ by difference.

EXPERIMENTAL

The preparation of the organomercurials and the purification of dithizone and other reagents has been described previously¹.

Stoichiometry of the magenta complexes

A series of solutions were prepared from 10 ml of a $1.2 \cdot 10^{-5}$ M solution of dithizone in carbon tetrachloride, 1 ml of 2.5 M sodium hydroxide, x ml of a $2.99 \cdot 10^{-5}$ M aqueous solution of *o*-carboxyphenylmercury(II) chloride and $(10-x)$ ml of water. After equilibration for several minutes the mixtures were centrifuged to separate the phases and the optical density of each aqueous phase was measured at 526 nm (the absorption maximum of the magenta complex) and at 470 nm (the maximum for the dithizonate ion, HDz⁻). The results are shown graphically in Fig. 1.

The equivalence point occurred at $x=3.8$ ml, *i.e.* a molar ratio of 1:1.06 for *o*-carboxyphenylmercury(II) chloride to dithizone.

Determination of the acid dissociation constant of primary phenylmercury(II) dithizonate

A series of solutions of 10^{-5} M primary phenylmercury(II) dithizonate were prepared in 52.75% (v/v) ethanol–water mixtures of differing pH and with the ionic strength adjusted to 0.1 M with sodium perchlorate. Their optical densities at 476 and 526 nm were measured at 25° (matched 1-cm silica cells) with a Unicam SP 500 spectrophotometer and the pH was measured with a Radiometer pH-meter calibrated with 0.05 M potassium hydrogen phthalate and 0.1 M borax. The results are shown in Fig. 4.

The composition of secondary phenylmercury(II) dithizonate

Two equivalents of phenylmercury(II) hydroxide (chosen as having the greatest solubility of salts of this cation) were equilibrated with 10 ml of a 0.006 M solution of dithizone in chloroform and sufficient sodium hydroxide solution was added to give a final volume of 10 ml. The calculated concentration of added hydroxyl ion was 0.044 M. The mixture was equilibrated for several minutes and after phase separation the concentration of hydroxyl ion in the aqueous phase was determined by titrating a 5-ml aliquot portion. No change in [OH⁻] had occurred.

One of us (A.M.K.) wishes to thank the National Research Centre of the United Arab Republic for study leave and financial assistance.

SUMMARY

Arylmercury(II) cations containing carboxy groups form with dithizone yellow 1:1 complexes of the type HOOC·R·Hg(HDz) which can be extracted quantitatively into carbon tetrachloride over a wide pH range. In alkaline media, water-soluble yellow complexes ⁻OOC·R·Hg(HDz) are formed and in strongly alkaline solutions these ionise further to give magenta-coloured anions, ⁻OOC·R·Hg(Dz)⁻. Phenylmercury(II) dithizonate, PhHg(HDz), ionises in very alkaline solution to give the magenta anion PhHg(Dz)⁻ and the acid dissociation constant, $pK=11.5$ (in 36–53% v/v ethanol–water; $\mu=0.1$ M NaClO₄) was determined spectrophotometrically.

In alkaline solution and in the presence of excess of organomercurial, dithizone yields a series of secondary dithizonates which are less stable and less soluble in organic solvents than the corresponding primary complexes; their spectra were recorded.

RÉSUMÉ

Les cations arylmercuriques(II) renfermant des groupes carboxy forment avec la dithizone des complexes 1:1 jaunes du type $\text{HOOC}\cdot\text{R}\cdot\text{Hg}(\text{HDz})$ pouvant être extraits quantitativement dans le tétrachlorure de carbone, sur une large échelle de pH. En milieu alcalin, il y a formation de complexes jaunes $-\text{OOC}\cdot\text{R}\cdot\text{Hg}(\text{HDz})$ solubles dans l'eau; en solution fortement alcalines, ils s'ionisent pour donner un anion magenta $-\text{OOC}\cdot\text{R}\cdot\text{Hg}(\text{Dz})^-$. (Exemple choisi le phénylmercure(II) dithizonate $\text{PhHg}(\text{HDz})$.) En solution alcaline et en présence d'un excès d'organomercuriel, la dithizone donne une série de dithizonates secondaires, moins stables et moins solubles dans les solvants organiques que les complexes primaires correspondants. Leurs spectres sont enregistrés.

ZUSAMMENFASSUNG

Aryl-Quecksilber(II)-Kationen, welche Carboxylgruppen enthalten, bilden mit Dithizon gelbe 1:1-Komplexe des Typs $\text{HOOC}\cdot\text{R}\cdot\text{Hg}(\text{HDz})$, welche quantitativ mit Tetrachlorkohlenstoff innerhalb eines weiten pH-Bereiches extrahiert werden können. In alkalischem Medium werden wasserlösliche gelb gefärbte Komplexe der Form $-\text{OOC}\cdot\text{R}\cdot\text{Hg}(\text{HDz})$ gebildet und in stark alkalischen Lösungen ionisieren diese weiter und geben magenta-gefärbte Anionen der Form $-\text{OOC}\cdot\text{R}\cdot\text{Hg}(\text{Dz})^-$. Phenyl-Quecksilber(II)-Dithizonat, $\text{PhHg}(\text{HDz})$, ionisiert in sehr alkalischer Lösung und gibt das magenta Anion $\text{PhHg}(\text{Dz})^-$. Die spektralphotometrisch bestimmte Säure-dissoziationskonstante ergab $\text{p}K = 11.5$ (in 36–53% Vol.-%igen Äthanol-Wasser; $\mu = 0.1 \text{ M NaClO}_4$). In alkalischer Lösung und in Gegenwart eines Überschusses von Organo-Quecksilber gibt Dithizon eine Reihe sekundärer Dithizonate, welche in organischen Lösungsmitteln weniger stabil und weniger löslich sind als die korrespondierenden primären Komplexe. Ihre Spektren werden angegeben.

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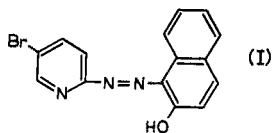
1-[(5-BROMO-2-PYRIDYL)AZO]-2-NAPHTHOL AS A POSSIBLE NEW CHROMOGENIC REAGENT

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During the past ten years, the analytical application of 2-pyridylazo compounds has been studied extensively¹⁻³. Two representatives of this group, 1-(2-pyridylazo)-2-naphthol (β -PAN) and 4-(2-pyridylazo)resorcinol (PAR), have proved to be very versatile reagents for metals. In a search for new sensitive spectrophotometric procedures for the determination of micro amounts of metal impurities in high-purity materials, a thorough study of some of the azo compounds containing halogen-substituted pyridine or naphthol has been made. In this paper, the possibilities of 1-[(5-bromo-2-pyridyl)azo]-2-naphthol (I, 5-Br- β -PAN) as an analytical reagent are described.



EXPERIMENTAL

Reagents

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

Buffer solution. Sodium acetate-acetic acid and ammonium chloride-ammonia solutions were used for pH adjustment.

Potassium cyanide (0.2 M), 0.2 M sodium fluoride, 10% sodium citrate and 0.1 M EDTA (disodium salt) solutions were used as masking reagents.

Organic solvents were purified by the usual methods.

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

Apparatus

Absorbance curves were measured with a Model EPS-3T Hitachi recording spectrophotometer with 1-cm cells; absorbances were measured with a Model EPV-2A Hitachi spectrophotometer with 1-cm cells. A Yanagimoto 42-A type pH meter was used.

Preparation of reagent

The reagent was prepared by coupling 2-naphthol with 5-bromopyridyldiazotate in ethanol with slow passing of carbon dioxide. The diazotate was prepared by adding a solution of butyl nitrite to a mixture of 5-bromo-2-aminopyridine and sodium amide under reflux.

*Bromination of 2-aminopyridine*⁴. Bromine (40 g) was added with stirring to a cooled solution of 18.8 g of 2-aminopyridine in 200 ml of ethanol, keeping the temperature below 20°. The crystalline precipitate was filtered, washed with ethanol, and dissolved in water. The solution was made alkaline with sodium hydroxide and extracted with ether. The ether residue was extracted twice with petroleum ether to remove dibromoaminopyridine and then crystallized from benzene (m.p. 137–8°, yellow powder).

Preparation of diazotate. Freshly prepared butyl nitrite (3.74 g) was added to a solution containing 6 g of 2-bromo-2-aminopyridine and 1.6 g of sodium amide in 120 ml of ethanol. The mixture was refluxed about 3 h and cooled, and the precipitated diazonium salt of 5-bromo-2-aminopyridine was filtered and dried in air.

Coupling reaction. 2-Naphthol (3.7 g) was dissolved in 30 ml of ethanol and a solution of 4.5 g of diazonium salt in 70 ml of ethanol was added. This mixture was heated to 40–50° for 4 h in a stream of carbon dioxide. The mixture was let cool overnight, and the precipitated orange-red needle-like crystals were filtered. If a little water was added to the filtrate, a further yield of crude dye could be obtained. Finally, the precipitate was recrystallized from 1:1 ethanol–water (m.p. 172–3°, orange-red needles).

Analysis. Calculated: C 54.8%, N 12.8%, H 3.07%, Br 24.3%. Found: C 54.6%, N 12.6%, H 3.1%, Br 24.1%.

RESULTS AND DISCUSSION

Acid dissociation constant

The reagent is almost insoluble in water, but readily soluble in various organic

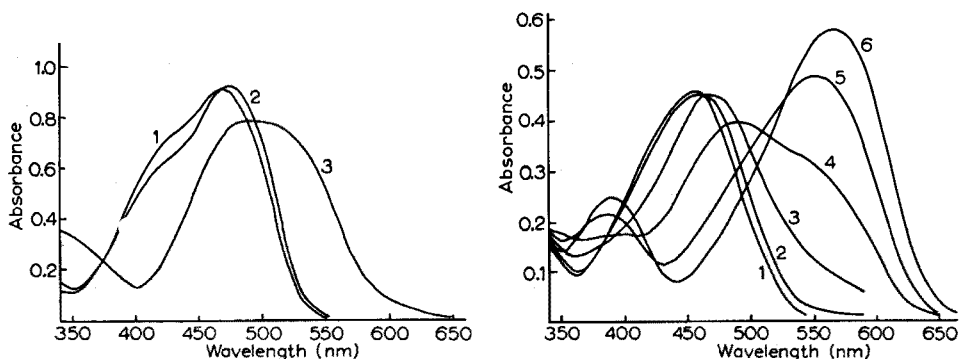


Fig. 1. Absorbance curves of 5-Br- β -PAN in 50% (v/v) aqueous dioxane. (1) pH = 1.0, (2) pH = 4.0, (3) pH = 13. $4.5 \cdot 10^{-5}$ M, $\mu = 0.1$ (KNO₃), 25°.

Fig. 2. Absorbance curves of 5-Br- β -PAN in sulfuric acid. $2.4 \cdot 10^{-5}$ M, Hammett acidity function - H₀. (1) 3.9, (2) 4.8, (3) 5.8, (4) 7.66, (5) 8.6, (6) 10.4.

solvents, including ethanol, acetone, dioxane, carbon tetrachloride, ether, and chloroform, as well as in strongly acidic or alkaline aqueous solution. This compound shows acid-base indicator properties and is yellow in acidic and neutral solution, and red in strongly alkaline solution; in concentrated sulfuric acid, it is violet. The absorbance curves of 5-Br- β -PAN in 50% (v/v) aqueous dioxane and in sulfuric acid are shown in Figs. 1 and 2.

Three species of 5-Br- β -PAN, H_2L^+ , HL and L^- , are involved in its acid-base behaviour; in strong sulfuric acid solution, two additional protonated species, H_3L^{2+} and H_4L^{3+} , probably occur, the extra protons being attached to the azo group. In sulfuric acid, the value of pK_a was obtained from the following equation:

$$pK_a = H_0 + \log \frac{\epsilon - \epsilon_1}{\epsilon_2 - \epsilon}$$

where H_0 is the Hammett acidity function of the sulfuric acid solution^{5,6}; ϵ_1 , ϵ_2 and ϵ are the molar absorptivities of a solution containing the two protonated species, and a mixture of the two species, respectively. The wavelength of maximum absorbance and the molar absorptivity of each species, and the pK_a values obtained are listed in Tables I and II.

TABLE I
VISIBLE SPECTRA OF THE 5-Br- β -PAN

	H_2L^+ $pH \sim 0$ $\lambda \text{ max (nm)}$ ($\epsilon \cdot 10^{-3}$)	HL $pH \sim 5$ $\lambda \text{ max (nm)}$ ($\epsilon \cdot 10^{-3}$)	L^- $pH \sim 14$ $\lambda \text{ max (nm)}$ ($\epsilon \cdot 10^{-3}$)	H_3L^{2+} $-H_0 \sim 4^a$ $\lambda \text{ max (nm)}$ ($\epsilon \cdot 10^{-3}$)	H_4L^{3+} $-H_0 \sim 10.5^a$ $\lambda \text{ max (nm)}$ ($\epsilon \cdot 10^{-3}$)
β -PAN	425 (16.2)	470 (17.2)	495 (13.2)	—	—
5-Br- β -PAN	450 (18.8)	475 (19.6)	500 (16.6)	460 (19.4)	570 (24.1)

^a In 1:1 (v/v) aqueous dioxane.

TABLE II
DISSOCIATION CONSTANTS OF THE 5-Br- β -PAN

	$pK_{H_2L^+}^a$	pK_{OH}^a	$pK_{H_3L^{2+}}$	$pK_{H_4L^{3+}}$
β -PAN	1.8	12.3	—	—
5-Br- β -PAN	~ 1.0	11.8	$\sim 3.9^b$	$\sim 7.6^b$

^a In 1:1 (v/v) aqueous dioxane.

^b Hammett's acidity function (in sulfuric acid).

Chelate formation

The chelate compounds are easily prepared by adding a few drops of a solution of 5-Br- β -PAN in methanol to solution of heavy metals. Generally, the solutions containing heavy metal showed a red colour under acidic, neutral or alkaline conditions, except for cobalt(III), palladium(II), vanadium(V) and iron(III). The ions that gave a colour or precipitate with the reagent are listed in Table III. The tests

were made by adding one drop of 0.1% reagent solution in methanol to 1 ml of the metal ion solution (0.1 mg/ml). For nickel and platinum metals, the test tube was heated to about 80° for a few minutes. The following ions failed to give a detectable precipitate or coloration at room temperature: lithium, beryllium, boron, sodium, magnesium, aluminium, potassium, calcium, chromium(III), germanium, arsenic, strontium, molybdenum, tin, barium, tungsten, thallium(I), tellurium, and almost all common anions.

TABLE III

COLOUR REACTION OF METALS WITH 5-Br- β -PAN IN AQUEOUS SOLUTION AND MASKING POSSIBILITIES

<i>Metals</i>	<i>Colour</i>	<i>Metals</i>	<i>Colour</i>
Sc ³⁺	Purple	Pd ²⁺	Green
V ⁵⁺	Light olive	Ag ⁺	Red brown
Mn ²⁺	Wine red	Cd ²⁺	Red
Fe ³⁺	Brown	In ³⁺	Red
Co ²⁺	Red	Sb ³⁺	Brown red
Co ³⁺	Green	RE ³⁺	Purple
Ni ²⁺	Purple	Hf ⁴⁺	Red
Cu ²⁺	Red purple	Pt ⁴⁺	Brown
Zn ²⁺	Red purple	Hg ²⁺	Red
Ga ³⁺	Red	Pb ²⁺	Red
Y ³⁺	Purple	Bi ³⁺	Red
Zr ⁴⁺	Red	Th ⁴⁺	Red
Nb ⁵⁺	Dark orange	UO ₂ ²⁺	Purple red

TABLE IV

REACTIVITY OF METALS WITH 5-Br- β -PAN IN THE PRESENCE OF MASKING REAGENTS

<i>Metals</i>	<i>KCN</i>	<i>Citrate</i>	<i>Fluoride</i>	<i>EDTA</i>
V ⁵⁺	—	—	+	—
Mn ²⁺	+	—	+	—
Fe ³⁺	—	—	—	—
Co ²⁺	—	+	+	—
Ni ²⁺	—	+	+	—
Cu ²⁺	—	+	+	—
Zn ²⁺	—	—	+	—
Ga ³⁺	—	—	—	—
Y ³⁺	+	—	—	—
Pd ²⁺	—	+	+	—
Sb ³⁺	+	—	—	—
Hg ²⁺	—	—	+	—
Pb ²⁺	+	—	+	—
Bi ³⁺	—	—	—	—
RE ³⁺	+	—	—	—
Hf ⁴⁺	—	—	—	—
UO ₂ ²⁺	+	—	+	+

Reactivity in the presence of masking reagents

An attempt was made to use the common masking reagents, such as EDTA, cyanide, fluoride, and citrate, in order to improve the selectivity of the reagent. Suitable amounts of neutral or slightly acidic metal ion solution were mixed with

5 ml of the masking reagent and 1 ml of methanolic 0.1% reagent solution, and the pH was adjusted before the mixture was stirred for few minutes. The results are shown in Table IV. EDTA prevented almost all metals tested from reacting with the reagent, except uranium. Cyanide prevented the reaction of metals other than manganese, antimony, lead, uranyl and rare earth metals. Fluoride prevented the reaction of iron and some other metals. Citrate had a masking effect similar to fluoride, except in the case of mercury.

Solvent extraction

The highly coloured chelate formed with many heavy metals under various conditions was useful for the detection of certain metals. These coloured chelates are soluble in various organic solvents (Table V).

TABLE V

SOLUBILITY AND COLOUR^a OF METAL CHELATES IN VARIOUS ORGANIC SOLVENTS

Metals	CHCl ₃	CCl ₄	Benzene	Ether	Isoamyl alcohol
Reagent	Yellow	Yellow	Yellow	Yellow	Yellow
V ⁵⁺	Olive	—	—	—	—
Mn ²⁺	Red	Red	Red	Red	Red
Fe ³⁺	Dull red	Dull red	Dull red	Dull red	Dull red
Co ²⁺	Red	Red	—	—	—
Co ³⁺	Green	Green	Green	Green	Green
Ni ²⁺	Red	Red	Red	Red	Red
Cu ²⁺	Red	Red	Red	Red	Red
Zn ²⁺	Red	Red	Red	Red	Red
Ga ³⁺	Red	Orange	Orange	Orange	Orange ^c
Pd ²⁺	Green	Green	Pale green	Pale green	Pale green
Cd ²⁺	Red	Red	Red	Orange red	Red
In ³⁺	Red	Orange-yellow	Red	Yellow	Yellow
RE ³⁺	Red	Orange red	Red	Red	— ^b
Hg ²⁺	Red	— ^b	— ^b	— ^b	— ^b
Bi ³⁺	— ^b	— ^b	— ^b	— ^b	— ^b
UO ₂ ²⁺	Red	— ^b	Orange-yellow	— ^b	— ^b

^a With excess of reagent.

^b Decomposed.

^c Purple aqueous phase.

Absorbance curve

Colorimetric determinations may be made by extraction with an organic solvent, or directly in an aqueous solution by adding alcohol or dioxane, or by adding gum arabic to prevent turbidity.

In this study, for comparison, the absorbance curves of the metal chelates in chloroform are shown in Figs. 3, 4 and 5. Most 5-Br-β-PAN complexes have absorption maxima lying between 550 nm and 570 nm, but some complexes absorb at longer wavelength (Fig. 3).

Effect of pH

A series of solutions containing definite amounts of the required metal and

1 ml of 0.1% reagent solution was prepared. Figure 6 shows the influence of hydrogen ion concentration on the extraction of metals with chloroform from aqueous solution. Although above pH 11 some metal complexes were formed in aqueous solution, the extractability was decreased, probably because hydroxy species were formed. The results clearly show that the chelate formation and extractability are strongly dependent on the acidity of the reaction medium.

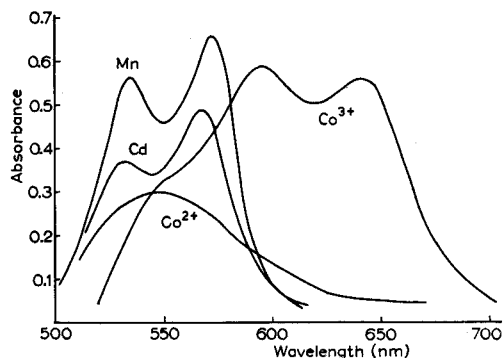
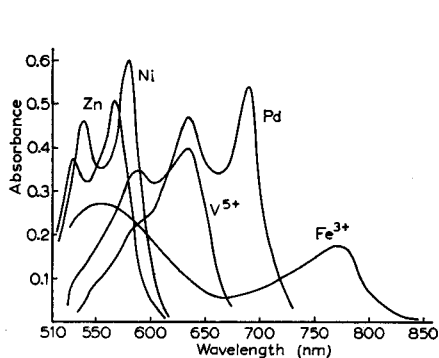


Fig. 3. Absorbance curves of metal-5-Br- β -PAN complexes in chloroform against a reagent blank. Reagent in large excess; 1-cm cells.

Fig. 4. Absorbance curves of metal-5-Br- β -PAN complexes in chloroform against a reagent blank. Reagent in large excess; 1-cm cells.

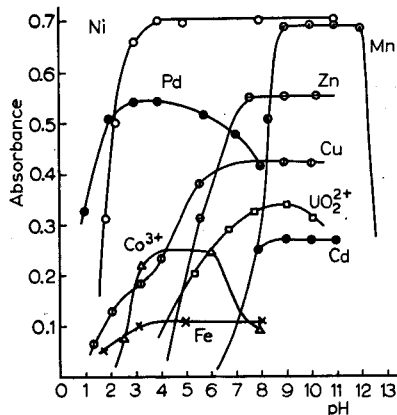
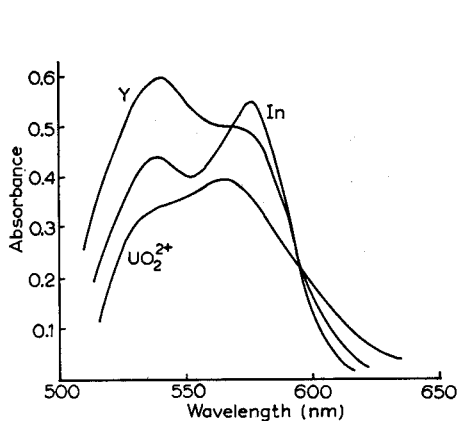


Fig. 5. Absorbance curves of metal-5-Br- β -PAN complexes in chloroform against a reagent blank. The curve for yttrium was obtained in ether medium. Reagent in large excess.

Fig. 6. Optimum pH for chloroform extraction. Cd 0.5, Co 0.5, Cu 0.5, Fe 2.5, Mn 0.54, Ni 0.58, Pd 3.2, UO_2^{2+} 1.5 and Zn 0.5 p.p.m. respectively. Mn was extracted with ether.

Beer's law and sensitivity

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

TABLE VI

THE MOLAR ABSORPTIVITIES OF SOME METAL CHELATES

Metals	Molar absorptivity $\epsilon \cdot 10^{-4}$		λ max (nm)	
	5-Br- β -PAN	β -PAN	5-Br- β -PAN	β -PAN
V(V)			570	570
	3.1 ^a	1.7 ^{a7}	630 ^a	615 ^a
Mn(II)	7.2 ^b	4.8 ^b	574	502
Co(II)	3.5	2.7 ^b	540	550
Co(III)	6.9 ^a	2.5 ^{a10}	595 ^a	590 ^a
			640	640
Ni(II)	8~9	5.0 ¹¹	582	570
Cu(II)	5.2	4.4 ¹²	572	564
Zn(II)	6.7	5.6 ^b	570	550
Pd(II)			635	626
	1.8 ^a	1.4 ^{a13}	695 ^a	678 ^a
Cd(II)	7.3	4.9 ¹⁴	568	555
In(III)	1.1	2.0 ¹⁴	575	560
Tm(III)	7.0 ^b	6.5 ^{b15}	540	530
UO ₂ ²⁺	6.6	2.3 ¹⁶	570	570

^a Determined at maximum wavelength.^b Ether solution.*Stripping into aqueous solution*

The selectivity of extraction and determination of metals could be increased, by back-washing or back-extraction. Potassium cyanide (0.2 M) allowed back-extraction of Cu, Zn, Ga, Pd, Cd, In, Hg(II) and Pb. Acetate buffer pH 4 allowed back-extraction of Mn(II), Y, Cd, Hg(II), Pb and rare earths. Mn(II), Cu, Zn, Y, Cd, In, Hg(II), Pb and rare earths could be back-extracted with 5% citrate solution.

Effect of temperature

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

Nature of complex

The empirical formula of the coloured complexes was determined by the continuous variation and the mole ratio method. Representative results are given in Fig. 7. It is evident that these complexes contain two molecules of reagent to one of metal.

The composition of some metal complexes can depend on the ratio of the reactants, and on the nature and acidity of the solvent. As an example, the copper(II) complex was investigated in detail. The absorbance curves of the bluish purple copper(II) complex in chloroform, extracted from aqueous solution of pH 3.4 showed only one absorption maximum (at 570 nm), the absorption maximum of the reagent itself occurring at 460 nm. The mole ratio method applied for a $7.4 \cdot 10^{-5}$ M reagent solution at 570, 590 and 610 nm, with the extraction procedure, clearly indicated the formula CuLX (X = Cl).

The absorbance curves of the reddish purple copper(II) complex extracted by chloroform from aqueous solutions of pH 10 were different from those obtained

at pH 3.4. In this case, two absorption maxima, at 540 and 570 nm, were clearly shown, and the mole ratio method at 570 and 590 nm clearly indicated the formula CuL_2 . The value for the molar absorptivity of the 1:2 complex was nearly twice that of the 1:1 complex, indicating that the absorption of these 5-Br- β -PAN complexes is solely due to the ligand molecule. The absorbance curves of the copper(II) complexes extracted by chloroform from aqueous solutions of various pH values and at a constant molar ratio of 1:2 for Cu: 5-Br- β -PAN, are shown in Fig. 8. These plots unequivocally show that the copper(II) complex formed depends on the pH of the reaction medium; generally, the MLX-type complexes are rather soluble in water, whereas the ML_2 -type complexes are almost insoluble.

Finally, as a typical example, the infrared spectra of the reagent and its palladium chelate are shown in Fig. 9. The results obtained suggest the coordination of the heterocyclic nitrogen and azo groups. It appears that 5-Br- β -PAN acts as a tridentate ligand, forming two stable 5-membered chelate rings by the use of the

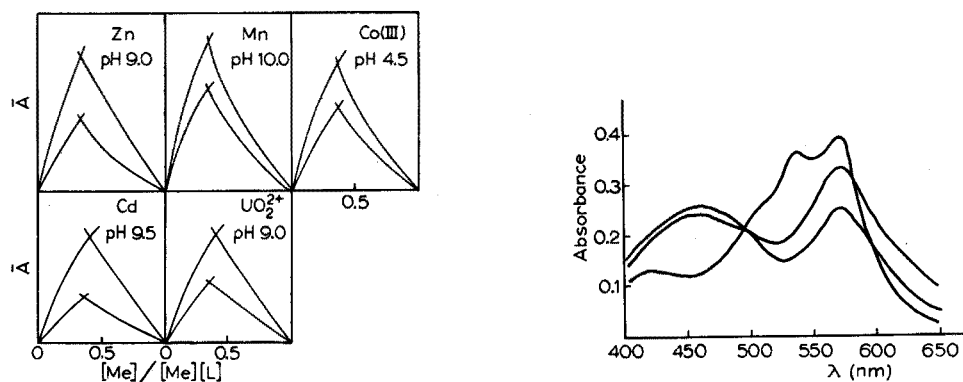


Fig. 7. Composition of the coloured complexes (at different wavelengths).

Fig. 8. Absorbance curves of copper(II)-5-Br- β -PAN complexes in chloroform, extracted from aqueous solutions of different pH ($1.85 \cdot 10^{-5}$ M reagent and $0.925 \cdot 10^{-5}$ M copper).

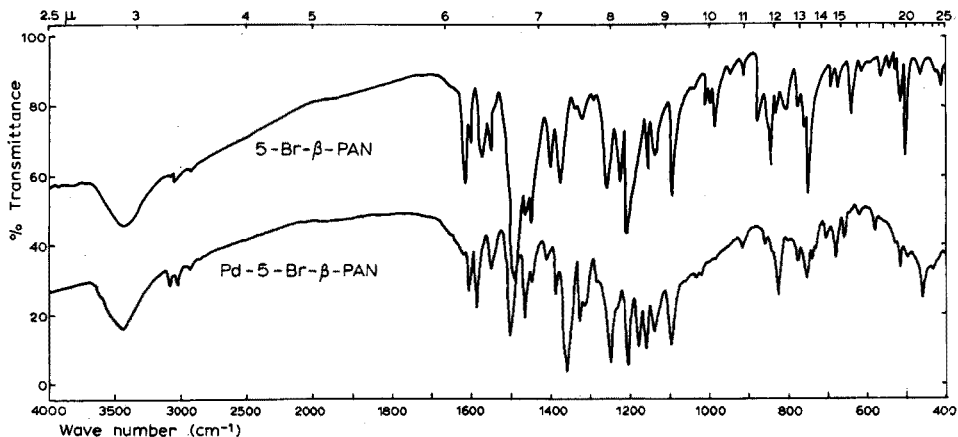


Fig. 9. The infrared spectrum of 5-Br- β -PAN and its palladium chelate (KBr tablet).

o-hydroxyl group, the heterocyclic nitrogen and the azo group, and that the commonest chelates are of the type ML and ML₂. Further work on the structure and stability of each metal complex is now in progress.

As an extraction and photometric reagent, 5-Br- β -PAN seems to be promising, because of its high molar absorptivity, the high stability of its complexes and the large bathochromic shift produced on chelation. Although the reagent is rather unselective, it can be improved by a judicious choice of pH, solvent, and masking reagents.

SUMMARY

The heterocyclic azo compound, 1-[(5-bromo-2-pyridyl)azo]-2-naphthol (5-Br- β -PAN), forms various coloured metal chelates, which can be extracted with different organic solvents. Most of the reacting metals form reddish chelates, except for cobalt(III) and palladium(II) (green), and vanadium(V) (olive). Chelate stability is greatly affected by pH. The molar absorptivities are usually considerably greater than those of the β -PAN chelates. A correct choice of pH, solvent and masking reagents allows 5-Br- β -PAN to be made reasonably selective.

RÉSUMÉ

Le composé azo hétérocyclique, 1-[(5-bromo-2-pyridyl)azo]-2-naphthol (5-Br- β -PAN), forme divers chélates métalliques colorés pouvant être extraits dans différents solvants organiques. La plupart des métaux réagissant donne des chélates rougeâtres, à l'exception du cobalt(III), du palladium(II) (vert) et du vanadium(V) (olive). La stabilité de ces chélates est fortement influencée par le pH. Les absorptions molaires sont généralement beaucoup plus grandes que celles des chélates β -PAN. Un choix correct du pH, du solvant et des réactifs de masquage permet au 5-Br- β -PAN d'être suffisamment sélectif.

ZUSAMMENFASSUNG

Die heterozyklische Azoverbindung 1-[(5-bromo-2-pyridyl)azo]-2-naphthol (5-Br- β -PAN) bildet zahlreiche gefärbte Metallchelate, welche mit unterschiedlichen organischen Lösungsmitteln extrahiert werden können. Die meisten der reagierenden Metalle bilden rötliche Chelate ausser Kobalt(III) und Palladium(II) (grün) und Vanadin(V) (olive). Die Chelatstabilität wird stark durch den pH-Wert beeinflusst. Der molare Extinktionskoeffizient ist im allgemeinen beträchtlich grösser als derjenige von β -PAN-Chelaten. Die richtige Wahl des pH-Wertes, des Lösungsmittels und maskierender Reagenzien macht das 5-Br- β -PAN zu einem brauchbaren selektiven Reagenz.

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Anal. Chim. Acta, 45 (1969) 279-288

ÜBER DAS VERHALTEN VON TERTIÄREN AROMATISCHEN AMINEN BEI DER EXTRAKTION VON URAN AUS NEUTRALEN UND SAUREN MEDIEN

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Die Spurenanalyse gewinnt immer mehr an Bedeutung für Anreicherungsverfahren und das Studium stofflicher Eigenschaften. Dabei wird den Extraktionen aus wässrigen Medien mit verschiedensten Agenzien eine besondere Stellung eingeräumt, da gerade diese es ermöglichen Elementtrennungen vorzunehmen, wobei die Trennverfahren wiederum in strenger Abhängigkeit zum Nernst'schen Verteilungssatz stehen. Spezifische Verfahren zur Extraktion von Uran mit tertiären aromatischen Aminen wurden bisher nicht entwickelt. RODDEN¹ zeigt in einer Publikation über die Analytik des Urans die vielfältigen Bestimmungsmöglichkeiten dieses Metalls auf und MOORE² befasst sich mit Methyldi-*n*-octylamin, Tri-*n*-Benzylamin und Methyldi-*n*-octylamin-xylol als Extraktanten für PuO₂²⁺, ²¹⁰Po, Zr und Pa aus sauren Lösungen. Eine umfangreiche Übersichtsliteratur hinsichtlich Lösungsmittelextraktionen mit Alkylaminen, hauptsächlich aliphatischen Aminen, stammt von COLEMAN *et al.*³

Uranylsulfatkomplexe extrahierte ALLEN⁴ mit Tri-*n*-octylamin und MOORE⁵ brachte Tri-*n*-isooctylamin bei Extraktionen von Uran und Plutonium aus salzsaurer Lösung zur Anwendung. Etwa auf gleicher Ebene liegt die Arbeit von MAECK⁶, der Elemente als quarternäre Propyl-, Butyl- und Hexylaminkomplexe extrahiert. In ähnlicher Richtung arbeiten WILSON *et al.*⁷, die Ammoniumhalogenide als mögliche Extraktanten einführen. SCRIBNER UND KOTECKI⁸ untersuchen die Extraktionswirkung von Trifluoracetylaceton-Isobutylamin gegenüber Uran. Besonders erwähnenswert ist auch die Arbeit von HECHT UND LEHNER⁹, die langkettige gerade und verzweigte aliphatische Amine zum Einsatz bringen.

Am eigenen Institut ausgearbeitete Verfahrenstechniken konnten auf die Extraktion von Niobium mit N-Benzylanilin übertragen werden¹⁰. Dabei wurde auch die spezifische Extraktion von Uran mit N-Benzylanilin und N-Butylanilin untersucht¹¹. Andere sekundäre und tertiäre aliphatische bzw. aromatische Amine wie etwa N,N-Diphenylanilin und N,N-Dibenzylanilin kamen dabei nur qualitativ zum Einsatz.

EXPERIMENTELLES

Für die Extraktion und Abtrennung des Urans von anderen Elementen durch tertiäre aromatische Amine, gelöst in Chloroform, hatten wir folgende Voraus-

setzungen geschaffen: die Testlösung enthielt jeweils $10 \mu\text{g U(VI)/ml}$, eingewogen als $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. Eingesetzt wurden allgemein $50 \mu\text{g U(VI)}$. Zur Prüfung des Verteilungskoeffizienten war es unerlässlich eine Zweiphasenkontrolle durchzuführen. Wir konnten nämlich zeigen, dass in einigen Fällen scheinbar gute Extraktionen vorlagen, das Uran in der wässrigen Phase jedoch blockiert bzw. komplexiert war und daher auch eine Bestimmung dieses Metalls in der organischen Phase nicht möglich war.

Die Zweiphasenkontrolle erfolgte spektralphotometrisch nach der PAR-Methode¹². Als Aminextraktionslösung verwendeten wir eine 0.5%ige Grundlösung (500 mg Amin gelöst in 100 ml Chloroform). Eine solche Extraktionslösung wird

TABELLE I

DIE ZUR URANEXTRAKTION VERWENDETEN TERTIÄREN AROMATISCHEN AMINE UND DEREN WIRKUNGSGRAD (%)

Nr.	0.5% Amin/ CHCl_3	System							
		Neutral		HCl		H_2SO_4		HNO_3	
		Extr. (%)	Effekt. Säurenorm.	Extr. (%)	Effekt. Säurenorm.	Extr. (%)	Effekt. Säurenorm.	Extr. (%)	Effekt. Säurenorm.
1	DMA	12	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
2	DÄA	22	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
3	DBA	29	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
4	DÄT	18	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
5	MDPA	10	0.5	24	5.0	18	0.5-5.0	0	—
6	BMA	14	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
7	ÄPBA	18	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
8	PDBA	24	5.0	24	5.0	35	5.0	34	—
9	MBDMA	38	0.5	28	0.5	34	0.5	37	—
10	BÄT	22	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
11	BMAP	30	0.5	15	0.5	1.6	7.0	65	—
12	ABA	16	5.0	16	0.5	27	5.0	25	—
13	MPBA	24	2.5	19	0.5	25	0.5	15	—
14	DAA	26	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
15	DMAZ	—	0.5-5.0	—	0.5-5.0	—	0.5-5.0	—	—
16	BDMÄDA	41 → 68	0.5	14	0.5	7	5.0	24	—
17	BDMABP	52 → 61	0.5-5.0	—	0.5	7	0.5-5.0	—	—
18	DMAMI	59 → 94	0.5	18.8	0.5	43.8	0.5-5.0	—	—
19	DMTA	51	5.0	12	5.0	9	0.5	17	—
20	DMHTA	33 → 49	0.5	18	0.5	8	0.5	10	—
21	DMNA	7	5.0	12	5.0	26	5.0	8	—

- 1 = N,N-Dimethylanilin.
 2 = N,N-Diäthylanilin.
 3 = N,N-Dibutylanilin,
 N,N-Di-*n*-Butylanilin.
 4 = N,N-Diäthyl-*m*-Toluidin,
 3-(Diäthylamino)-Toluol.
 5 = N-Methyl-Diphenylamin.
 6 = N-Benzyl-N-Methylanilin.
 7 = N-Äthyl-N-Phenylbenzylamin,
 N-Äthyl-N-Benzylanilin.
 8 = N,N-Dibenzylanilin,
 N-Phenyl-Dibenzylamin.
 9 = N-(α -Methylbenzyl)-Dimethylamin.
 10 = N-Benzyl-N-Äthyl-*m*-Toluidin.
 11 = 3-(Benzylmethylamino)-1-Propanol.

- 12 = Acetyl-*n*-Butylanilin.
 13 = N-Methyl-N-Propargyl-Benzylamin.
 14 = N,N-Diallylanilin.
 15 = *p*-N,N-Dimethylaminozimtaldehyd.
 16 = 4,4'-Bis-(Dimethylamino)-
 Benzophenon.
 17 = N-Benzyl-N,N-Dimethyläthylen
 Diamin.
 18 = 3-(Dimethylamino)-Methylindol.
 19 = N,N-Dimethyltryptamin,
 3-(2-Dimethylaminoäthyl)-Indol.
 20 = N,N-Dimethylhomotryptamin,
 3-(γ -Dimethylaminopropyl)-Indol.
 21 = N,N-Dimethylnicotinamid.

jeweils aus den tertiären aromatischen Aminen hergestellt, die in Tabelle I aufgeführt sind. Diese Amexlösung war zunächst ausreichend um Extraktionsmaxima festzustellen. An diesen Punkten wird dann die günstigste Aminkonzentration ermittelt, um eine eventuelle Steigerung der Extraktion zu erzielen. Es zeigte sich, dass nur Extraktionswerte von über 50% interessant sind, um hinsichtlich variabler Aminkonzentration eingehender untersucht zu werden.

EXTRAKTIONSSCHEMA

Nach vorheriger Festlegung der Eichkurve werden die Extraktionen in 100-ml Scheidetrichter durchgeführt. Dabei sind mit 0.5%iger Amin-Chloroformlösung und genereller Schütteldauer von 5 Minuten die nachfolgenden Lösungen extrahierbar:

<i>Vergleichslösung</i>	<i>Testlösung</i>
5 ml H ₂ O	5 ml U(VI)-Lösung = 50 µg U(VI)
5 ml N-Säure	5 ml N-Säure
10 ml 0.5% Amin/CHCl ₃	10 ml 0.5% Amin/CHCl ₃

Nach der Phasentrennung werden

(a) Die wässrigen Medien von Test- und Vergleichslösung mit DNP (2,4-Dinitrophenol) neutralisiert (siehe DNP als Neutralisationsindikator). Nach Zugabe von 5 ml Triäthanolaminpuffer (pH 8) und 2 ml 0.2 %iger PAR-Lösung wird mit Wasser auf 50 ml aufgefüllt und im Zeiss-Spektralphotometer PMQ II bei 530 nm in 5-cm Küvetten vermessen.

(b) Die organischen Phasen von Test- und Vergleichslösung entweder:

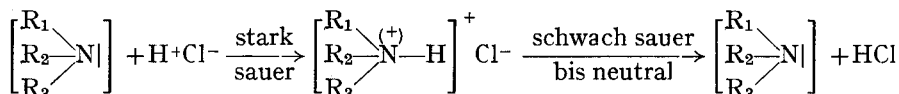
1. Mit Wasser, Lauge, Säure bzw. Gemischen reextrahiert,
2. In Platinschalen verdampft und verglüht, oder
3. Durch direkte Aufnahme von UO₂²⁺ mit Säure während des Verdampfens und anschließender PAR-Methode spektrophotometrisch bestimmt. Nach experimenteller Bestimmung der Extraktionsmaxima veränderten wir auch die Aminkonzentration, um eine Steigerung der Uranextraktion zu erzielen.

Uran lässt sich in neutraler bzw. schwach saurer Lösung mit PAR gut direkt bestimmen. Stark saure Medien werden mit 2,4-Dinitrophenol (DNP) als Neutralisationsindikator versetzt und so der PAR-Methode zugänglich gemacht. Es ergab sich, dass die Bestimmung von Uran(VI) in organischer Phase von Amin zu Amin verschieden erfolgen musste. Entweder war nur eine Reextraktion mit Wasser, Säure oder Lauge möglich, oder man musste nach Verdampfen bzw. Verglühen der organischen Phase in der Platinschale und nachträglicher Aufnahme in Säure das Metall bestimmen.

Auch das Überschichten der organischen Phase im Platingefäß mit Säure, nebst anschließender Verdampfung der Chloroformschicht bei ca. 60°, wobei Uran in der wässrigen Phase verbleibt, konnte zur Bestimmung des Metalls verwendet werden. DNP diente wieder als Indikator. Dieser wurde deshalb gewählt, weil er die Lösung noch schwach sauer hält und so eine vorzeitige Fällung von Diuranat verhindert. Sein Vorhandensein hat keinerlei Einfluss auf die Uranbestimmung mit PAR. Konnte in einigen Fällen das Metall der organischen Phase nur teilweise oder

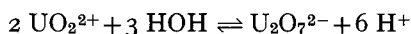
überhaupt nicht bestimmt werden, so lag eine Maskierung des Urans vor. Bei echter Extraktion war jedoch eine Zweiphasenbestimmung möglich.

Extraktionen aus alkalischer-, phosphor- und essigsaurer Lösung waren nicht möglich. Für die PAR-Bestimmung empfiehlt es sich, die Ausgangslösung schwach sauer zu halten, da etwa ausfallendes Diuranat stört. Bleibende Trübungen oder Niederschläge sind wahrscheinlich die Folge eines sich im wässrigen Medium rückspaltenden Amines. In saurem Bereich entsteht das leichtlösliche Aminsalz, das auch teilweise in wässriger Phase zu finden ist. Nähert man sich nun dem Neutralpunkt, wird dieses Salz in das freie Amin zurückgespalten, welches dann die Trübung verursacht:



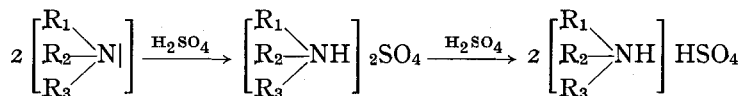
Trotz dieser Trübungen konnte man nach Zugabe von PAR an dem Farbunterschied Test: Vergleich erkennen, ob Uran extrahiert wurde oder nicht.

In Uranyl-salzlösungen besteht bekanntlich das pH-abhängige Gleichgewicht:

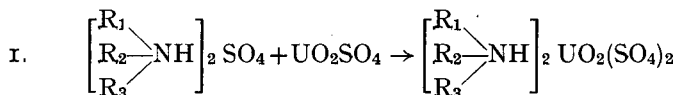


Im alkalischen Medium entsteht ein Niederschlag von Diuranat. Weinsäure verhindert diese Fällung unter Bildung eines löslichen Komplexes, der aber für die Extraktion ungeeignet ist. Diese gelingt wegen Niederschlagsbildung nicht aus den vorhin erwähnten Medien, zudem lässt sich mit Essigsäure der Bestimmungs-pH = 8 der PAR-Methode nicht halten.

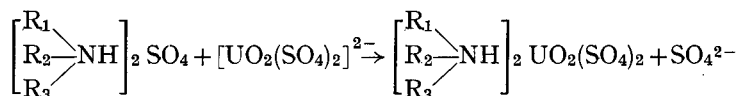
Das zur Extraktion eingesetzte tertiäre Amin reagiert nun allgemein, demonstriert am Beispiel der Schwefelsäure, wobei zunächst das Normalsulfat und dann das Hydrogensulfat entsteht:



Für die weitere Reaktionsfolge stehen 2 Möglichkeiten zur Diskussion:



2. Austausch von Sulfat gegen den anionischen Uranyl-sulfatkomplex in wässriger Lösung:



Der eigentliche Extraktionsvorgang dürfte je nach Säurekonzentration nach (1) oder (2) ablaufen. Das komplexierte Uran(VI) kann wiedergewonnen werden durch Austausch mit Chlorid—bzw. Nitration oder durch Hydrolyse des Aminsalzes.

EXTRAKTIONSERGEBNISSE

Unter Einhaltung der im Extraktionsschema angegebenen Richtlinien gelangten wir zu Daten, die in Tabelle I zusammengefasst sind. Extrahiert wurde aus neutralen und 0.5 bis 5.0 normal sauren Medien. Das entsprechende Amin war jeweils in Chloroform gelöst. DMAZ konnte in keinem Fall brauchbare Ergebnisse liefern, da bei allen Versuchen gallertartige Polymerisationsprodukte entstanden. Solche Lösungen waren spektralphotometrisch nicht zu vermessen.

Von den in Tabelle I aufgeführten tertiären aromatischen Aminen ist hinsichtlich ihrer Extraktionsfähigkeit folgendes beachtenswert:

(a) *HCl-System*. DMA-, DÄA-, DBA-, DÄT-, BMA-, ÄPBA-, BÄT-, DAA- und BDMABP-Lösungen ergeben im salzsauren Medium Trübungen oder Niederschläge durch Aminrückspaltung. Den gleichen Effekt gab eine MPBA-Lösung in 5 N HCl. Maximalextraktion ist mit einer 1.5 %igen MBDMA-Chloroform-Lösung in 0.5 N HCl mit 28% gegeben. Der Extraktionsdurchschnitt liegt bei 18.3%.

(b) *H₂SO₄-System*. DMA-, DÄA-, DBA-, DÄT-, BMA-, ÄPBA-, BÄT- und DAA-Lösungen verursachen Trübungen oder Niederschläge. Bei einer MPBA- und BDMABP-Lösung kann die Bestimmung aus erwähnten Gründen nicht durchgeführt werden. Maximalextraktion ergibt eine 0.5%ige DMAMI-Lösung aus 0.5 N H₂SO₄ mit 43.8%. Der Extraktionsdurchschnitt beträgt hier 20.1%.

(c) *HNO₃-System*. DMA-, DÄA-, DBA-, DÄT-, BMA-, ÄPBA-, BÄT-, DAA-, BDMABP- und DMAMI-Lösungen ergeben ebenfalls Trübungen oder Niederschläge. DMHTA-Lösung war auch aus vorerwähntem Grunde bei 2.5 und 5 N HNO₃ nicht verwendbar. Maximalextraktion mit 44% ergab sich bei Anwendung einer 0.5%igen BMAP-Lösung in 5 N HNO₃. Durchschnittlich werden 23.5% Uran extrahiert.

(d) *Neutral-wässriges System*. BDMÄDA erzielte als 0.5%ige Lösung 41% Extraktion. Mit einer 2%igen Lösung konnte dieser Wert noch auf 68% gesteigert werden. Eine nähere Untersuchung ergab jedoch, dass Uran(VI) in wässriger Phase blockiert vorlag. BDMABP liefert als 0.5%ige Lösung einen Extraktionswert von 52%. Mit einer 2%igen Lösung konnte dieser noch auf 61% gesteigert werden.

DMHTA 0.5%ig, erzielt 33%ige Extraktion. Mit 0.1%iger Amin-Lösung erhält man 49%ige Extraktion.

DMAMI 0.5%ig, extrahierte 59% Uran. Höhere und tiefere Aminkonzentrationen erwiesen sich als schlechtere Extraktanten. Hinsichtlich des Extraktionsvorganges ergab sich eine starke Abhängigkeit von der Säurekonzentration (Abb. 1).

Wir stellten zunächst Lösungen innerhalb des pH-Bereiches von 4.04–6.5 her und führten damit die Extraktionen durch. Nach mehrmaligen Einzelbestimmungen ergaben sich folgende Ergebnissen (siehe Tabelle II). Bei pH 5.1–5.7 werden 94–100% U(VI) von der organischen Phase übernommen. Das Metall ist nach Reextraktion mit 10 ml Wasser und 2 ml 1 N HCl gut zu bestimmen.

Die Werte sind bei Erstextraktion mit –6 bis 0% Fehlergrenze gut reproduzierbar und liegen noch im üblichen Bereich.

Im Rahmen dieser Versuche wurde auch das Verhalten des Uranylcarbonatkomplexes hinsichtlich der Extraktion mit Aminen erprobt. NaHCO₃ und (NH₄)₂CO₃ bilden mit Uranylsalzen leicht lösliche Komplexe, die in saurer Lösung zerstört werden. Wir haben nun das Uranylsalz der Testlösung (10 µg U(VI) pro ml) mit gesättigter (NH₄)₂CO₃-Lösung in den Komplex überführt und versucht, diesen mit

einer 1.5%igen MBDMA-Lösung zu extrahieren. Dabei kamen wir zu einer Maximalextraktion von 82%, die durch eine anschließende PAR-Bestimmung bestätigt wurde. Um sicher zu gehen, inwieweit MBDMA an diesem Vorgang integrierend mitbeteiligt ist, wurde auch eine Extraktion mit Reinchloroform allein durchgeführt.

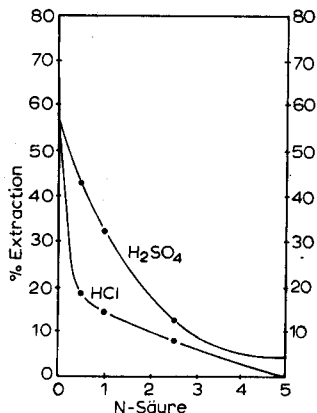


Abb. 1. Prozentuale Abhängigkeit der Extraktion des U(VI) mit 0.5% DMAMI in Chloroform von der effektiven Säurenormalität.

TABELLE II

URANEXTRAKTION INNERHALB DES pH 4.04–6.5 MIT ANSCHLIESSENDER SPEKTRALPHOTOMETRISCHER BESTIMMUNG

pH-Wert	Extinktion des Uran-PAR-Komplexes		$\mu\text{g U(VI)}$ organ. Phase	Extraktion (%)
	wässr. Phase	organ. Phase		
4.04	0.278	0.435	31	62
4.60	0.075	0.638	45	90
5.10	0.042	0.0671	47	94
	0.000	0.713	50	100
5.40	0.043	0.670	47	94
	0.000	0.713	50	100
5.70	0.042	0.671	47	94
	0.000	0.713	50	100
6.50	0.158	0.555	39	78

Dabei ergab sich der gleiche Wert von 82%, womit bewiesen war, dass das Amin an der Extraktion nicht beteiligt ist. Der Komplex wird also allein von Chloroform extrahiert. Nach viermaliger Wiederholung dieses Vorganges war eine Maximalextraktion von 99.8% gegeben.

Wir untersuchten auch den Einfluss des Uranylphosphatniederschlages hinsichtlich der Extraktion. Die erwartete Unregelmässigkeit in der Verteilung des Niederschlages auf beide Phasen bei wechselnder Säurenormalität trat nicht ein, vielmehr liess sich, wie Tabelle III zeigt, eine lineare Beziehung zwischen Extraktion des $(\text{UO}_2)_3(\text{PO}_4)_2$ und der effektiven Säurekonzentration herstellen. Hier führten wir die Uranbestimmung mit PAR jeweils bei pH 6–7 durch. Vorgelegt wurden jedesmal 50 $\mu\text{g U(VI)}$, die Schütteldauer betrug bei allen Versuchen 5 Minuten. Als

Extraktionslösung verwendeten wir generell 10 ml 0.5%ige ABA-Chloroformlösung.

Das Uran konnte nach dem Extraktionsvorgang in wässriger Phase einwandfrei bestimmt werden. Auch in organischem Medium konnte es nach Verdampfen und Verglühen des organischen Solvens in einer Platinschale, anschliessender Aufnahme in 5 ml 1 N HCl und Neutralisation mit DNP auf pH 5–6 bestimmt werden. Bei grösseren Säurenormalitäten zeigten sich schwankende Extraktionswerte. Hier war daher eine genaue Uranbestimmung nicht mehr möglich.

TABELLE III

PHASENVERTEILUNG VON $(\text{UO}_2)_3(\text{PO}_4)_2$ NACH EXTRAKTION MIT ABA IN CHCl_3

Effektive Säurenorm.	Extinkt. Messung Test/Vergleich		$\mu\text{g Uran(VI)}$		Extraktion %
	H_3PO_4	wässr.	organ.	wässr.	
0.0	0.616	0.109	42	8	16
0.5	0.725	0.003	50	0	0
1.0	0.605	0.123	41.5	8.5	17
2.5	0.384	0.344	27	23	46
5.0	0.229	0.499	16	34	68
8.0	0.132	0.596	9	41	82
10.0	0.0		0	50	100
22.5	0.0		0	50	100

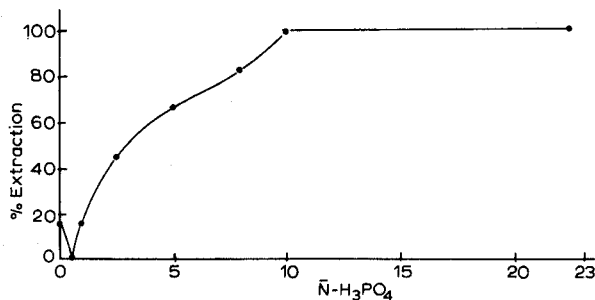


Abb. 2. Abhängigkeit der prozentuellen Extraktion des $(\text{UO}_2)_3(\text{PO}_4)_2$ von der effektiven Säurenormalität.

In verdünnt vorliegenden Lösungen sind die Phasen noch farblos klar. Im organischen Solvens konnte Uran mit 8-Hydroxychinolin oder Chinalizarin nachgewiesen werden. Milligrammengen Uran rufen zunächst eine Gelbfärbung der wässrigen Phase hervor, die mit fortschreitender Extraktion geringer wird, sowie eine leichte Trübung beider Phasen, die aber beim Verdünnen wieder verschwindet. Nur Chloroform zeigte hinsichtlich des Phosphatniederschlages eine transferierende Wirkung, gelöstes Amin ist bedeutungslos.

Über die Verwendung von 2,4-Dinitrophenol (DNP) bei Extraktionen

DNP ist als Neutralisationsindikator im Zusammenhang mit Extraktionsvorgängen des Urans gut verwendbar, da sein Umschlag nahe dem Neutralbereich erfolgt. Viele Extraktionen finden im sauren Medium statt, welches später neutrali-

siert werden muss, um das Metall einer spektralphotometrischen Messung zugänglich zu machen.

Wir konnten zeigen, dass DNP nicht absorbiert und somit durch sein Vorhandensein die Extinktionsmessungen in keiner Weise beeinflusst.

ZUSAMMENFASSUNG

Tertiäre aromatische Amine zeigen gegenüber Uran(VI) ein recht unterschiedliches Extraktionsverhalten. Im Neutralbereich haben alle ein mehr oder minder grosses Extraktionsvermögen. In saurer Lösung ergeben sich teils nicht vermessbare Trübungen, teils gut durchführbare Extraktionen. Je weiter im Amin der Stickstoff vom Kern entfernt, oder je verzweigter die Kette ist, umso besser werden die Ergebnisse. Von 21 untersuchten Aminen extrahierte DMAMI, gelöst in Chloroform, am besten.

SUMMARY

Tertiary aromatic amines behave in different ways in the extraction of uranium(VI). In neutral media all the amines tested show more or less high extractabilities. In acidic media, turbidities are obtained in some cases, and reasonable extractions in other cases. The more distant the nitrogen from the amine nucleus, or the more ramified the chain, the better is the extraction. Out of 21 amines examined, 3-(dimethylamino)-methylindole in chloroform proved to be the best extracting agent.

RÉSUMÉ

Les amines aromatiques tertiaires, utilisées pour l'extraction de l'uranium, présentent un comportement tout à fait différent suivant le milieu. En solution neutre, toutes ces amines ont un pouvoir d'extraction plus ou moins élevé. Par contre, en milieu acide, on observe dans certains cas des troubles non mesurables et dans d'autres cas des extractions convenables. On constate que plus l'azote de l'amine est éloigné du noyau, ou plus la chaîne est ramifiée, meilleurs sont les résultats. Parmi les 21 amines examinées, la solution de 3-(diméthylamino)-méthylindole dans le chloroforme constitue le meilleur réactif d'extraction.

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EXTRACTION OF PLATINUM METALS BY HIGH-MOLECULAR-WEIGHT AMINES. RHODIUM(III) SYSTEMS

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In recent work, the authors developed spectrophotometric methods for the determination of palladium¹ and platinum² by the extraction of the chlorostannous complexes with high-molecular-weight amines (HMWA). In the present work a study of rhodium(III) systems, rhodium(III)-tin(II) chlorocomplexes and rhodium(III)-hydrochloric acid was undertaken. The results of the investigations on these systems are reported below.

EXPERIMENTAL

Apparatus

A Hilger Uvispek Spectrophotometer SP 700 was used.

Reagents

Rhodium solution. A 0.01% (w/v) solution was prepared by dissolving the required amount of "specpure" ammonium chlororhodite $(\text{NH}_4)_3\text{RhCl}_6 \cdot 1.5\text{H}_2\text{O}$ (Johnson and Matthey Ltd.) in 1 M hydrochloric acid. An additional standard was prepared by fusing finely divided rhodium metal with potassium pyrosulphate in a silica crucible until all the metal was brought into solution and dissolving the melt in 1 M hydrochloric acid.

Tin(II) chloride solution. Tin(II) chloride dihydrate (23 g) was dissolved in 100 ml of 2.5 M hydrochloric acid.

Tri-n-octylamine. A 0.2 M solution in thiophene-free benzene was used without additional purification.

All other chemicals were of AnalaR Grade.

RHODIUM(III)-TIN(II) CHLOROCOMPLEXES

Formation of rhodium(III)-tin(II) chlorocomplexes and extraction by tri-n-octylamine

Hydrochloric acid solutions of rhodium(III) develop a reddish colour when heated with tin(II) chloride³. YOUNG *et al.*⁴, in an investigation of chlorocomplexes formed by five platinum metals, identified the dark-red solution produced on the interaction of rhodium(III) with tin(II) chloride as being due to a tetravalent anion $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_2)_4]^{4-}$. A second complex species, yellow in colour, in addition to the red species is obtained, if the solution containing the red complex is diluted with water.

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Conditions for the formation of both are indicated below.

Formation of the red species. In the present work, the procedure of MAYNES AND MCBRYDE⁵ was followed for the formation of the red species. Samples containing rhodium(III) in a solution 1.4 M in hydrochloric acid and 0.3 M in tin(II) chloride were heated for 1 h in a bath of boiling water and diluted to 50 ml with 2 M hydrochloric acid. The colour of the solution before and after dilution was distinctly red and showed an absorption maximum at 470 nm.

Investigations on the extractability of the complex were carried out. The red coloured complex was transferred to a separatory funnel, 5 ml of 0.2 M tri-*n*-octylamine in benzene were added, the system was shaken on a mechanical shaker for 2 min and the phases were allowed to separate. The aqueous phase was colourless and no rhodium could be detected, indicating quantitative extraction into the amine phase. One surprising feature, however, was observed. The amine phase was yellow in colour, indicating that the red coloured species existing in the aqueous phase was not extracted in the same form as present before extraction in the aqueous phase. Further confirmation of this was observed by examining the absorption spectrum of the yellow amine extract which did not resemble the absorption spectrum obtained by MAYNES AND MCBRYDE⁵ for the red species. In the latter the maximum absorption occurred at 470 nm. All attempts to extract the red species into the amine phase as the red coloured species failed.

Formation of the yellow species. Studies were carried out on the red species obtained when rhodium(III) and tin(II) were heated together in 1.4 M hydrochloric acid and subsequently diluted. It was found that conversion from the red to the yellow species occurred when the hydrochloric acid concentration fell below 0.4 M. Formed in this way, the yellow form attained optical constancy very slowly. The absorption spectrum of this solution showed a maximum around 415 nm.

When attempts were made to extract the yellow species into HMWA, turbidity and precipitation of the tin salt occurred which resulted in no separation of the two phases. An attempt was then made to obtain the yellow species directly in aqueous phase, instead of by dilution of the red species. Rhodium(III) and tin(II) were heated together on a boiling water bath for 1 h in hydrochloric acid solutions of different concentrations (1.4–11.6 M). With hydrochloric acid concentrations in the range 1.4–6 M, the colour was distinctly red, but, in hydrochloric acid concentrations in the range 7–11.6 M, the colour was yellow. The colour was more pronounced, the more concentrated the hydrochloric acid, maximum colour intensity being obtained in concentrated hydrochloric acid. As the yellow species has not previously been used for the determination of rhodium, and it would appear to possess one analytical advantage at least over the red species, *viz.*, greater sensitivity, its extractability into HMWA was investigated, the following procedure being used for the formation of the yellow species.

Procedure. Transfer a suitable aliquot of rhodium(III) solution (20–40 μ g), contained in a small volume of 0.1–0.5 ml to a 100-ml beaker. Add 7 ml of concentrated hydrochloric acid and 1 ml of tin(II) chloride solution and cover the beaker with a cover glass. Place the beaker in a boiling water bath for 1 h and dilute with water to 50 ml.

Extractability of the yellow species. The yellow coloured solution obtained by the above procedure was transferred to a separatory funnel and 5 ml of 0.2 M tri-*n*-

octylamine in benzene added. The system was shaken for 2 min and the phases were allowed to separate. The colourless aqueous phase was tested for rhodium, but no trace was ever found, indicating quantitative extraction of the complex. The amine phase was filtered into a 10-ml flask and the volume made up to 10 ml with benzene. A second extraction was found to be unnecessary. An amine blank was extracted similarly. The absorption spectrum measured against the amine blank (Fig. 1) showed a definite absorption maximum at 415 nm. The spectrum is identical to that obtained by transformation of the red species, discussed earlier.

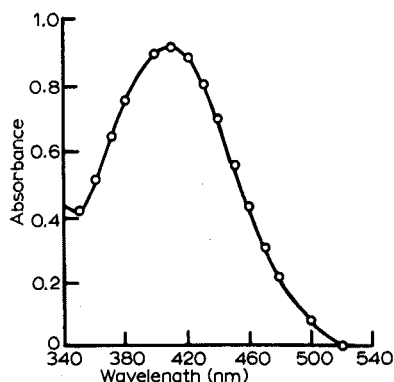


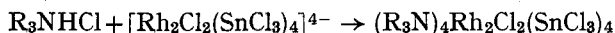
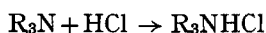
Fig. 1. The absorption spectrum of rhodium(III)-tin(II) chlorocomplex extracted by 0.2 *M* tri-*n*-octylamine in benzene.

Discussion

In the study of the extractability and absorption spectra of the two rhodium-tin chlorocomplex species, several factors of importance emerged. The red species was not extractable into amine as the red species, changing colour to yellow on extraction. The absorption spectrum of the yellow amine phase extracted from the red species formed in aqueous solution in no way resembled that of the red species, but was identical with the absorption spectra of the yellow species in aqueous phase. Further, the red species changed its colour to yellow in aqueous phase on dilution with water. The red species has been reported to be anionic⁴.

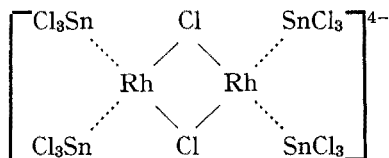
The yellow species obtained by dilution of the red species was not extractable into the organic amine phase, owing to the low acid concentration in the aqueous phase. Instead, the yellow species was obtained directly by the interaction of rhodium(III) and tin(II) in presence of concentrated hydrochloric acid. This was found to be extractable into the amine phase, and its spectrum revealed its identity to (i) the yellow species obtained from the red species by dilution with water, and (ii) the yellow species obtained on extraction of the red species.

YOUNG, GILLARD AND WILKINSON⁴ isolated a salt of the anionic tin chlorocomplex of rhodium. This anionic complex has been formulated as $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$ and hence the overall extraction may be represented by the following equations:

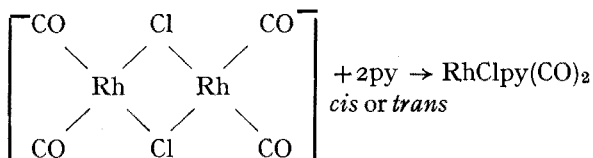


It is somewhat difficult to propose actual structures, but the situation might be represented in the following way:

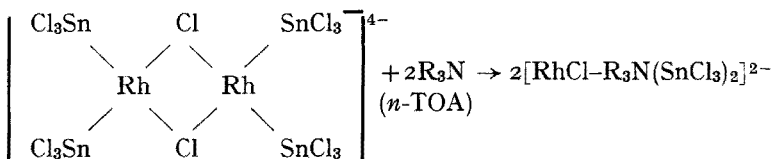
The structure of the red species has the form⁴:



The structure of the yellow species is more difficult to envisage. However, examples are known which are somewhat similar and may give a lead. The carbonyl chloride or a corresponding bridged olefin complex such as that of norbornadiene, can be cleaved by ligands such as amines to planar rhodium complexes as follows:



Thus it is possible that, on treating the red species in the present work with HMWA, a cleavage of the red compound occurs in the following way,



giving the yellow solution. Further, being negatively charged, it is extracted into HMWA in the usual way. When the yellow species is formed in aqueous solution, the species first formed may be represented as $2[\text{RhCl} \cdot \text{H}_2\text{O}(\text{SnCl}_3)_2]^{2-}$. This will still be yellow in colour and possesses negative charge. On treatment with amine it is suggested that water is replaced by the stronger amine ligand giving rise to $2[\text{RhCl} \cdot \text{R}_3\text{N}(\text{SnCl}_3)_2]^-$ as before, which is then extracted into the HMWA to give the same result as that obtained on extracting the red species with HMWA as described above.

RHODIUM(III)-HYDROCHLORIC ACID SYSTEMS

Extractability of the rhodium(III)-hydrochloric acid system

A study of the extractability of rhodium(III) from solutions of differing hydrochloric acid concentrations with liquid anion exchangers was undertaken. Equal volumes of rhodium(III) in the aqueous phase were shaken with 0.2 M tri-*n*-octylamine in a 25-ml flask for 2 min on a mechanical shaker. The two phases were allowed to separate and suitable aliquots of each phase were used to determine the amount of rhodium distributed between organic and aqueous phases. In preliminary experiments, rhodium in the aqueous phase was determined by the tin(II) chloride method^{3,6}. The red product obtained in this reaction between rhodium and tin(II) chloride gave reproducible results for large amounts of rhodium, but was unsatisfactory for the

determination of smaller amounts. The yellow coloured species produced by transformation of the red species on dilution with water was also examined analytically, but did not give an optically stable solution. However, the procedure based on the extraction of the yellow species into tri-*n*-octylamine in benzene, as outlined above, was found to be very satisfactory. Reproducible results were obtained. The extracted species produced an optically stable solution which maintained its stability for more than a week. The sensitivity of the method was also increased about 20-fold. The extent of extraction of rhodium as a function of the hydrochloric acid concentration in the range 0.1–11.6 *M* was then examined; 500 μg of rhodium(III) was extracted with 0.2 *M* tri-*n*-octylamine in benzene. The extraction curve exhibited a maximum of 84.8% extraction at 0.1 *M* hydrochloric acid concentrations, but rhodium(III) was not quantitatively extracted into the organic amine phase at any acid concentration; only traces (1.2–1.7%) of rhodium were extracted from an aqueous phase 2–3 *M* in hydrochloric acid and there was no extraction at acidities above 4 *M*. This behaviour of rhodium(III) in extractability does not indicate the absence of an anionic chloro-complex of rhodium, rather it conforms to a common characteristic of trivalent transitional metals which form trivalent complex anions.

Extractability of platinum(IV) and palladium(II) from hydrochloric acid solutions

The extractability of platinum and palladium as a function of hydrochloric acid in the range 0.1–11.6 *M* was examined in the same manner as for rhodium. In the case of platinum, maximum extraction occurred at lower hydrochloric acid concentrations (Fig. 2). For palladium, the percentage extraction with tri-*n*-octylamine in benzene was essentially 100% in the hydrochloric acid concentration range of 0.1–6 *M*, and decreased gradually to about 50% in concentrated hydrochloric acid.

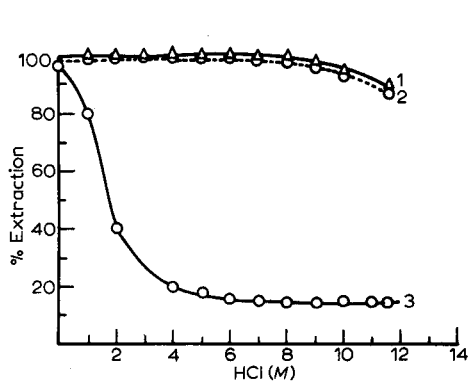


Fig. 2. The extraction of platinum(IV) from hydrochloric acid solutions by various amines in benzene. 1. Tri-*n*-octylamine; 2. tri-*n*-hexylamine; 3. primene 81-R.

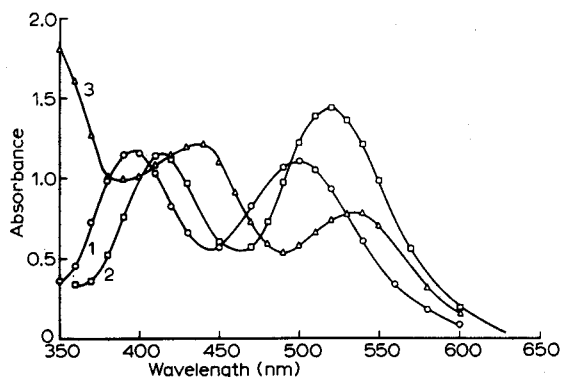


Fig. 3. Comparison of the absorption spectra of rhodium(III) (1) in 0.1 *M* HCl, (2) in concentrated HCl and (3) extracted from 0.1 *M* HCl by tri-*n*-octylamine in benzene.

Identification of the absorbing rhodium(III) species

The absorption spectra of aqueous solutions containing the same amounts of rhodium(III) are shown in Fig. 3.

It will be observed that in hydrochloric acid media, the spectra (curves 1 and 2)

are almost identical (maxima 500–520 and 400–410 nm), with very slight shifts in the positions of the absorption peaks, *e.g.*, the peak at 400 nm in curve 1 is shifted to 410 nm in curve 2. The slight shifts are undoubtedly due to the change in acid concentration. The absorption spectra of the hexachlorocomplex of rhodium has been examined by JØRGENSEN⁷, who showed that bands at 518 and 412 nm are characteristic of the $[\text{RhCl}_6]^{3-}$ species. The identical spectra in 0.1 *M* and 11.6 *M* hydrochloric acid suggest, therefore, one absorbing species. For the amine-extracted species (Fig. 3, curve 3), two absorption peaks are again obtained, at 530 nm and 440 nm, which would appear to indicate that, while there may be a solvent effect, the spectrum is not due to any different absorbing species.

Separation of rhodium from platinum and palladium

The results of the extraction experiments showed that, while platinum and palladium are readily extracted into the organic amine phase by tertiary amines from a very wide range of hydrochloric acid concentrations, rhodium is extracted into the amine phase only from very low acid concentrations. This difference in extractability provides a basis for the separation of rhodium from platinum and palladium in which the chlorocomplexes of palladium and platinum are quantitatively extracted into the amine phase, while rhodium is left unextracted in the aqueous phase.

Investigations showed that the following procedure was satisfactory.

Procedure. Take the mixture of the three metals in a hydrochloric acid solution with a concentration in the range 3.5–6.5 *M*. Shake for 2 min with an equal volume of 0.2 *M* tri-*n*-octylamine in benzene on a mechanical shaker. Allow the phases to separate and draw off a suitable aliquot of the aqueous phase. Determine the rhodium present in this aliquot spectrophotometrically by the procedure for the yellow rhodium-chloro-tin species outlined above, as follows.

Determination of rhodium. Transfer the aliquot to a 100-ml beaker and treat with 7 ml of concentrated hydrochloric acid and 1 ml of tin(II) chloride solution. Cover the beaker with a cover glass to avoid excessive loss of acid and heat on a boiling water bath for 1 h. Dilute the yellow solution obtained (maximum colour development requires 1 h) to 50 ml with water and extract with 5 ml of 0.2 *M* tri-*n*-octylamine in benzene by shaking the two-phase system in a 100-ml separatory funnel for 2 min.

Separate the extracted yellow species from the aqueous phase and measure the

TABLE I
ANALYSIS OF "UNKNOWN" SAMPLES

No.	Rhodium (μg)		Error (μg)	Other elements present (μg)
	Present	Found		
1	200	200	0	—
2	0	0	0	Pd, 200; Pt, 200
3	200	202	+2	Pt, 200
4	200	200.5	+0.5	Pt, 200
5	200	201	+1	Pd, 200
6	200	198	-2	Pd, 200; Pt, 200
7	300	303	+3	Pd, 300; Pt, 300
8	500	500	0	Pd, 500; Pt, 500
9	100	100.5	+0.5	Pd, 100
10	250	250	0	Pt, 250

optical density at 415 nm. Determine the amount of rhodium present from a standard calibration curve prepared by the same procedure with varying amounts of rhodium. The calibration graph obeyed Beer's law over the range 0–8 p.p.m. of rhodium.

Results. As a check on the method, the "unknowns" shown in Table I were analysed.

*Interferences*². The following cations and anions cause no interference in the determination of rhodium: osmium(IV), ruthenium(IV), indium(IV), cobalt(II), nickel(II), iron(III), sulphate, nitrate and perchlorate.

SUMMARY

The complexes formed by rhodium(III) and tin(II), and by rhodium(III) in hydrochloric acid solutions and their extractability by tri-*n*-octylamine have been studied. Hydrochloric acid solutions of rhodium(III) developed a red colour when heated with tin(II) chloride, but a yellow species was obtained by dilution of solutions of the red complex with water. By heating rhodium(III) with tin(II) in 7–11.6 *M* hydrochloric acid, the yellow species was obtained directly in aqueous solution. A procedure was developed for the extraction of the yellow complex from aqueous solution with tri-*n*-octylamine. A mechanism for the extraction of both species is proposed. The extractabilities of the Rh(III)–HCl, Pt(IV)–HCl and Pd(II)–HCl systems by tri-*n*-octylamine depend on the hydrochloric acid concentration; rhodium could be separated from platinum and palladium leading to a sensitive, reproducible analytical method for the determination of rhodium by means of the extracted yellow complex in tri-*n*-octylamine.

RÉSUMÉ

Dans un travail récent les auteurs ont développé des méthodes spectrophotométriques pour le dosage du palladium et du platine par extraction des complexes chlorostanneux avec des amines à poids moléculaire élevé. Ils examinent maintenant les systèmes chlorocomplexes de rhodium(III) et d'étain(II), et rhodium(III)–acide chlorhydrique. Les résultats de ces recherches sont donnés.

ZUSAMMENFASSUNG

Die in salzsauren Lösungen gebildeten Komplexe von Rhodium(III) und Zinn(II) und von Rhodium(III) alleine und ihre Extrahierbarkeit durch Tri-*n*-octylamin wurden untersucht. Salzsaure Lösungen von Rhodium(III) entwickeln eine rote Farbe, wenn sie mit Zinn(II)-chlorid erhitzt werden; beim Verdünnen dieser Lösungen mit Wasser entsteht eine gelbe Farbe. Beim Erhitzen von Rhodium(III) mit Zinn(II) in 7–11.6 *M* Salzsäure erhält man die gelbe Farbe direkt in wässriger Lösung. Es wurde ein Verfahren entwickelt, um den gelben Komplex aus der wässrigen Lösung mit Tri-*n*-octylamin zu extrahieren. Ein Mechanismus für die Extraktion beider Spezies wird vorgeschlagen. Die Extrahierbarkeit hängt von der Salzsäurekonzentration ab. Es ist möglich, Rhodium neben Platin und Palladium empfindlich und reproduzierbar zu bestimmen durch Extraktion des gelb gefärbten Komplexes mit Tri-*n*-octylamin.

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VOLATILE CHELATES OF THE ALKALI METALS

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The volatility of complexes of transition metals with ligands such as acetylacetone has been successfully exploited by various workers, in particular SIEVERS¹, in the separation and identification of these metals by gas chromatography; the complexes exhibited the greatest volatility when the ligand contained fluorine atoms, as in the case of tri- and hexafluoroacetylacetone. The possibility of carrying out similar separations of alkali metal chelates was first investigated by BELCHER *et al.*² who studied the sublimation behaviour of the alkali metal derivatives of tri- and hexafluoroacetylacetones, acetoacetanilides, ethyl-*o*-benzoylbenzoate and *o*-hydroxyacetophenone. These studies were later extended and it was shown that the alkali metal chelates of trifluoroacetylacetone, hexafluoroacetylacetone, dipivaloylmethane and trifluoroacetyl-pivaloylmethane had suitable properties of volatility and apparent thermal stability for gas-chromatographic purposes³. However, in no case could separations of the alkali metal chelates be achieved by gas chromatography. In work described below, the reasons for these failures were studied by means of mass spectrometry. The preparation of new volatile alkali metal chelates and their gas-chromatographic behaviour were also investigated.

EXPERIMENTAL

Preparation of alkali metal chelates

The derivatives of lithium, sodium and potassium were prepared by adding an equimolar quantity of the diketone to an aqueous solution of the alkali metal hydroxide. The alkali metal chelate was extracted with ethyl acetate or ether and the extract dried. The solvents were removed by evaporation and the residue was purified by sublimation where possible. The rubidium and caesium derivatives were prepared in a similar manner from their carbonates at 70°.

In addition to the alkali metal chelates mentioned in the introduction, the alkali metal derivatives of the following β -diketones were prepared:

1,1,1,2,2-Pentafluoro-6,6-dimethylheptan-3,5-dione (pentafluoropropanoyl-pivaloylmethane; PPM).

1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyloctan-4,6-dione (heptafluorobutanoyl-pivaloylmethane, HPM).

The abbreviations refer to the enolate ion used in the formation of the metal complex.

Instrumentation

The mass spectra were recorded before and after sublimation, with an A.E.I. MS9 mass spectrometer. The infrared spectra were recorded before and after sublimation, with a Perkin-Elmer Model 21 infrared spectrophotometer. The gas chromatographic behaviour was studied with a Pye Series 104 gas chromatograph fitted with a flame ionisation detector.

RESULTS

Mass spectrometry

All the alkali metal chelates studied were sufficiently volatile to permit the recording of their mass spectra at temperatures of about 200° when a direct insertion probe was used. A typical mass spectrum is shown in Fig. 1. It can be seen that in addition to peaks arising from the expected 1:1 complex, there are various peaks at

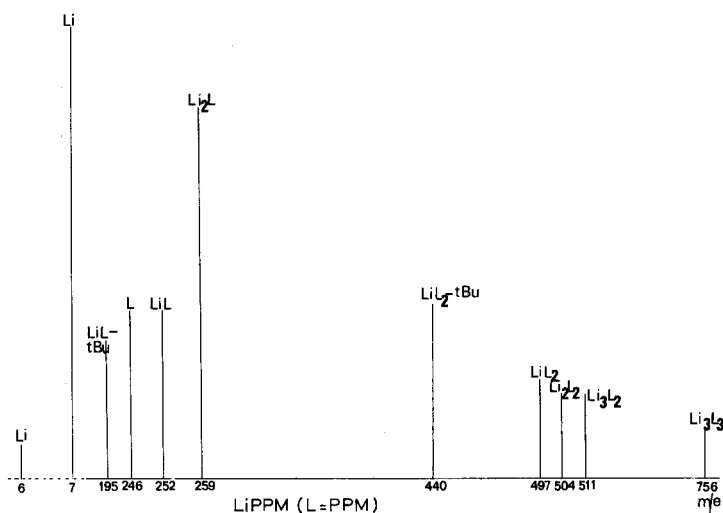


Fig. 1. Mass spectrum of the lithium chelate of pentafluoropropanoypivaloymethane (L=PPM).

higher m/e values corresponding to polymeric ions containing at least three alkali metal atoms. It is not possible to decide whether these structures exist in the alkali metal chelate lattice or whether they are formed in the evaporation and ionisation processes. An ion of particular interest has the formula M_2L^+ (where M is an alkali metal and L is the enolate ion of the β -diketone ligand). In this ion, the second alkali metal atom does not replace a hydrogen atom in the ligand but must be held by secondary forces. Some of the difficulties encountered in the chromatography of alkali metal chelates are probably due to this polymerisation, but the mass spectra showed a further complication.

There appeared to be a ready exchange of alkali metals between chelates. Thus, for example, after a sample of a lithium chelate had been admitted to the mass spectrometer, the spectrum recorded, and the sample removed, the subsequent introduction of a sample of a sodium chelate led to a composite spectrum with peaks arising

from both chelates and from polymeric ions containing the two metals. When a potassium chelate was then introduced, the spectrum showed peaks corresponding to ions in which all three metals were present. Figure 2 shows the spectrum of the sodium chelate of heptafluorobutanoylpivaloylmethane which had been introduced into the mass spectrometer source after an examination of the lithium and potassium chelates of the same ligand. This ready exchange of alkali metal atoms was found to occur with all the alkali metal complexes of the β -diketones used. The exchange reactions obviously take place on metal surfaces within the mass spectrometer and similar effects may be expected to occur on metal surfaces in any gas-chromatographic apparatus. Clean mass spectra could be obtained only by scavenging the ion source with a high pressure of the parent diketone before the recording of the mass spectrum of each alkali metal chelate.

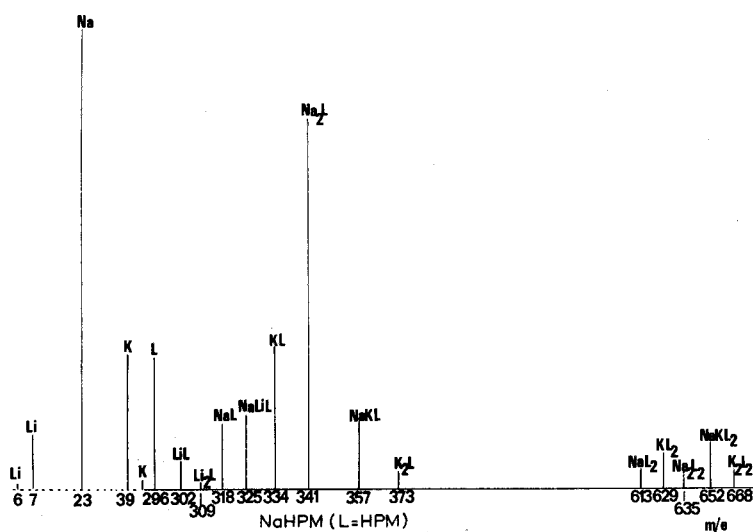


Fig. 2. Mass spectrum of the sodium chelate of heptafluorobutanoylpivaloylmethane after an examination of the lithium and potassium chelates (L = HPM).

Integrated ion-current technique

The application of the integrated ion-current technique to the determination of submicrogram amounts of various metal chelates has been described previously⁴⁻⁷. In spectra of the alkali metal chelates, the alkali metals provided the most abundant ions; these peaks were therefore chosen for the application of the technique to the lithium, sodium and potassium derivatives of pentafluoropropanoylpivaloylmethane and heptafluorobutanoylpivaloylmethane. The reference compound, heptacosafuoro-tri-*n*-butylamine, used in other studies of metal chelates was unsuitable for the present work and was replaced in each case by an inert gas of appropriate mass (Table I). Quantitative measurements were made by taking a solution of the appropriate alkali metal hydroxide, adding the diketone and extracting the chelate into ether. Aliquots of the ethereal solution were introduced directly into the mass spectrometer and the integrated ion-current curve at the appropriate alkali metal ion peak was recorded and measured. Straight line calibration graphs were obtained relating the peak area

to the initial quantity of alkali metal hydroxide. Amounts of alkali metal between 10^{-6} and 10^{-9} g were measured in this way at low instrumental gain; the sensitivities are shown in Table I.

Gas chromatography of alkali metal chelates

While many of the alkali metal derivatives of β -diketones are considered to be ionic in character, when the β -diketone contains fluorine atoms then the corresponding chelates exhibit appreciable covalent character. The two highly fluorinated ligands (PPM and HPM) examined in the present work provided lithium, sodium and potassium chelates which sublimed at lower temperatures than those described previously³, but the rubidium and caesium chelates did not sublime below 210° . The identical nature of the infrared and mass spectra before and after sublimation showed that there was no decomposition of the chelates.

TABLE I

INTEGRATED ION-CURRENT DATA FOR THE ALKALI METAL β -DIKETONATES

Complex	Ion used	Reference gas	Sensitivity (area in $\text{mm}^2/\mu\text{g}$ sample)
Li-PPM	$^6\text{Li}^+$	$^4\text{He}^+$	49
Na-PPM	Na^+	$^{20}\text{Ne}^+$	206
Li-HPM ^a	$^6\text{Li}^+$	$^4\text{He}^+$	48
Na-HPM	Na^+	$^{20}\text{Ne}^+$	220
K-HPM	$^{39}\text{K}^+$	$^{40}\text{Ar}^+$	823

^a The low sensitivity for lithium can be attributed to the use of the ^6Li isotope.

TABLE II

SUBLIMATION TEMPERATURES OF ALKALI METAL COMPLEXES (0.1 torr)

Complex	Temperature of commencement of sublimation ($^{\circ}$)	Temperature of more rapid sublimation ($^{\circ}$)	I.R. and mass spectra before and after sub- limation	Retention time ^a (sec)
Li-PPM	140	150	Identical	31
Na-PPM	160	180	Identical	40
K-PPM	170	190	Identical	85
Li-HPM	130	150	Identical	33
Na-HPM	140	160	Identical	33
K-HPM	170	190	Identical	81

^a On a 3-ft column containing silicone gum on Universal B at 200° .

Complexes of lithium, sodium and potassium with these two ligands were chromatographed separately and in mixtures, on a 3-ft Teflon column (0.125 in int. diam.) containing Universal B support (Phase Separations Ltd.) coated with 2.5% E301 silicone gum at a temperature of 200° (with nitrogen as carrier gas). The results (Table II) show that the retention times are very similar for chelates of the same metal. The retention times for chelates of different metals differ adequately, but when mixtures are chromatographed under the same conditions, the individual peaks are

not resolved. This is considered to result from the exchange reactions taking place at the working temperature, and would indicate that the chromatographic separation of alkali metal complexes of this type is not possible.

SUMMARY

Alkali metal derivatives of pentafluorodimethylheptan-3,5-dione and heptafluorodimethyloctan-4,6-dione are described. Their mass spectra were examined and the integrated ion-current technique was used to determine quantities of the alkali metal chelates down to 10^{-9} g. The volatility and stability of these chelates were studied. Gas-chromatographic separation of mixtures of alkali metal β -diketonates does not appear to be feasible because of undesirable exchange reactions.

RÉSUMÉ

On décrit les dérivés alcalins de la pentafluodiméthylheptane-3,5-dione et de l'heptafluodiméthylheptane-4,6-dione. On examine leur spectre de masse; la technique courant ionique intégré est appliquée au dosage des chélates alcalins en quantités de l'ordre de 10^{-9} g. On examine également la volatilité et la stabilité de ces chélates. Une séparation de β -dicétonates alcalins par chromatographie gazeuse ne semble pas réalisable en raison des réactions secondaires.

ZUSAMMENFASSUNG

Alkalimetallderivate von Pentafluorodimethylheptan-3,5-dion und Heptafluorodimethyloctan-4,6-dion werden beschrieben. Ihre Massenspektren werden geprüft und mit Hilfe der integralen Ionenstromtechnik die Mengen des Alkalimetallchelats bis hinab zu 10^{-9} g bestimmt. Die Flüchtigkeit und Stabilität dieser Chelate wurde untersucht. Eine gaschromatographische Trennung von Mischungen der Alkalimetall- β -diketonate scheint wegen unerwünschter Austauschreaktionen nicht geeignet zu sein.

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UTILISATION DE LA TRILAURYLAMINE EN CHROMATOGRAPHIE DE PARTAGE

PARTIE I. SÉPARATION ANALYTIQUE DU NEPTUNIUM DES SOLUTIONS CONCENTRÉES EN URANIUM

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L'analyse de traces de neptunium-237 dans les solutions concentrées en uranium, solutions souvent polluées par d'autres éléments radioactifs, nécessite la séparation sélective et quantitative du neptunium dont l'activité spécifique est faible. Dans le cas d'un échantillon très radioactif les méthodes basées sur l'extraction par solvants¹⁻³ semblent difficilement applicables. En effet, l'obtention de facteurs de décontamination élevés nécessite plusieurs équilibres successifs. La précision de la méthode est alors diminuée par les inévitables pertes de réactifs au cours de la manipulation. Ceci explique l'application quasi-universelle des méthodes chromatographiques à ces séparations analytiques.

Un premier groupe de méthodes utilise la faible charge et la faible aptitude à la complexation du neptunium(V) NpO_2^+ . Peu chargé, cet ion est élué préférentiellement au plutonium(IV) et à l'uranium(VI) des résines échangeuses de cations par les solutions nitriques diluées^{4,5}. De même, en chromatographie de partage utilisant le phosphate de tributyle, cet ion peu complexé est élué préférentiellement au plutonium et à l'uranium^{6,7}. Cependant le neptunium, recueilli dans les premières fractions de l'élution, est souvent contaminé. Les modifications de l'élution proposées pour remédier à cet inconvénient compliquent sensiblement la manipulation.

Les méthodes du second groupe, basées sur la grande aptitude à la complexation du neptunium(IV) évitent la plupart de ces contaminations. Ainsi on peut séparer le neptunium par chromatographie sur résine échangeuse d'anions en solution nitrique réductrice^{5,8-10}. Toutefois la récupération quantitative du neptunium impose d'opérer à une acidité nitrique élevée. Ceci abaisse les facteurs de séparation neptunium-uranium et neptunium-plutonium (instabilité du plutonium(III) en milieu nitrique). Ici encore les solutions envisagées compliquent les manipulations. La chromatographie de partage utilisant la thénoyltrifluoroacétone (TTA) en solution chlorhydrique réductrice¹¹ évite ces inconvénients. Cependant elle nécessite un changement de milieu avec les échantillons nitriques des installations de traitement des combustibles irradiés et le neptunium obtenu est encore pollué par certains produits de fission (en particulier le zirconium).

Ce document décrit une méthode de séparation par chromatographie de partage utilisant la trilaurylamine (TLA). Les amines tertiaires ont déjà été appliquées à de nombreuses séparations chromatographiques sur colonnes¹²⁻¹⁵. Compte

tenu de ses propriétés extractives^{16,17} (affinité et sélectivité élevées pour les éléments transuraniens tétravalents) la trilaurylamine doit permettre d'utiliser un mode opératoire simple (fixation—lavage—élution). De plus, la possibilité d'opérer avec une solution peu concentrée en anions nitrate, favorise la réduction du plutonium à l'état trivalent, ce qui laisse présager une bonne décontamination sans perte de neptunium.

TECHNIQUES EXPÉRIMENTALES

Préparation de la poudre échangeuse

Nous avons utilisé la trilaurylamine de qualité nucléaire fournie par les Etablissements Rhône-Poulenc. Elle est déposée sur des grains de Kel-F (CFCl—CF₂)_n Voltalef-300-CHR fournis par la Société Ugine. Afin d'assurer un fonctionnement hydrodynamique satisfaisant de la colonne, nous avons dû broyer et tamiser les grains (granulométrie 50–100 mesh) et déposer de l'octanol-2 (5% en poids par rapport au Kel-F) avec la trilaurylamine afin que les grains soient mouillés par les solutions aqueuses. Le Kel-F peut être remplacé par du gel de silice de même granulométrie préalablement traité aux vapeurs de dimethyldichlorosilane.

La préparation de la poudre est la suivante: on introduit dans une fiole à vide 5 g de poudre prétraitée, 0,250 g d'octanol-2, le poids de trilaurylamine correspondant au pourcentage désiré sur les grains et 10 ml de benzène. On évapore le benzène sous vide en agitant et reprend deux fois avec 10 ml de benzène jusqu'à sec.

L'analyse systématique de différents échantillons¹⁸ a prouvé l'homogénéité de la poudre obtenue. Le rendement de l'opération dépend du pourcentage pondéral de la trilaurylamine par rapport au support. Le Tableau I indique le pourcentage réellement déposé sur les grains (% TLA)_f en fonction du pourcentage introduit dans la fiole (% TLA)_i.

TABLEAU I

DÉPÔT DE LA TRILAURYLAMINE SUR LA POUDRE

(% TLA) _i	5	10	20	30	40
(% TLA) _f	5	10	19	27	34

Préparation des colonnes

Nous utilisons des colonnes en verre thermostatées de 4 mm de diamètre munies à la partie inférieure d'un capillaire de platine.

Le mode opératoire est le suivant. Emplir la colonne, bouchée à sa partie inférieure, d'une solution nitrique. Introduire les grains de Kel-F en suspension (éventuellement ajouter une goutte d'octanol-2) et les tasser en exerçant une pression au sommet de la colonne. Quand le remplissage atteint la hauteur désirée, introduire un tampon de laine de verre au dessus des grains et achever le tassement en pressant sur ce tampon. Faire passer 2 ml de solution nitrique 2 N sur la colonne.

Tous les résultats indiqués dans ce document se rapportent à une colonne de 4 mm de diamètre et 40 mm de hauteur contenant 220 mg de Kel-F sec. Le volume interstitiel de la colonne, déterminé à l'aide de ¹⁵⁵Eu est égal à 240 µl.

Le débit de la solution correspond à un flux de $0.1 \text{ ml.cm}^{-2}.\text{min}^{-1}$. Les manipulations sont effectuées à 30° afin d'éviter la cristallisation du nitrate de trilaurylammonium sur les grains.

Radioisotopes utilisés

Le comportement de différents éléments lourds a été étudié par radiométrie- α de ^{237}Np , ^{239}Pu , ^{238}U et ^{231}Pa . Le neptunium et le plutonium ont été purifiés par extraction à la trilaurylamine en solution nitrique^{16,17}, l'uranium par extraction à la trilaurylamine en solution chlorhydrique diluée¹⁹, et le protactinium par extraction à la trilaurylamine en solution chlorhydrique concentrée²⁰. La pureté radiométrique de chacun de ces émetteurs a été vérifiée par spectrométrie- α .

Le comportement du thorium a été étudié par radiométrie- β de ^{234}Th (UX_1) séparé de l'uranium naturel par échange d'anions en solution hydroalcoolique nitrique²¹.

ÉTUDES PRÉLIMINAIRES

Ces études doivent préciser le schéma opératoire suivant :

fixation du neptunium(IV) en solution nitrique réductrice (sulfamate ferreux 0.1 M) (volume V_F) ;

lavage de la colonne avec une solution nitrique réductrice (sulfamate ferreux 0.01 M) afin d'éliminer les éléments faiblement fixés ou retenus dans le volume interstitiel de la colonne et de parfaire la décontamination en plutonium par déplacement chromatographique de l'équilibre plutonium(III)-plutonium(IV) (volume V_L) ;

élution du neptunium décontaminé par une solution sulfo-nitrique (volume V_E).

Nous avons étudié le partage du neptunium entre la poudre échangeuse et les solutions aqueuses nitriques réductrices (sulfamate ferreux 0.1 M) afin de déterminer les conditions optimales de la séparation (choix de la composition de la poudre échangeuse, de l'acidité et de la concentration aqueuse de l'uranium). En raison de difficultés analytiques nous avons dû employer des concentrations de neptunium assez importantes. Les coefficients de partage $P(\text{Np(IV)})$ indiqués ci-dessous correspondent à une concentration du neptunium dans la poudre équivalente à 1 mg de neptunium par g de trilaurylamine. Ils sont rapportés au g de poudre et au ml de solution aqueuse.

Choix de la concentration en trilaurylamine

La Fig. 1 indique les variations du coefficient de partage avec l'acidité aqueuse et le pourcentage pondéral de trilaurylamine fixée sur le Kel-F. Le solvant adsorbé est un mélange de trilaurylamine et d'octanol-2. Si nous calculons les coefficients de partage rapportés au g de trilaurylamine, nous constatons que les valeurs obtenues décroissent lorsque le pourcentage pondéral d'octanol-2 dans le solvant adsorbé croît. Ces variations sont conformes aux propriétés extractives des mélanges ternaires trilaurylamine-octanol-2-dodécane^{16,17}.

Puisque le coefficient de partage croît avec le pourcentage de trilaurylamine adsorbé, nous devons choisir le pourcentage maximum compatible avec un bon mouillage des grains, soit $\text{TLA/Kel-F} = 19\%$.

Choix de la composition de la solution de fixation

La Fig. 2 indique les variations du coefficient de partage du neptunium avec la concentration aqueuse de l'uranium. La décroissance du coefficient de partage lorsque la concentration de l'uranium croît est plus importante pour une acidité aqueuse 4 N que pour une acidité 2 N. Sous réserve d'une récupération quantitative du neptunium, les conditions choisies sont celles qui permettent de décontaminer en

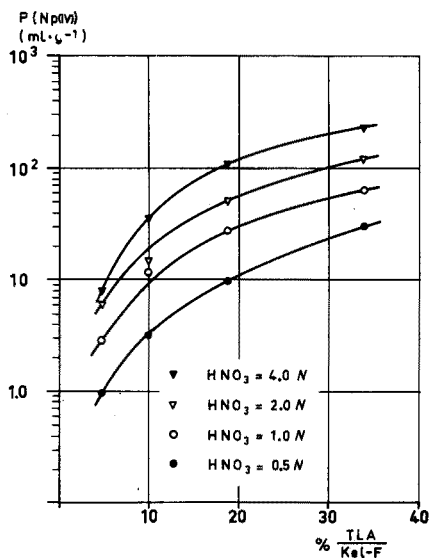


Fig. 1. Variations du coefficient de partage du neptunium avec le pourcentage de TLA adsorbée.

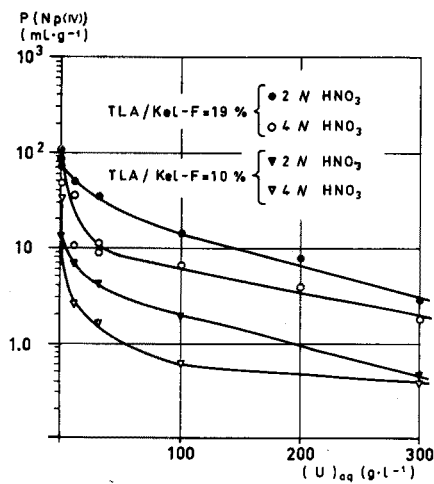


Fig. 2. Variations du coefficient de partage du neptunium avec la concentration de l'uranium.

une seule opération la quantité maximale de cet élément. Pour un échantillon dont le rapport neptunium/uranium est fixé, nous choisissons les conditions qui permettent de passer la plus grande quantité d'uranium à travers la colonne sans fuite de neptunium au bas de celle-ci. Le volume maximal admissible de solution influente étant égal au volume de rétention de la colonne, il faut choisir la composition de cette solution pour que le produit du volume de rétention par la concentration de l'uranium soit maximal.

En première approximation, nous pouvons assimiler le volume de rétention au volume théorique de rétention, lequel est proportionnel au coefficient de partage du neptunium²². Il faut donc opérer dans des conditions telles que le produit du coefficient de partage du neptunium par la concentration de l'uranium dans l'influent soit maximal. Les variations de ce produit sont indiquées sur la Fig. 3. Il apparaît que les conditions optimales pour la fixation correspondent à une solution influente d'acidité 2 N contenant entre 60 et 200 g d'uranium par l.

Choix de la composition de la solution de lavage

Afin de faciliter la réduction du plutonium à l'état trivalent sans abaisser exagérément le coefficient de partage du neptunium, nous avons choisi (Fig. 1) de

laver la colonne avec une solution d'acide nitrique 1 N contenant un réducteur. Lorsque le fer gêne l'analyse radiométrique du neptunium recueilli dans l'éluat, il est possible:

soit de chasser le fer retenu dans le volume interstitiel de la colonne en lavant celle-ci avec un petit volume (0.5 ml) de solution d'acide nitrique 1 N;

soit de remplacer le sel ferreux par l'acide ascorbique à la même molarité.

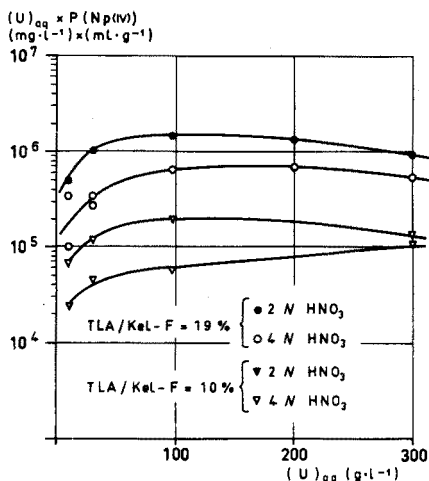


Fig. 3. Choix de la composition de la solution de fixation.

Choix de la solution éluante

A la suite d'essais préliminaires avec des solutions sulfo-nitriques de compositions différentes, nous avons choisi d'éluier le neptunium fixé sur la colonne avec 1 ml de la solution sulfo-nitrique suivante: acide sulfurique 1 N + acide nitrique 0.18 N.

SÉPARATION SUR COLONNES

Ces essais ont été effectués pour déterminer les performances de la séparation dans les conditions opératoires choisies. Dans toute cette étude nous avons utilisé les solutions suivantes:

Fixation: solution A d'acidité nitrique 2 N contenant 95 g.l⁻¹ d'uranium, 0.1 mole.l⁻¹ de sulfamate ferreux et des quantités variables d'éléments lourds (Pa, Th, Np, Pu).

Lavage: solution B d'acidité nitrique 1 N contenant 0.01 mole.l⁻¹ de sulfamate ferreux.

Elution: solution C: mélange sulfo-nitrique de composition indiquée plus haut.

Volume utile de rétention

Ce volume utile ne peut être directement déduit des études précédentes car: le nombre d'étages théoriques équivalent à la colonne est fini,

le coefficient de partage limite du neptunium est sans doute supérieur à celui que nous avons mesuré (concentration du neptunium élevée).

Le Tableau II indique le pourcentage de neptunium recueilli pour différents volumes de solution influente, la colonne étant lavée avec 1 ml de solution B et éluée avec 1 ml de solution C. Ce pourcentage étant obtenu avec une précision de l'ordre de $\pm 5\%$, nous avons vérifié que nous pouvons séparer quantitativement le neptunium contenu dans 10 ml de solution A, influente. Les pertes dans le fixat sont indécélables par spectrométrie- α .

TABLEAU II

VOLUME UTILE DE RÉTENTION

V_F (ml)	0.5	2	5	10
% Np	98	103	104	96

Influence du lavage sur la décontamination en émetteurs- α

Nous avons étudié le comportement de différents éléments lourds susceptibles d'être adsorbés sur la colonne. Compte tenu de la faible affinité des amines tertiaires pour les éléments trivalents en solution nitrique²³ les éléments transplutoniens (américium, curium ..) sont séparés du neptunium. Nous nous sommes limités aux éléments suivants: thorium, protactinium, uranium, plutonium.

Les résultats indiqués sur la Fig. 4 correspondent à 1 ml de solution de fixation,

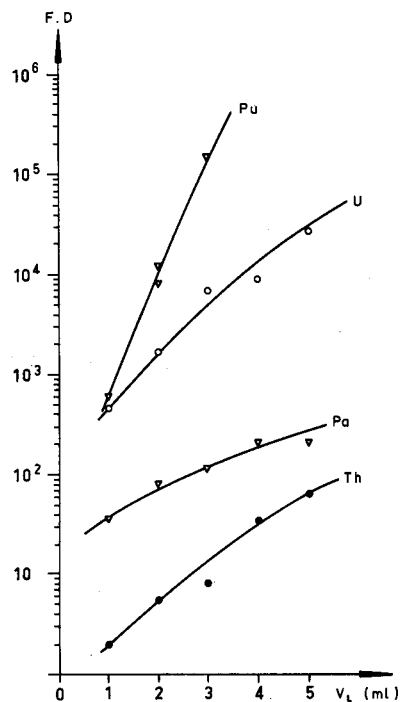


Fig. 4. Variations des facteurs de décontamination avec le volume de lavage ($V_F = 1$ ml).

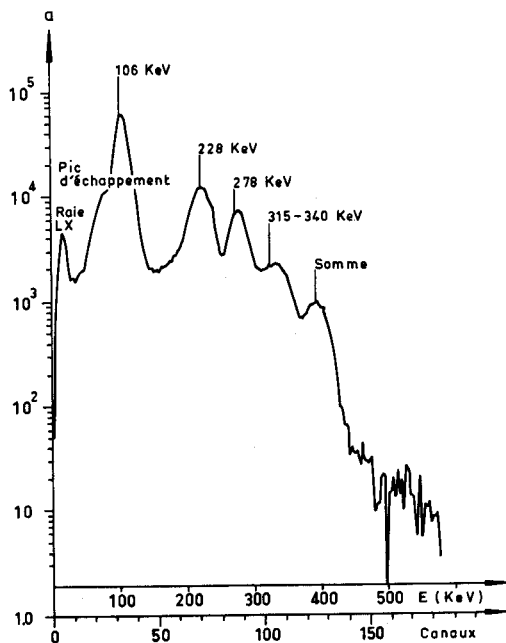


Fig. 5. Spectre- γ du ^{239}Np obtenu.

la colonne étant lavée avec un volume variable de solution B et éluée avec 1 ml de solution C. Le facteur de décontamination (F.D) est égal au rapport de la quantité d'élément contenue dans la solution influente à celle recueillie dans l'éluat.

Remarques. Le facteur de décontamination global obtenu dépend du volume de solution de fixation. Ainsi, le volume de lavage étant maintenu constant et égal à 1 ml, le facteur de décontamination en uranium croît continûment de $5 \cdot 10^2$ à $30 \cdot 10^2$ si le volume de fixation croît de 1 à 4 ml. Le facteur de décontamination en thorium peut être sensiblement amélioré par lavage de la colonne avec 1 ml de solution chlorhydrique 7 N²⁴.

Sélectivité par rapport aux produits de fission. Préparation de ²³⁹Np

Nous avons irradié des pastilles d'uranium naturel et d'uranium appauvri (0.04% ²³⁵U) dans le réacteur ZOE (réacteur EL.1 de Fontenay-aux-Roses) et séparé le neptunium-239 formé dans les échantillons. L'irradiation correspond à $1.8 \cdot 10^{12}$ fissions par g d'uranium, conditions dans lesquelles le rapport de la masse d'uranium à celle de neptunium est supérieur à 10^{10} .

Les spectres- γ des éluats obtenus (Fig. 5) indiquent une bonne sélectivité par rapport aux produits de fission présents dans l'échantillon et montrent que la méthode permet aisément la préparation de neptunium-239 radiométriquement pur.

MODE OPÉRATOIRE

Le mode opératoire décrit ci-dessous est applicable à une colonne contenant 270 mg d'une poudre de composition pondérale 78.5% Kel-F + 5% octanol-2 + 16.5% trilaurylamine. Il suppose que l'échantillon a été ajusté aux concentrations suivantes: acide nitrique 2 N, uranium $< 100 \text{ g.l}^{-1}$, sulfamate ferreux 0.1 M.

Faire passer un volume $V_F = 10$ ml de solution sur la colonne préalablement équilibrée avec une solution nitrique 2 N (le volume V_F est fixé par la concentration du neptunium-237 souhaitée dans l'éluat). Laver la colonne avec un volume V_L de solution 1 N d'acide nitrique contenant 0.01 mole.l⁻¹ de sulfamate ferreux (le volume V_L dépend des facteurs de décontamination souhaités), puis avec 0.5 ml de solution nitrique 1 N. Dans le cas de l'analyse de combustibles nucléaires irradiés, le volume est fixé à $V_L = 3$ ml.

Eluer la colonne avec 1 ml de solution sulfo-nitrique (acide sulfurique 1 N + acide nitrique 0.18 N). Déterminer par radiométrie et spectrométrie- α la concentration du neptunium dans l'éluat.

Nous remercions vivement Monsieur CHANDANSON qui a effectué les irradiations de pastilles d'uranium dans le réacteur ZOE. Les analyses radiométriques ont été effectuées par Monsieur R. POTTIER. Nous avons apprécié la contribution technique de Monsieur R. AYACHE à ce travail.

RÉSUMÉ

L'étude du partage du neptunium(IV) entre la trilaurylamine adsorbée sur poudre de Kel-F et les solutions aqueuses nitriques concentrées en uranium permet de définir les conditions opératoires d'une séparation des traces de neptunium par

chromatographie de partage. La séparation s'effectue par fixation du neptunium d'une solution HNO_3 2 N-Fe(II) 0.1 M-U $\leq 100 \text{ g.l}^{-1}$ sur une colonne de poudre TLA- HNO_3 -Kel-F. Après lavage par une solution réductrice d'acidité nitrique 1 N, le neptunium est élué par une solution sulfo-nitrique. Cette méthode, très sélective par rapport aux produits de fission, à l'uranium et au plutonium a été appliquée à des solutions dans lesquelles $\text{U/Np} > 10^{10}$. Ses limites sont fixées par la sensibilité des méthodes d'analyse du neptunium en solution aqueuse diluée. Elle s'applique aisément à la préparation de ^{239}Np radiométriquement pur.

SUMMARY

The partition of neptunium(IV) between nitric acid-uranyl nitrate solutions and Kel-F powder coated with a trilaurylammonium nitrate solution has been studied in order to determine the optimum operating conditions for separating neptunium from uranium. The reversed-phase partition chromatography was performed by passing a 2 N HNO_3 -0.1 M iron(II) solution containing up to 100 g.l^{-1} of uranium, through a column of TLA- HNO_3 -Kel-F beads. After washing the column with N nitric acid containing iron(II) sulphamate, the neptunium is eluted with a sulfuric acid-nitric acid mixture. The method is very selective for neptunium(IV), and allows a good separation from fission products, plutonium and uranium. It has been applied to solutions in which the weight ratio U/Np is greater than 10^{10} , and to the preparation of radiometrically pure ^{239}Np .

ZUSAMMENFASSUNG

Die Verteilung von Neptunium(IV) zwischen salpetersauren Uranylnitratlösungen und Kel-F-Puder, welches mit Trilauryl-ammoniumnitratlösung benetzt ist wurde untersucht, um die optimalen Arbeitsbedingungen für die Trennung des Neptuniums von Uran zu bestimmen. Zur Trennung wurde eine Lösung aus 2 N HNO_3 , die 0.1 M Eisen(II) und bis zu 100 g.l^{-1} Uran enthielt über eine Kolonne mit Kel-F gegeben, das mit salpetersäurem TLA beladen war. Nach dem Waschen der Kolonne mit 1 N Salpetersäure, die Eisen(II)-Sulphamat enthielt, wurde das Neptunium mit einem Gemisch aus Schwefelsäure und Salpetersäure eluiert. Die Methode ist für Neptunium(IV) sehr selektiv und erlaubt eine gute Trennung von den Spaltprodukten Plutonium und Uran. Das Verfahren wurde für Lösungen angewendet in dem das Gewichtsverhältnis U/Np grösser als 10^{10} ist und zur Herstellung von radiochemisch reinem ^{239}Np .

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UTILISATION DE LA TRILAURYLAMINE EN CHROMATOGRAPHIE DE PARTAGE

PARTIE II. SÉPARATION ANALYTIQUE CONJOINTE DU NEPTUNIUM ET DU PLUTONIUM DE L'URANIUM

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Il est souvent intéressant de déterminer l'activité résiduelle α due aux isotopes du neptunium (^{237}Np) et du plutonium ($^{238}\text{Pu} + ^{239}\text{Pu} + ^{240}\text{Pu}$) dans l'uranium recyclé provenant des usines de traitement des combustibles irradiés. Outre les isotopes de l'uranium naturel, ce produit peut contenir les isotopes ^{232}U , ^{233}U et ^{236}U , ainsi que les descendants des quatre familles radioactives. A cet effet nous avons étudié la séparation analytique conjointe de ces deux éléments par chromatographie de partage utilisant la trilaurylamine (TLA).

Nous avons déjà appliqué cette méthode à la séparation analytique du neptunium dans l'uranium¹. Dans ce document nous nous limiterons à indiquer et à justifier les modifications apportées au mode opératoire afin d'obtenir une récupération quantitative du plutonium avec le neptunium.

TECHNIQUES EXPÉRIMENTALES

Les préparations de la poudre de Kel-F imprégnée de trilaurylamine (TLA/Kel-F = 19%) et des colonnes sont identiques à celles indiquées dans la publication citée en référence 1. Tous les résultats consignés dans ce document se rapportent à des colonnes de diamètre 4 mm et hauteur 40 mm fonctionnant à 30° sous un flux 1 ml.cm⁻².min⁻¹.

Les essais préliminaires sur des solutions synthétiques ont été effectués avec des solutions de ^{237}Np et ^{239}Pu purifiées par extraction à la trilaurylamine en milieu nitrique^{2,3}.

Les éluats sont analysés par comptage- α et spectrométrie- α dans une chambre à grille.

ÉTUDE PRÉLIMINAIRE

Choix de la composition de la solution influente

La récupération conjointe du neptunium et du plutonium exige que ces deux éléments soient extraits simultanément à l'état tétravalent. Compte tenu des potentiels normaux apparents des couples neptunium(IV)–neptunium(V) et plutonium(III)–plutonium(IV), ces deux éléments ne peuvent coexister quantitativement à l'état tétravalent en solution nitrique diluée.

Cependant la présence de trilaurylamine, complexant énergétique des espèces tétravalentes, déplace suffisamment les équilibres d'oxydo-réduction pour permettre l'extraction partielle simultanée du neptunium(IV) et du plutonium(IV). Ainsi un procédé d'extraction a été proposé², le potentiel d'oxydo-réduction en solution aqueuse étant fixé à l'aide d'un mélange de sels ferreux et ferrique.

Nous inspirant de ce procédé nous avons étudié l'influence du rapport molaire des espèces ferriques et ferreuses dans la solution influente sur la fixation du plutonium sur la colonne au cours des manipulations suivantes: passage sur la colonne de 2.8 ml de solution influente de composition (U) = 71.5 g.l⁻¹, (NO₃⁻) = 3.55 M, (H⁺) = 1.4 N, (Fe(III)) = 0.5 M, (Fe(II)) variable, ²³⁷Np et ²³⁹Pu en traces; lavage de la colonne avec 3 ml de solution nitrique 1 N (décontamination en uranium); élution de la colonne avec 1 ml de solution sulfo-nitrique (1 N acide sulfurique + 0.18 N acide nitrique).

La Fig. 1 indique le pourcentage de plutonium recueilli dans l'éluat. Dans tous les cas la récupération du neptunium est quantitative, les pertes étant indécélabables par spectrométrie- α . Lorsque le rapport de la concentration du sel ferrique à celle du sel ferreux est supérieure à 90 la méthode proposée permet de recueillir tout le neptunium et tout le plutonium contenus dans 200 mg d'uranium.

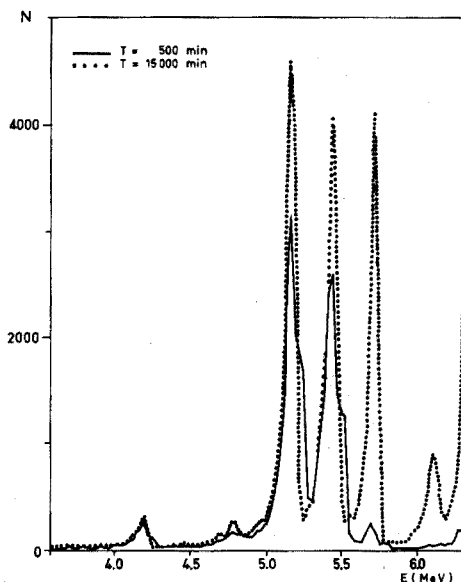
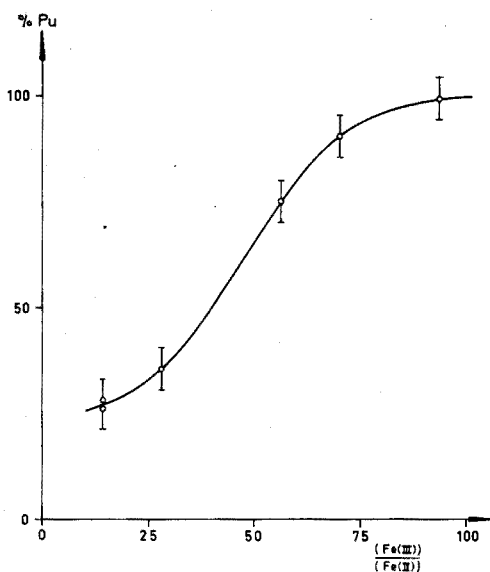


Fig. 1. Influence du rapport Fe(III)/Fe(II) sur la fixation du plutonium.

Fig. 2. Spectre- α d'un éluat après simple lavage nitrique.

Insuffisance du lavage nitrique

Nous avons effectué des séparations sur une solution d'uranium recyclé selon le mode opératoire précédent, le rapport de la concentration du sel ferrique à celle du sel ferreux étant égal à 93.5. Les résultats obtenus par analyse radiométrique- α de l'éluat sont peu reproductibles. Celui-ci contient de nombreux émetteurs- α d'énergies différentes de celles correspondant aux isotopes de l'uranium, du neptunium et du plutonium. Les intensités relatives de ces émissions varient avec le temps T écoulé

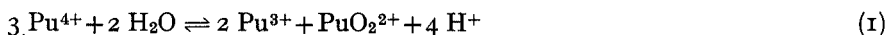
entre la séparation et la mesure radiométrique. La Fig. 2 donne un exemple de spectre obtenu.

Logiquement, ces émissions proviennent des produits de filiation de l'uranium. En effet, comme nous l'avons indiqué¹ la méthode utilisée élimine peu le thorium (le facteur de décontamination est voisin de 10). Les isotopes du thorium présents dans l'éluat produisent par filiation des émetteurs- α parasites.

Lavage chlorhydrique

Compte tenu de la grande instabilité des complexes chlorhydriques du thorium, il est possible d'éluer sélectivement cet élément de la colonne en lavant cette dernière par 1 ml de solution chlorhydrique concentrée (7 N) après le lavage à l'acide nitrique 1 N. Avec ce mode opératoire nous constatons la disparition des émissions- α parasites. Cependant la récupération du plutonium dans l'éluat n'est plus quantitative, celle du neptunium le restant.

Les coefficients de partage du neptunium tétravalent étant inférieurs à ceux du plutonium(IV)³, la fuite du plutonium au cours du lavage chlorhydrique résulte nécessairement d'un changement de valence de cet élément. En l'absence d'oxydant et de réducteur énergiques il est logique d'attribuer ce fait à la dismutation du plutonium(IV) selon la réaction:



En effet, au début du lavage chlorhydrique la solution interstitielle est une solution moyennement acide (diffusion de la solution nitrique 1 N dans la solution chlorhydrique 7 N). La présence de triaurylamine, complexant énergétique des transuraniens hexavalents en solution chlorhydrique⁴, favorise la dismutation. Celle-ci provoque une fuite de plutonium(III) au pied de la colonne.

Une augmentation de l'acidité de la solution interstitielle avant l'introduction des anions chlorure doit déplacer l'équilibre de dismutation en faveur du plutonium(IV). Pour cela il suffit de réacidifier la colonne avec 0.5 ml de solution nitrique 7 N avant le lavage chlorhydrique. Nous avons vérifié que nous obtenons ainsi quantitativement le neptunium et le plutonium dans l'éluat, les pertes étant inférieures à 1%.

MODE OPÉRATOIRE ET RÉSULTATS

Mode opératoire

Fixation. Prendre 2 ml d'échantillon nitrique 2 N contenant 200 mg d'uranium; ajouter 15 μl d'une solution de sulfamate ferreux 1 M, puis 0.7 ml d'une solution de nitrate ferrique 2 M; passer cette solution à travers la colonne.

Lavage et élution. Laver successivement la colonne avec 3 ml de solution nitrique 1 N, puis 0.5 ml de solution nitrique 7 N, puis 1 ml de solution chlorhydrique 7 N. Eluer la colonne avec 1 ml de solution sulfurique 1 N et nitrique 0.18 N.

Radiométrie. Comptage et spectrométrie- α sous un angle solide 2π d'une aliquote de l'éluat. La contribution des isotopes ²³³U et ²³⁴U dans le domaine d'énergie voisin de 4.8 MeV (énergies de ²³⁷Np) est calculée à partir de l'activité due à l'isotope ²³⁸U. A cet effet le spectre radiométrique- α dû aux différents isotopes de l'uranium est déterminé après extraction de l'uranium par l'acétate d'éthyle⁵.

Résultats

Nous avons effectué une série de neuf séparations et analyses sur une même solution d'uranium recyclé. La Fig. 3 donne un exemple de spectre obtenu par radiométrie d'un éluat. Le Tableau I indique l'activité- α due aux isotopes du neptunium et du plutonium (a) mesurée sur une aliquote de l'éluat (50 μ l).

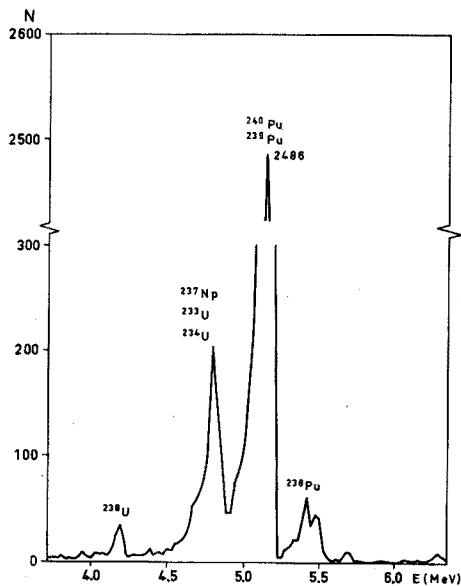


Fig. 3. Spectre- α d'un éluat après lavages nitrique et chlorhydrique.

TABLEAU I

RÉSULTATS DES ANALYSES SUCCESSIVES D'UN ÉCHANTILLON

Analyse	1	2	3	4	5	6	7	8	9
a (c/min)	10.26	10.44	9.80	9.48	9.82	9.77	9.31	9.89	9.42

Il résulte de ces mesures que nous avons pu déterminer l'activité (a) égale à 1960 désintégrations- α par min et par g d'uranium avec un écart quadratique moyen égal à 3.9%. Ceci correspond à un intervalle de confiance à 95% égal à 9%.

Les analyses radiométriques ont été effectuées par Monsieur R. POTTIER. Nous avons apprécié la contribution technique de Monsieur R. AYACHE à cette étude.

RÉSUMÉ

Une séparation analytique conjointe du neptunium et du plutonium dans l'uranium est proposée. Elle utilise le partage de ces deux éléments entre une colonne de Kel-F imprégné de TLA et les solutions aqueuses nitriques. La séparation s'effectue par fixation du neptunium et du plutonium tétravalents d'une solution nitrique,

l'ajustage des valences étant effectué avec un mélange d'ions ferreux et ferriques. Après lavage par des solutions nitriques, puis chlorhydrique, la colonne est éluée par une solution sulfo-nitrique. Le neptunium et le plutonium sont analysés par radiométrie- α de l'éluat.

SUMMARY

A simultaneous separation of neptunium and plutonium from uranium is proposed, involving the partition of these two elements between a column of Kel-F coated with a trilaurylammonium nitrate solution and aqueous nitrate solutions. Neptunium(IV) and plutonium(IV) are fixed from a nitrate solution containing iron(II)-iron(III) to adjust the valence states. After washing the column with nitric and hydrochloric solutions, the neptunium and plutonium are eluted with a sulfuric-nitric acid mixture, and the analysis is completed by α -radiometry.

ZUSAMMENFASSUNG

Eine gleichzeitige Abtrennung des Neptuniums und Plutoniums vom Uran wird vorgeschlagen. Dabei wird die Verteilung dieser zwei Elemente zwischen einer Kolonne aus Kel-F, welche mit Trilaurylammoniumnitratlösung benetzt ist und einer wässrigen salpetersauren Lösung herangezogen. Neptunium(IV) und Plutonium(IV) werden aus der salpetersauren Lösung aufgenommen. Sie enthält zur Stabilisierung der Wertigkeit Eisen(II) und Eisen(III) in einem bestimmten Mengenverhältnis. Nach dem Waschen der Kolonne mit salpeter- und chlorwasserstoffsaurer Lösungen wird das Neptunium und Plutonium mit einer Mischung aus Schwefel- und Salpetersäure eluiert und die Analyse α -radiometrisch abgeschlossen.

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Anal. Chim. Acta, 45 (1969) 321-325

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF COBALT IN VARIOUS MATERIALS WITH ZINC DIETHYLDITHIOCARBAMATE

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Nitroso-R-salt has been widely used as a reagent for the photometric determination of microgram amounts of cobalt¹. However, the reagent reacts with many metals, and cobalt must be separated previously. The separation of cobalt by extraction as the diethyldithiocarbamate has been reported as a useful method for the analysis of uranium^{2,3}, but this technique is tedious and time-consuming because the organic reagent added must be decomposed before the photometry.

It is known that cobalt cannot be displaced from its diethyldithiocarbamate by mercury(II) or copper(II) ion, while other metal chelates are affected by these ions⁴. The exceptional property of this cobalt chelate has been successfully used for the determination of radioactive cobalt in reactor coolant water⁵. The property has also been applied to the photometric determination of cobalt by measuring the absorbance of cobalt diethyldithiocarbamate extracted in the organic solvent^{6,7}. Interfering metals extracted with cobalt were removed by washing the organic phase with mercury(II) salt solution; however, mercury(II) diethyldithiocarbamate remains in the organic phase, and absorbs at 325 nm, where the cobalt chelate has a large absorption maximum. For this reason, a wavelength of 367 or 650 nm was chosen for the absorbance measurement. The method has not been used in practice owing to its poor sensitivity.

In the present investigation, cobalt was extracted with a benzene solution of zinc diethyldithiocarbamate; the organic phase was washed with potassium cyanide solution, copper sulfate solution, and again with potassium cyanide solution, and the cobalt was determined by measuring the absorbance of the extract at 325 nm.

EXPERIMENTAL

Apparatus

Absorbance measurements were made in 1-cm quartz cells with a Shimadzu QR-50 spectrophotometer. The pH was measured with a Horiba M-5 glass electrode pH meter. An Iwaki Model KM shaker and 200-ml Squibb-type separatory funnels were used.

Reagents

Standard cobalt solution. Prepare a stock solution of cobalt by dissolving

accurately weighed amounts (100 mg) of pure cobalt metal in 6 *N* hydrochloric acid by heating. Prepare working solutions by suitable dilution.

Zinc diethyldithiocarbamate in benzene. Use a 1% (w/v) solution. Prepare the zinc chelate as follows. Dissolve ca. 15 g of sodium diethyldithiocarbamate in 700 ml of water and filter the solution to remove traces of insoluble residues. Stir and precipitate zinc diethyldithiocarbamate by slow addition of 15 g of zinc sulfate in 100 ml of water. Filter the precipitate, wash with dilute ammonia solution and water, air-dry and store in a desiccator.

Other reagent solutions. Prepare solutions of copper sulfate heptahydrate (2%), potassium cyanide (1%), and other reagents from reagent-grade chemicals.

Procedure

Use a slightly acidic sample solution, containing 1–15 μg of cobalt. Add 20 ml of 50% (w/v) ammonium citrate solution and adjust the pH to 9.0–9.5 with dilute ammonia solution. Transfer the solution to a separatory funnel, add exactly 10 ml of the benzene solution of zinc diethyldithiocarbamate and shake for 20 min. Remove the aqueous phase. Wash the organic phase with 25 ml of 1% potassium cyanide solution by shaking for 2 min, and then with 25 ml of water. Add 25 ml of 2% copper sulfate solution to the organic phase, shake for 2 min, remove the aqueous phase and wash again with 25 ml of 1% potassium cyanide solution. Transfer the benzene phase to an Erlenmeyer flask containing 1 g of anhydrous sodium sulfate and swirl to remove droplets of water. Measure the absorbance of the organic phase at 325 nm, against a reagent blank as the reference.

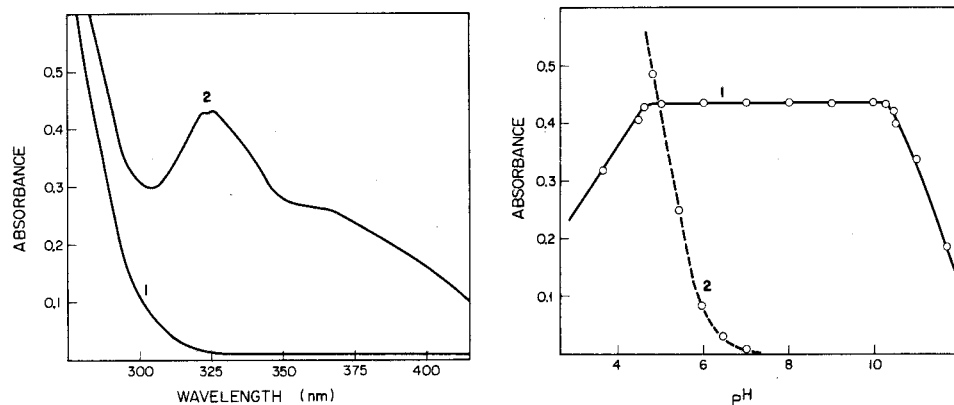


Fig. 1. Absorption spectra for benzene extract of cobalt diethyldithiocarbamate. (1) Reagent blank against benzene; (2) 10 μg of Co against reagent blank. Volume of organic phase: 10 ml.

Fig. 2. Effect of pH on extraction of cobalt and iron diethyldithiocarbamate. (1) 10 μg of Co; (2) 5 mg of Fe. Volume of organic phase: 10 ml.

The calibration curve was prepared by taking 1–20 μg of cobalt and extracting as mentioned above. A linear relationship was obtained up to 15 μg of cobalt. The absorbance per μg of cobalt at 325 nm was found to be 0.0438 in a 1-cm cell. The absorption spectra are shown in Fig. 1.

RESULTS AND DISCUSSION

Reagent

Sodium diethyldithiocarbamate is generally used as an analytical reagent because of its solubility in water. However, many metals form chelates with the reagent in aqueous phase and interfere with the formation of cobalt chelate. The interferences are reduced by the use of a solution of zinc diethyldithiocarbamate in benzene, which does not react with iron and uranium in the recommended pH range. Moreover, zinc diethyldithiocarbamate can be easily removed by washing with potassium cyanide solution. On the other hand, cobalt forms the diethyldithiocarbamate with the reagent quantitatively, and is extracted in benzene. The cobalt chelate in benzene is not affected by washing with cyanide solution.

Less than 100 μg of cobalt can be quantitatively extracted into benzene by shaking with 10 ml of a 0.1% zinc diethyldithiocarbamate solution, but 10 ml of a 1% solution is recommended, in order to reduce interferences.

Masking agent

When the sample solution contains hydrolyzable metals, it is necessary to add a proper masking agent. Ammonium citrate was examined; the addition of 20 ml of 50% (w/v) ammonium citrate solution was effective in masking up to 20 mmole of metals, and the citrate did not interfere with the extraction of cobalt.

Effect of pH

Cobalt diethyldithiocarbamate can be quantitatively extracted in the pH range of 5–10 (Fig. 2). This pH range is almost unaffected by the presence of metals in the solution to be analyzed and the addition of citrate. In the procedure, a pH range of 9.0–9.5 was used because below pH 9, the extraction of iron increased, and prevented extraction of cobalt.

Shaking time

If cobalt diethyldithiocarbamate is formed in the aqueous phase, the chelate

TABLE I
IONS WITHOUT EFFECT ON COBALT DETERMINATION

<i>Ion</i>	<i>Amount (mg)</i>	<i>Cobalt found^a (μg)</i>	<i>Ion</i>	<i>Amount (mg)</i>	<i>Cobalt found^a (μg)</i>
Bi ³⁺	0.5	10.2	Cr ³⁺	200	10.0
Pb ²⁺	0.5	10.2	Mg ²⁺	200	10.0
Ag ⁺	1	10.0	Th ⁴⁺	200	9.9
Cd ²⁺	1	10.0	U ⁶⁺	200	9.8
Cu ²⁺	1	10.0	V ⁵⁺	200	9.8
Mn ²⁺	1	10.5	W ⁶⁺	200	10.0
Mo ⁶⁺	1	10.1	Zr ⁴⁺	200	10.0
Ni ²⁺	1	10.0	F ⁻	5	9.9
Zn ²⁺	1	10.0	PO ₄ ³⁻	20	10.0
Fe ³⁺	5	10.0	NO ₃ ⁻	1000	10.0
Sc ³⁺	5	10.1	SO ₄ ²⁻	1000	10.0
Al ³⁺	200	9.8	Cl ⁻	1000	10.0
Be ²⁺	200	9.8	ClO ₄ ⁻	1000	10.0

^a Each solution contained 10.0 μg of cobalt.

TABLE II
PREPARATION OF SAMPLE SOLUTION

Sample	Amount ^a (g)	Preparation
U metal	5	Dissolve in 20 ml of hydrochloric acid and 20 ml of potassium chlorate solution (4%) by heating.
U ₃ O ₈	5	Dissolve in 10 ml of hot nitric acid (1 + 1) containing a few drops of hydrofluoric acid. Evaporate to dryness, and dissolve the residue in 1 ml of perchloric acid. Evaporate nearly to dryness.
Al metal	0.5	Dissolve in 10 ml of hot concentrated hydrochloric acid.
Be metal	2	Treat with 10 ml of hydrochloric acid (1 + 1) carefully. Add 10 ml of hydrochloric acid and dissolve completely by heating. After dissolution, add 75 ml of ammonium citrate solution (50%).
Zircaloy	2	Dissolve in 20 ml of sulfuric acid and 20 ml of ammonium sulfate (50%) by heating. Add 1 ml of nitric acid, when free sulfur appears.

^a Maximum permissible amount.

TABLE III
RECOVERY OF ADDED COBALT

Material	Amount (g)	Cobalt (μg)			Recovery
		Added	Found		
U [UO ₂ (NO ₃) ₂ ·6H ₂ O]	5	0	1.2	1.3	—
		2.0	3.2	3.1	1.9
		5.0	6.1	6.2	4.9
		10.0	11.5	11.4	10.2
Th [Th(NO ₃) ₄ ·6H ₂ O]	5	0	0.8	0.8	—
		1.0	1.9	1.9	1.1
		2.0	2.9	2.9	2.1
		5.0	5.9	5.8	5.1
10.0	11.0	11.0	10.2		
Al [99.99% metal]	0.5	0	0.1	0.1	—
		1.0	1.1	1.1	1.0
		2.0	2.1	2.1	2.0
		5.0	5.1	5.0	5.0
10.0	10.1	10.3	10.1		
Be [BeSO ₄ ·4H ₂ O]	2	0	1.9	2.0	—
		1.0	3.2	3.0	1.1
		2.0	4.1	4.0	2.1
		5.0	7.0	7.0	5.0
10.0	12.0	12.4	10.2		
Zircaloy (Sn 1.4% Cr 0.2 Fe 0.1)	2	0	1.6	1.7	—
		1.0	2.6	2.7	1.0
		2.0	3.6	3.7	2.0
		5.0	6.5	6.5	4.8
10.0	11.6	11.7	10.0		

is extracted rapidly by benzene. However, if a benzene solution of zinc diethyldithiocarbamate is used, the extraction is slow and it is necessary to shake vigorously for about 15 min to extract cobalt quantitatively.

Interferences

In the experiments performed, the metals extracted by benzene are bismuth, cadmium, copper, indium, lead, mercury, molybdenum, nickel, palladium, platinum, and silver. These metals in large amounts prevent the extraction of cobalt. If the amounts of metals extracted are a few milligrams, they can be removed as follows. Cadmium, copper, nickel, and silver are easily removed with zinc by washing with potassium cyanide solution. The other metals mentioned, with the exception of mercury, palladium, and platinum, can be replaced by copper by shaking the extract with copper sulfate solution, and the copper chelate formed in the benzene phase can be removed by washing with potassium cyanide. Absorbances of 1 μg each of mercury, palladium and platinum, were equivalent to 0.25, 0.01, and 0.1 μg of cobalt, respectively. Table I lists the noninterfering ions tested, but these amounts do not represent the maximum permissible amounts.

Applications

The procedure was applied to the determination of cobalt in uranium, thorium, aluminum, beryllium, and zircaloy. The preparations of the sample solutions are summarized in Table II. Table III shows the recoveries of cobalt added to uranium, thorium, aluminum, beryllium, and zircaloy. The results obtained on some samples by the procedure are given in Table IV.

TABLE IV
DETERMINATION OF COBALT IN SOME SAMPLES

Material	Co (p.p.m.)		Standard deviation
	Present	Found	
U ₃ O ₈			
JAERI-U ₁ , No. 3	2.6	2.4, 2.6, 2.6	
No. 4	1.5	1.2, 1.4, 1.7	
JAERI-U ₂	8.7	8.5	0.20 (n = 10)
ThO ₂			
NBL-26, No. 5	2	2.2	0.14 (n = 10)
No. 6	1	1.1, 1.2	
Be metal			
NBL-85	4	4.0	0.13 (n = 5)
NBL-86	22	22, 23, 23	
Zircaloy	50	50, 50	

SUMMARY

Cobalt is extracted with a benzene solution of zinc diethyldithiocarbamate. The excess of reagent and metals such as copper and nickel extracted with cobalt are

removed by washing the organic phase with potassium cyanide solution. Other metals such as bismuth and lead are replaced by copper by shaking the organic phase with copper sulfate solution; the copper in the organic phase is removed by potassium cyanide solution. The absorbance of cobalt diethyldithiocarbamate in the organic phase is then measured at 325 nm. Down to $1 \mu\text{g}$ of cobalt in a few grams of uranium, thorium, aluminum, beryllium and zircaloy can be readily determined.

RÉSUMÉ

Le cobalt est extrait avec une solution benzénique de diéthylthiocarbamate. L'excès de réactif, ainsi que les métaux tels que cuivre et nickel extraits avec le cobalt sont éliminés par lavage de la phase organique à l'aide d'une solution de cyanure de potassium. D'autres métaux, tels que bismuth et plomb sont déplacés par le cuivre en traitant la phase organique avec une solution de sulfate de cuivre; le cuivre dans la phase organique est ensuite éliminé par le cyanure de potassium. L'absorption du diéthylthiocarbamate de cobalt dans la phase organique est mesurée à 325 nm. On peut ainsi doser facilement jusqu'à $1 \mu\text{g}$ de cobalt dans l'uranium, le thorium, l'aluminium, le béryllium et le zircaloy.

ZUSAMMENFASSUNG

Kobalt wird mit einer benzolischen Lösung von Zinkdiäthylthiocarbamat extrahiert. Ein Überschuss des Reagenzes und solcher Metalle wie Kupfer und Nickel, welche mit dem Kobalt extrahiert werden, werden durch Waschen der organischen Phase mit Kaliumcyanidlösung reextrahiert. Andere Metalle, wie Wismut oder Blei werden durch Schütteln der organischen Phase mit Kupfersulfatlösung entfernt. Durch Absorption des Kobaltdiäthylthiocarbamats in der organischen Phase bei 325 nm können bis hinab zu $1 \mu\text{g}$ Kobalt in Uran, Thorium, Aluminium, Beryllium und Zircaloy schnell bestimmt werden.

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SHORT COMMUNICATIONS

Analyse spectrographique des impuretés dans les échantillons d'oxydes mixtes (U-Pu)O₂ par la méthode de distillation avec entraîneur dans l'arc électrique

L'utilisation de la méthode de distillation fractionnée dans l'arc électrique¹ pour l'analyse des combustibles nucléaires (U-Pu)O₂ pose un problème d'étalonnage. En effet, si la méthode donne de bons résultats pour l'uranium, pour lequel il est relativement facile de constituer une gamme d'étalons, il n'en est pas de même pour le plutonium en raison de la difficulté de fabriquer des étalons (immobilisation de quantités importantes de plutonium, contrôle analytique délicat en raison du travail en boîte à gants).

Par ailleurs, les échantillons mixtes pouvant présenter divers rapports uranium/plutonium, il devrait être nécessaire de constituer autant de systèmes d'étalonnage indépendants. Une étude comparative des deux matrices pures a été effectuée en vue de déterminer s'il était possible de choisir des conditions expérimentales telles qu'on puisse doser facilement les impuretés dans une matrice (U-Pu)O₂ par interpolation entre les systèmes d'étalonnage uranium pur et plutonium pur.

Techniques expérimentales

Appareillage et conditions d'excitation.

- Spectrographe : Jarrell-Ash (Europe) Mark IV type Ebert 3.40 m.
Source : Arc continu, intensité stabilisée de 12 A.
Dispersion : Réseau 1200 traits/mm donnant une dispersion de 2.5 Å/mm.
Région spectrale: 2300 à 3500 Å dans le 1er ordre.
Electrodes : Pechiney ongles bleu. Profondeur du cratère: 7.5 mm. Diamètre de la contre-électrode: 3.5 mm.
Fente : 15 μ. Devant la fente est placé un diaphragme et un secteur à 7 échelons.
Emulsion : Kodak SA 1.
Préflambage : 5 sec.
Pose : 40 sec avec l'entraîneur Ga₂O₃; 25 sec avec l'entraîneur AgCl + LiF (4 + 1).

Réalisation des étalons. Prise des spectres. Les produits utilisés sont des oxydes d'uranium et de plutonium calcinés à 900°. Les étalons sont obtenus en y ajoutant des quantités convenables d'oxydes Johnson-Matthey—5 ou 6 éléments par étalon—telles que les teneurs en impuretés varient entre 0 et 1000 p.p.m. L'homogénéisation des mélanges se fait pendant 70 h environ.

Les entraîneurs choisis sont l'oxyde de gallium (2%) pour les éléments courants sauf l'aluminium pour lequel on utilise 5% du mélange AgCl + LiF (4 + 1).

La prise d'essai est de 100 mg; la poudre est fortement tassée dans le cratère de graphite, en ménageant une cheminée centrale. Pour obtenir un tassage efficace, il est nécessaire d'utiliser des pointes de tasseur s'adaptant parfaitement à la densité de l'échantillon, c'est-à-dire de 2.5 mm de hauteur; le cratère peut alors être retourné

et doucement tapoté pour rejeter les fines particules non agglomérées à l'ensemble de la charge qui, sans cela, restent collées sur les bords du cratère et sont responsables d'une sortie du plutonium dans les premières secondes de pose. Toutes ces opérations sont effectuées dans des boîtes à gants sous atmosphère d'azote à faible hygrométrie (teneur en eau inférieure à 50 p.p.m.).

Résultats et discussion

Comparaison uranium-plutonium. Cinq étalons uranium et cinq étalons plutonium ont permis d'obtenir les deux systèmes de droites d'étalonnage extrêmes. Les Figures 1, 2, 3 montrent quelques unes de ces courbes. On remarque qu'elles sont différentes mais parallèles; elles sont distribuées relativement aux deux matrices de manière identique les unes par rapport aux autres.

La détermination des impuretés se fait donc avec une sensibilité indépendante de la matrice, mais avec des limites de détection différentes. Il en résulte qu'il est possible de doser les impuretés contenues dans le plutonium au moyen d'étalons

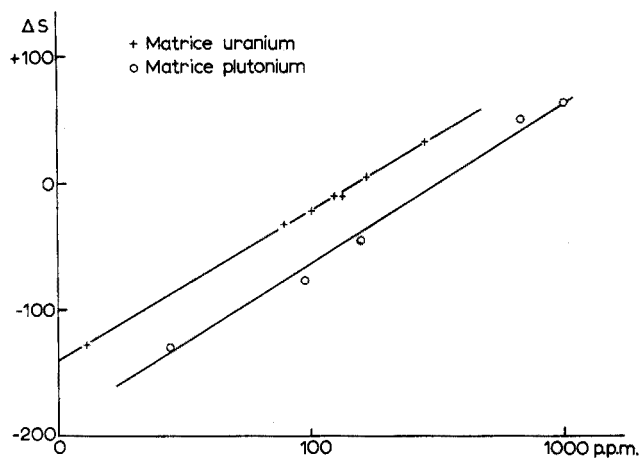


Fig. 1. Courbes d'étalonnage du fer (2599 Å).

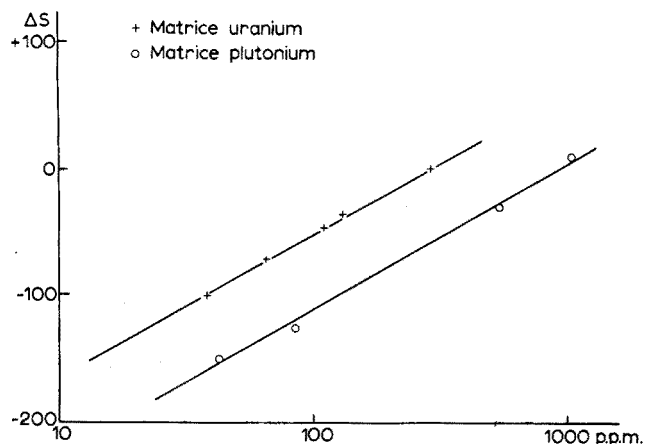


Fig. 2. Courbes d'étalonnage du nickel (3002 Å).

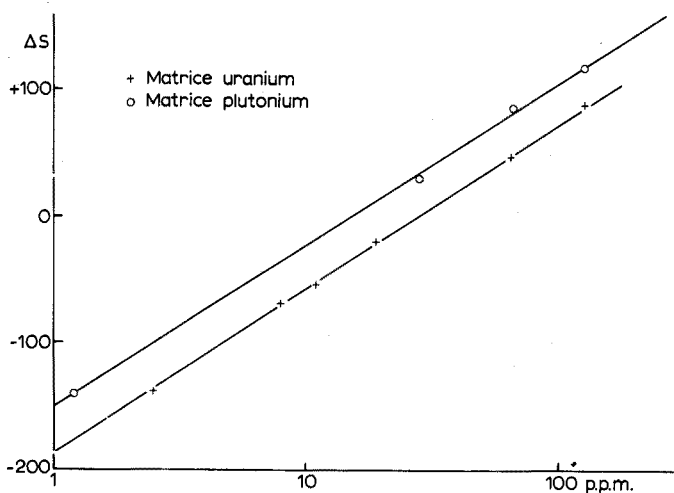


Fig. 3. Courbes d'étalonnage du manganèse (2801 Å).

TABLEAU I

VALEURS DU COEFFICIENT k , RAPPORT DES CONCENTRATIONS PLUTONIUM/URANIUM POUR UNE VALEUR DONNÉE DU FACTEUR ANALYTIQUE

Élément	Fe	Cu	Mn	Ni	Ag	B	Co	Mg	Cr
k	2.5	1.5	0.5	3	1	1.5	3	2.5	7

TABLEAU II

COMPARAISON DES RÉSULTATS THÉORIQUES ET EXPÉRIMENTAUX OBTENUS POUR LES ÉCHANTILLONS MIXTES (U-Pu) O_2

	Fe	Si	Nr	Ni	Al
ΔS oxyde de plutonium	-68	-15	-72	-113	-180 non détectable
ΔS oxyde d'uranium	-24	+124	-16	-36	-17
50% U (ΔS théorique)	-46	+54	-44	-80	-100
50% Pu (ΔS expérimental)	-50	+39	-41	-85	-90
75% U (ΔS théorique)	-35	+90	-28	-58	-56
25% Pu (ΔS expérimental)	-31	+86	-22	-57	-41

uranium; il suffit de multiplier par un facteur k dépendant de l'élément la teneur trouvée au moyen des étalons uranium pour obtenir la valeur de la teneur correspondant à une matrice de plutonium.

Le Tableau I indique quelques valeurs de ces facteurs k obtenus avec l'appareillage et les conditions expérimentales indiquées ci-dessus.

Emission des impuretés dans une matrice mixte (U-Pu) O_2 en fonction du rapport uranium/plutonium. A partir de deux étalons de plutonium pur et d'uranium pur, on a réalisé les deux mélanges suivants: 50% U_3O_8 + 50% PuO_2 et 75% U_3O_8 + 25% PuO_2 . Les résultats densitométriques de quelques uns des éléments courants

—les facteurs analytiques ΔS étant obtenus par la méthode de BRECKPOT²—sont donnés dans le Tableau II. On a mis en évidence, d'une part le ΔS théorique correspondant à une interpolation des résultats trouvés pour l'uranium et le plutonium purs, d'autre part la valeur expérimentale correspondante.

Si l'on tient compte de la précision des déterminations, la similitude des valeurs théoriques et expérimentales montre que l'interpolation est bien réalisable.

On peut alors déterminer, à partir de l'étalonnage uranium pur, le facteur k_e qui donnera la concentration en impuretés dans l'échantillon mixte analysé.

Soit C_p : concentration cherchée en impureté de l'échantillon;

C_U : concentration en impuretés de l'échantillon évaluée à l'aide de l'étalonnage uranium;

C_{Pu} : concentration en impuretés de l'échantillon évaluée à l'aide de l'étalonnage plutonium;

p : concentration en plutonium de l'échantillon;

k : rapport des concentrations en impuretés des matrices plutonium et uranium pures pour un même facteur analytique;

k_e : rapport de la concentration cherchée pour l'échantillon mixte à la concentration obtenue à l'aide de l'étalonnage uranium pour le même facteur analytique.

On a

$$p = \frac{Pu}{U + Pu} \quad , \quad k = \frac{C_{Pu}}{C_U} \quad \text{et} \quad k_e = \frac{C_p}{C_U}$$

d'où

$$\log k = \log C_{Pu} - \log C_U$$

$$\log k_e = \log C_p - \log C_U$$

et

$$\log C_e = \log C_U + p(\log C_{Pu} - \log C_U)$$

soit finalement

$$\log k_e = \log C_U + p \log k - \log C_U$$

ou

$$k_e = k^p \quad \text{avec} \quad 0 \leq p \leq 1.$$

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Neutron activation analysis of high-purity selenium

Part IV. Simultaneous determination of chlorine, bromine and iodine

In previous papers, the determination by neutron activation analysis of bromine¹, tellurium², phosphorus, sulfur and chlorine³ in high-purity selenium has been reported. A simultaneous γ -spectrometric determination of the halogens, chlorine, bromine and iodine seemed interesting. Tracer experiments showed that during the dissolution of selenium in hot concentrated nitric acid, the halogens can be volatilized quantitatively and that *ca.* 99% recovery can be obtained by absorption in ice-cooled silver nitrate solution. After the precipitation of the silver halides, the application of high-resolution γ -spectrometry allows the simultaneous determination of chlorine, bromine and iodine.

Nuclear data

The pertinent nuclear data of selenium, bromine and chlorine as well as possible nuclear interferences were given in previous papers¹⁻³. Table I summarises those nuclear data pertaining to the present investigation.

TABLE I

SOME NUCLEAR DATA OF CHLORINE, BROMINE, IODINE AND SELENIUM⁴

Stable isotope	Activation cross section (barns)	Isotope formed	Half-life	Most important γ -energies (keV) and relative intensities
³⁷ Cl	0.15	³⁸ Cl	37.3 min	1642.0 (100); 2166.8 (70)
⁸¹ Br	1.5	⁸² Br	35.9 h	554.3 (80); 619.0 (50); 698.3 (33); 776.6 (100); 827.8 (30); 1007; 1043.9 (37); 1082; 1317.2 (38); 1474.7 (28); 1650
⁷⁹ Br	1.4	^{80m} Br	4.38 h	37.0 (100)
	4.3	⁸⁰ Br	17.6 m	511.0; 617.0 (100); 665.7 (15); 704.3 (3)
¹²⁷ I	5.6	¹²⁸ I	25.0 m	442.7 (100); 526.3 (9); 743.5 (1)
⁸² Se	0.05	^{83m} Se	70 sec	
	0.004	⁸³ Se	25 m	
	Daughter	⁸³ Br	2.4 h	520.9 (4.5); 529.3 (100); 552.5 (1.5); 648.4 (0.95); 681.0 (0.27)

Chlorine can be readily determined by means of the peaks at 1642.0 and 2166.8 keV for which interferences are unlikely. An important interfering activity in the ⁸²Br measurement appeared to be due to ⁸³Br, daughter of ^{83m}Se. An analysis by scintillation spectrometry can be based on γ -rays of high energy and low abundance but this severely affects the sensitivity of the bromine determination. High-resolution Ge-Li spectrometry, however, allows the simultaneous measurement of ³⁸Cl, ⁸²Br and ¹²⁸I in the presence of ⁸³Br. The intense full energy peak of ⁸²Br at 776.6 keV can be used for the determination of bromine. A measurement based on the 617.0-keV peak of ⁸⁰Br is about 5 times more sensitive for the irradiation conditions used, but the

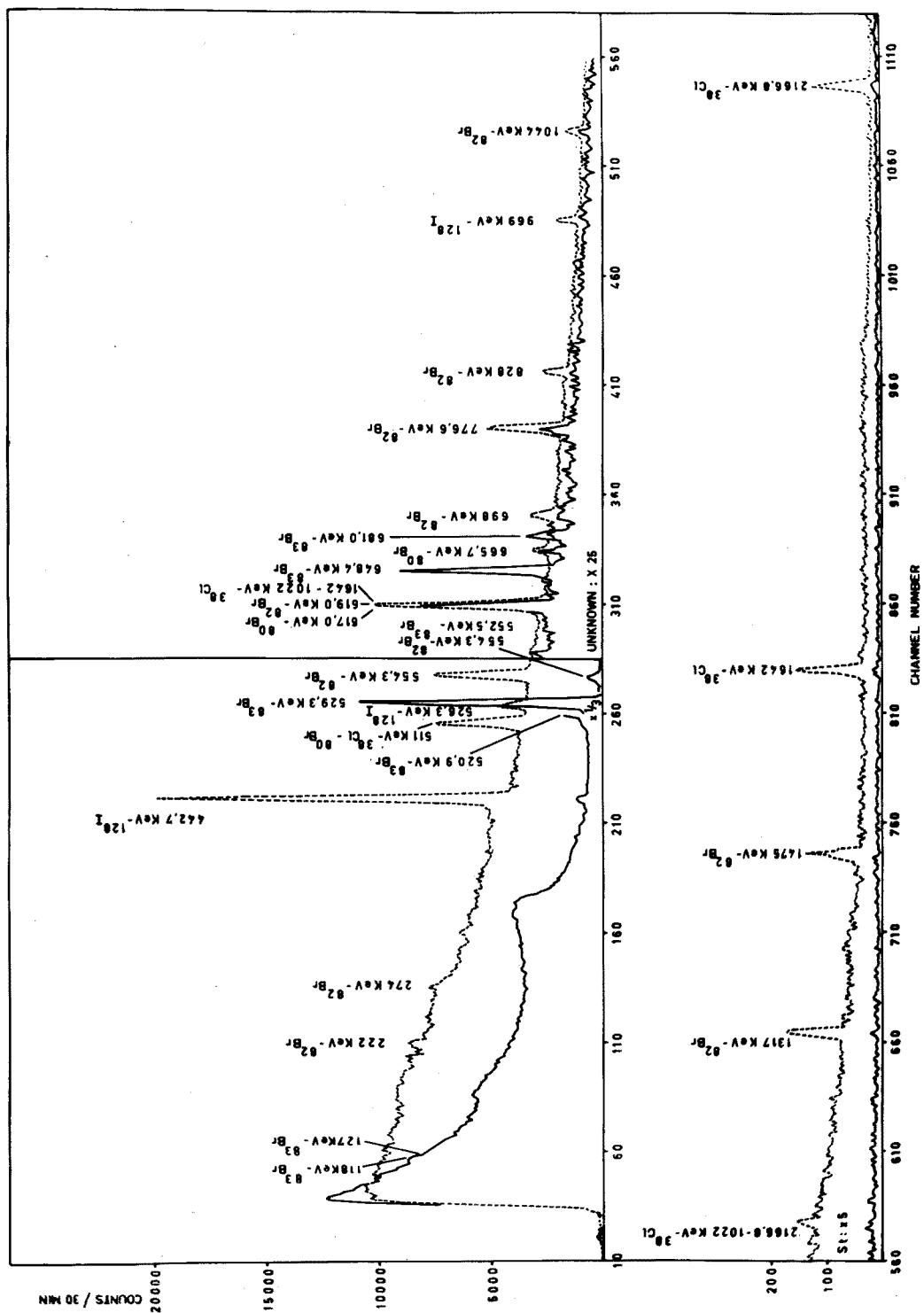


Fig. 1. γ -Spectra of silver halide precipitates separated from an unknown sample (—) and a standard sample (---). The standard sample contains 87.7 μg chlorine, 110 μg bromine and 64.8 μg iodine.

double escape radiation of ^{38}Cl at 1620 keV interferes. Furthermore, a decay correction at this energy can hardly be applied, since it is determined by the half-life of the isotopes $^{80\text{m}}\text{Br}$ (4.38 h) and ^{80}Br (17.6 min). The activity ratio of the two isotopes is unknown and varies during the relatively long measurement (30 min). The analysis of bromine cannot be based on the measurement of the full energy peak at 554.3 keV of ^{82}Br , because the γ -radiation at 552.5 keV of ^{83}Br interferes. For the analysis of iodine, the intense peak at 442.7 keV should be used since the less abundant peak at 526.3 keV is also affected by ^{83}Br radiation.

Irradiation conditions, preparation of standards and chemical procedure

Selenium (2 g) is irradiated together with chlorine, bromine and iodine standards (3.14 mg of ammonium chloride, 2.97 mg of ammonium bromide and 1.70 mg of potassium iodide) during 30 min at a flux of $8 \cdot 10^{10}$ n/cm².sec. After irradiation the sample is etched twice with 4 N nitric acid to remove surface contaminants and transferred to an all-glass distillation apparatus. The selenium is dissolved in 40 ml of 14 N nitric acid and 5 mg of chloride, bromide and iodide carrier is added. During the dissolution, the halogens are volatilised by means of a moderate gas stream of carbon dioxide and collected in 20 ml of 0.015 N silver nitrate and 0.5 N nitric acid. The condenser is heated with an infrared lamp to volatilise condensed iodine. The distillate is filtered on a fritted glass disk and the precipitate washed four times with 0.1 N nitric acid and once with alcohol and ether. Because time is not available to dry and weigh the selenium after the etch, the selenium loss is determined one day after the end of irradiation from the ratio of the ^{75}Se activities present in the nitric acid and in the etching solution.

The mixture of the standards is dissolved in 100 ml of water. To an aliquot of 5 ml is added 1 ml of 0.3 N silver nitrate. The halogens are precipitated in about 2 N nitric acid and separated as described above.

Counting

Figure 1 shows the γ -spectrum of the silver halide precipitate separated from 2 g of selenium which had been irradiated as described above. The precipitate is measured for 30 min with a 42-cm³ coaxial Ge(Li) detector operating at 750 V bias (energy resolution: 4.3 keV for the 1332.4 keV peak of ^{60}Co) coupled to a Tennelec TC 130 preamplifier and TC 200 amplifier used at single integration and differentiation constants of 1.6 μsec , and an Intertechnique CA 13 4096 channel analog-to-digital converter with a BM 96 4096-channel memory.

The count rates under the peaks at 1642.0 and 2166.8 keV, at 776.6 keV and at 442.7 keV are summed respectively for the determination of chlorine, bromine and iodine.

Figure 1 shows also a γ -spectrum of a mixture of chlorine, bromine and iodine standards.

Results and discussion

Results for two selenium samples are listed in Table II. The results for chlorine and bromine are compared with those obtained by NaI(Tl) scintillation γ -spectrometry^{1,3}. The results for bromine were obtained after decay of the chlorine activity¹. The standard deviation on the simultaneous determinations of chlorine, bromine and

TABLE II

DETERMINATION OF CHLORINE, BROMINE AND IODINE IN SELENIUM (p.p.m.)

Sample	Measurement	Chlorine	Bromine	Iodine
I	Ge(Li) Simultaneous determination	0.54	$0.97 \pm 0.2(21\%)$	$0.54 \pm 0.08(15\%)$
		<u>0.59</u>	<u>$1.28 \pm 0.22(17\%)$</u>	<u>$0.68 \pm 0.11(16\%)$</u>
		0.57	1.13	0.61
	NaI(Tl) Previous deter- mination ^{1,3}	$0.66 \pm 0.02(3.0\%)$	$1.07 \pm 0.02(1.9\%)$	
		<u>$0.68 \pm 0.03(4.4\%)$</u>	<u>$0.89 \pm 0.01(1.1\%)$</u>	
		0.67	<u>$1.11 \pm 0.02(1.8\%)$</u>	
		1.02 ± 0.07		
II	Ge(Li) Simultaneous determination	0.51	$2.33 \pm 0.30(13\%)$	$0.84 \pm 0.08(9.5\%)$
		<u>0.36</u>	<u>$2.01 \pm 0.30(15\%)$</u>	<u>$0.68 \pm 0.07(10\%)$</u>
		0.44	2.17	0.76
	NaI(Tl) Previous deter- mination ^{1,3}	$0.40 \pm 0.03(7.5\%)$	$2.20 \pm 0.02(0.9\%)$	
		<u>$0.32 \pm 0.04(13\%)$</u>	<u>$1.95 \pm 0.03(1.5\%)$</u>	
		0.36	<u>$2.05 \pm 0.03(1.5\%)$</u>	
		2.07 ± 0.07		

iodine is almost exclusively due to the counting statistics. Owing to the higher counting efficiency of the NaI(Tl) detector, the reproducibility of those determinations is better.

In the simultaneous determination of the halogens, the standard deviations for chlorine cannot be given owing to the low count rates at 1642.0 and 2166.8 keV (< 100 counts). In the experimental conditions the net count rate due to ³⁸Cl is about the same as the background. According to the conventions of CURRIE⁵ the detection limits (L.D.) for bromine and iodine are respectively 0.6 and 0.14 p.p.m.

Because radiochemically pure halide activities were separated, the detection limits can, however, be reduced if a higher neutron flux is applied. The reduction of the limits for chlorine and bromine is proportional to the increase of the flux. Owing to the presence of the ⁸³Br activity in the halide precipitate, the detection limit of iodine only reduces with the square root of the increase of the neutron flux. For example, an irradiation for 30 min at a neutron flux of 10^{12} n/cm².sec would result in detection limits of 0.05, 0.04 and 0.06 p.p.m. for bromine, iodine and chlorine, respectively.

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A rapid method for the determination of fluorine in silicate rocks and minerals

Fluorine is a difficult element to determine in silicate rocks and minerals, and existing methods are both time-consuming and require special apparatus. This note describes a simple method which the authors have found satisfactory for the analysis of silicates containing moderate or large amounts ($>0.1\%$) of fluorine.

The procedure is based on the application of the colorimetric alizarin fluorine blue method¹. Elements liable to cause interference with this method can be removed by a simple chemical separation, without recourse to the preliminary distillation usually required to separate fluorine from interfering elements in rocks. The first stage, that of fusion and separation of interfering elements, is adapted from the preliminary stages of the Berzelius method, as described by HILLEBRAND *et al.*². The colorimetric method used for the fluorine determination involves the measurement of the purple complex formed between the fluoride ion and the lanthanum chelate of alizarin fluorine blue (3-aminomethylalizarin-N,N-diacetic acid), and advantage has been taken of the availability of a commercial preparation containing the necessary colorimetric reagents together with a pH buffer mixture. Details of the method of analysis are given below.

Reagents

Alizarin fluorine blue reagent. Dissolve 25 g of alizarin fluorine blue lanthanum complex preparation (Hopkin and Williams Ltd, Chadwell Heath, Essex) in a mixture of 150 ml of propan-2-ol and 350 ml of distilled water. Filter before use.

Standard fluoride solution. Dissolve 0.0663 g of sodium fluoride in 1 l of distilled water to give a solution containing 30 μg of fluorine/ml.

Procedure

Weigh out exactly 1 g of powdered rock into a platinum crucible, add six times the sample weight of anhydrous sodium carbonate (A.R. grade), and mix. Cover the crucible and fuse over a Meker burner for 20 min. Digest the fusion cake in 100 ml of hot distilled water, filter through Whatman 41 filter paper, and wash the residue with hot water. Collect the filtrate in a 250-ml beaker. Add approximately 2 g of powdered ammonium carbonate (A.R. grade), digest on a water bath for 30 min, allow to cool, and add another 1 g of ammonium carbonate. Allow to stand for 12 h, and then filter through Whatman 41 filter paper into a 1-l conical flask, washing with dilute ammonium carbonate solution. Add a few drops of methyl orange to the filtrate, and then make the solution just acid by the careful addition of 1+1 hydrochloric acid, stirring vigorously after the effervescence has ceased. Make the solution up to 500 ml in a graduated flask, and store in a polythene bottle until ready for the colorimetric determinations.

Determination of fluorine. Transfer 1.00 ml of solution to a 50-ml volumetric flask, add 20 ml of alizarin fluorine blue reagent solution, and dilute to volume. Pipette 1-ml aliquots of standard fluoride solution (containing 30 μg of fluoride) into 50-, 100-, and 200-ml graduated flasks, and treat with corresponding amounts of reagent solution. Prepare a reagent blank, consisting of 20 ml of reagent solution diluted to 50 ml. Allow to stand for 1 h and then measure the optical densities of

the solutions at 630 nm in 1-cm cells, using distilled water in the reference cell. Plot a calibration curve from the measurements of blank and standard solutions. The reagent blank has a high optical density and the similar appearance of unknown, standard, and reagent blank solutions need not cause concern. The reagent is a reddish-purple colour, which becomes bluish-purple in the presence of large amounts of fluorine.

Results

Experiments on a reference mixture of basic igneous rocks to which known amounts of sodium fluoride were added showed that recovery of fluorine from the fusion and separation process was complete, and no interference by other elements was detected. The method has been used successfully for the analysis of silicate rocks containing fluorine-bearing minerals, and also for micas and amphiboles. Table I lists the results obtained by the proposed method on fluorine-bearing samples previously analysed by other methods.

TABLE I

COMPARISON OF RESULTS OBTAINED BY THE PROPOSED METHOD WITH THOSE OBTAINED BY CONVENTIONAL METHODS*

Sample	Proposed method (% F)	Conventional methods (% F)
Granodiorite GSP-1	0.36	0.38, 0.39
Biotite LAB 354	0.87	0.79
Aplite LAB 361	1.39	1.39
Muscovite C6	2.51	2.35

* The samples are from the following sources: the granodiorite GSP-1 is a U.S.G.S. reference sample, described by FLANAGAN³; the biotite LAB 354 and aplitite LAB 361 are from the collection of the Institute of Geological Sciences, London, and are listed as nos. 28 and 598 respectively in the compilation of analyses given by GUPPY⁴; the muscovite C6 was analysed by J. N. WALSH by means of the WILLARD-WINTER distillation method⁵.

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A rapid dimethylglyoxime method for the determination of nickel(II) in sea water^{*,**}

Dimethylglyoxime (DMG) has long been used for sequestering nickel from small volumes of ammoniacal citrate solutions of metal ions followed by spectrophotometric determination¹. A modification of this method is described whereby traces (0.5–40 $\mu\text{g/l}$) of nickel(II) may be determined in sea water, and other natural waters, without the usual time-consuming pre-concentration methods^{2,3}. No heating is necessary, and only readily available chemicals are used. Interference from other ions and masking requirements are minimal. The complete analysis of a 750-ml sample of sea water for nickel requires less than 45 min, which is considerably faster than the 3–4 h recently reported for a spectrophotometric method with pyridine-2-aldehyde-2-quinolyldiazone⁴. The accuracy of the method is a function of the amount of nickel in the solution being analyzed and, if present in the lower range (ca. 0.5 $\mu\text{g/l}$), can be improved by increasing the sample size. The limit of detection in a 750-ml sample of sea water is about 0.35 $\mu\text{g/l}$. The absence of any salt effect makes it possible to determine the calibration curve and reagent blanks in distilled water.

Reagents

All solutions were prepared from analytical grade reagents. Aqueous solutions were prepared with deionized (mixed-bed) distilled water. All are stable with time unless otherwise noted.

Stock nickel solution. Dissolve 2.0000 g of pure nickel sheet in hydrochloric acid and dilute to 2000 ml (1 mg/ml).

Standard nickel solution. Dilute 1 ml of stock solution to 1000 ml (1 $\mu\text{g/ml}$). Prepare fresh solution daily.

Instrumentation

Spectrophotometer, Cary 14 recording. Matched quartz cells of 10.0 cm path length.

Calibration curve

Prepare a calibration curve by adding appropriate amounts, 0.5 ml to 10 ml (0.7–13 p.p.b.) for sea water determinations, of the standard nickel solution to 750-ml aliquots of sea water, or distilled water, and carrying out the analytical procedure. Subtraction of the appropriate blank from each of the absorbance values should result in a straight line passing through the origin with a slope of about $4.3 \cdot 10^{-2}$ absorbance units per μg of nickel.

Procedure

To a 750-ml aliquot of sea water filtered through a HA millipore filter (0.45 μ), add 25 ml of aqueous 20% (w/v) sodium citrate reagent and 5 ml of 1% (w/v) DMG in 95% ethanol, and adjust the pH to 9–10 with 4–5 drops of concentrated ammonium hydroxide. In a separatory funnel fitted with a Teflon stopcock, extract

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the nickel dimethylglyoximate once into 10 ml of chloroform followed by three more extractions into 5-ml portions of chloroform. Collect all the extracts (*ca.* 20 ml) into a small separatory funnel. Take care not to transfer any of the viscous film, or foam, which may form between the aqueous and the organic layers. Back-extract the nickel ion into three 5-ml portions of 1 *M* hydrochloric acid; shake for 30 sec for each extraction. Add 1.0 ml of saturated bromine water and leave the solution for 15 min to insure complete oxidation to nickel(IV). During this oxidation quantitatively transfer the solution to a 50-ml beaker. Decant slowly to allow any chloroform, carried over from the previous step, to evaporate. At the end of the 15 min, adjust the pH of the solution to 10.4 ± 0.05 (allow for the heat of neutralization) and develop the nickel(IV) complex with 1.0 ml of the DMG reagent. Quantitatively transfer the solution to a 50-ml volumetric flask, make up to volume, and read the absorbance at 442 nm in 10-cm cells against a blank carried through the same procedure. For maximum precision, the same length of time should elapse between development and reading for all samples.

Discussion and results

Reagent blank. The absence of a salt effect, which was demonstrated by identical calibration curves obtained from both sea water and distilled water, suggested that the reagent blank could be obtained by adding the reagents to distilled water, carrying out the analytical procedure, and measuring the absorbance. The values received over a period of time varied slightly and averaged 0.033 absorbance units. If the same procedure is applied to sea water to which no nickel is added the absorbance measured should be the sum of two contributions: the reagents and the nickel originally present in the sea water. This value may be referred to as the sea water blank in order to avoid confusion with the reagent blank. The sea water blank, when measured repeatedly, yielded values which ranged from 0.033 to 0.055 absorbance units. Partition of the sea water blank to permit evaluation of the two components (absorbance due to reagents and nickel originally present) could furnish useful information. For example, if the reagent blank, measured either in distilled water or in nickel-free sea water with no interfering ions present, is zero or very close to this value, the absorbance obtained upon analysis of the sea water sample would be due primarily to the species of interest. On the other hand, if the absorbance due to the reagents is significant, it should be subtracted from the sea water blank in order to obtain the contribution of the species present. In this study partition of the sea water blank was accomplished by two different methods: extrapolation and masking in order to provide an independent confirmation of the reagent blank obtained from distilled water and to enable comparison with the sea water blank.

Extrapolation. To a large volume of sample water (*ca.* 10 l), add enough stock nickel solution to bring the concentration to about 10 $\mu\text{g/l}$. The exact concentration need not be known. Accurately measure 100-ml, 200-ml, 400-ml, and 800-ml samples of this water and analyze them for nickel by the procedure outlined above. Take care to use exactly the same volume of reagents in each sample as will be used in the experimental determination. Plot the absorbance of the samples against the volume, and extrapolate to zero volume (Fig. 1). The absorbance at this point, due to the reagents, is 0.030 absorbance units and is in good agreement with the absorbance of the blank determined in nickel-free water (0.033 absorbance units).

Masking. The nickel(IV) ion does not form an extractable complex with dimethylglyoxime. This makes it possible to mask chemically the nickel in the sample water by oxidizing it to the tetravalent state. Adjust the pH of 750 ml of sample

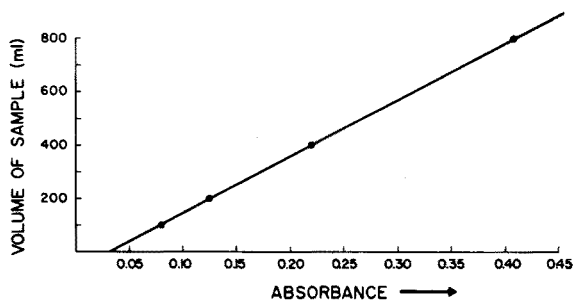


Fig. 1. Determination of reagent blank by extrapolation.

water to about 5 with several drops of concentrated (12 *M*) hydrochloric acid. Add 10 ml of saturated bromine water and let stand 15 min. Adjust the pH of the solution to 9.5 with ammonium hydroxide and extract as outlined above. The absorbance of the blank obtained in this manner matched the blank determined by either of the other methods, within experimental uncertainty, and amounted to 0.025–0.030 absorbance units, which is again in good agreement with the results obtained from distilled water and by extrapolation. The absorbance is evidently due largely to the reagents, indicating that very little nickel(II) was present in the freshly collected and analyzed surface sea water from Koko Head, Oahu. Confirmation was supplied by permitting other acidified samples of the same sea water to age and carrying out the analytical procedure for nickel after definite time intervals. In general, the nickel concentration increased steadily and significantly presumably as a result of the release of organically bound nickel. This aspect will be dealt with separately elsewhere.

Interfering ions. Copper and cobalt are known to form dimethylglyoxime complexes¹. Neither, however, interferes when present in concentrations greater than eighty times that normally found in sea water. The cobalt complex is not appreciably soluble in chloroform, and the copper dimethylglyoximate is not stable in strongly ammoniacal solutions. Iron is prevented from interfering by the citrate present in the solution, which also prevents emulsification in the basic medium. Manganese, if present in significant amounts relative to the nickel, may lead to low results. The manganese(II) ion may be oxidized by the oxygen present in the solution, and, in turn, oxidize the nickel(II) ion to the unextractable nickel(IV) ion. This can be prevented, if necessary, by adding 5 ml of hydroxylamine hydrochloride (10% w/v in water) to the solution before extraction. Zinc, in concentrations of at least 200 $\mu\text{g/l}$, does not interfere.

Reproducibility. In order to establish the reproducibility of the method three separate calibration curves were determined over a 4-week period. Two of the curves were prepared with sea water and, to test for a salt effect, the third was determined in deionized distilled water. The slopes were $4.27 \cdot 10^{-2}$ and $4.30 \cdot 10^{-2}$ in sea water, and $4.24 \cdot 10^{-2}$ in deionized distilled water, as determined by the method of least squares. The data for one such curve are summarized in Table I together with the

standard deviation for each point calculated from the formula, $\sigma = (\sum d^2 / (n - 1))^{1/2}$, for each point.

TABLE I
SEA WATER CALIBRATION CURVE^a

	1.0 μg	2.0 μg	4.0 μg	5.0 μg	10.0 μg
	0.045	0.083	0.170	0.215	0.427
	0.043	0.084	0.172	0.211	0.429
	0.046	0.085	0.173	0.213	0.430
	0.043	0.083	0.177	0.212	0.424
	0.044	0.081	0.172	0.212	0.430
A (Mean)	0.045	0.083	0.173	0.213	0.428
Fract. std. dev. (%)	3.3	1.4	1.5	1.4	1.2
σ	0.0015	0.0012	0.0026	0.0030	0.0050

^a All absorbance values are less blank; sample volume of 750 ml of filtered sea water.

Precision. The fractional standard deviation⁵ indicates a precision of *ca.* 1.5% at a concentration of 2 $\mu\text{g/l}$ which is in the neighborhood of the concentration of total nickel found in Hawaiian water². The precision decreases to *ca.* 7% if the concentration is in the 0.5 $\mu\text{g/l}$ range.

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Utilization of surfactants in a.c. polarographic analysis

The presence of maxima on conventional d.c. polarograms affects the height and shape of the corresponding a.c. polarographic waves. Usually a d.c. polarographic maximum gives rise to an increase in the current of the main a.c. wave, but a separate peak may also appear on the polarogram. Even where no maximum is visible on the d.c. step, the process which gives rise to maxima may nevertheless be proceeding, although to a minor extent¹. In d.c. polarography the maxima are easily suppressed by addition of a surface-active substance to the electrolyte. However, even traces of

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surfactants usually decrease the rate of the electron-transfer reaction and lead to a lowering or even disappearance of a.c. polarographic waves. Hence, surfactants are usually avoided in a.c. polarography².

Several studies have been made of the effect of surfactants on the reduction of cadmium and lead ions. Thus, RANGLES AND SOMERTON^{3,4} found that the presence of gelatin decreased the rate constant for the reduction of these cations. TANAKA *et al.*⁵ studied the effect of polyoxyethylene lauryl ether (LEO) on a.c. polarographic waves of lead and cadmium in 1 *M* potassium nitrate containing 0.001 *M* nitric acid. They claim that the peak current remains practically constant up to a concentration of $2 \cdot 10^{-5}$ *M* LEO, but decreases rapidly with a further increase of the concentration of this surfactant. In the presence of $2 \cdot 10^{-4}$ *M* LEO the waves of both lead and cadmium disappear.

Recent investigations⁶⁻⁹ indicate that the rate of the electron-transfer reaction is not affected, or sometimes even increased, in the presence of certain ionic surfactants with a charge opposite to that of the depolarizer. The present work was carried out in order to test the effect of various ionic surfactants on a.c. polarographic waves of lead and cadmium and to find a maximum suppressor more suitable than gelatin and LEO for a.c. polarographic determination of uncomplexed cations.

Apparatus and reagents

Polarograms were recorded with a Metrohm E 261 R Polarecord connected to a Metrohm E 393 A-C modulator. An Ag/AgCl/saturated KCl electrode served as reference electrode and a tungsten electrode was employed as auxiliary electrode. All a.c. polarograms were obtained with an a.c. amplitude of 10 mV r.m.s. The capillary characteristics of the dropping mercury electrode, measured in 0.1 *M* potassium nitrate (open circuit) at a mercury height of 50 cm, were $m = 3.62$ mg/sec and $t = 2.63$ sec. All experiments were performed at $25 \pm 0.1^\circ$. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis.

A 0.1 *M* potassium nitrate solution containing 0.001 *M* nitric acid was used as supporting electrolyte. Stock solutions of lead, cadmium, copper and zinc were prepared by dissolving the appropriate amount of reagent-grade metal nitrates in distilled water. The following surfactants were used:

1. Sodium dodecylsulphate (L. Light and Co., Ltd., England).
2. Aerosol AY, sodium diamylsulphosuccinate (American Cyanamide Co., New York, U.S.A.).
3. Benax 2A-1, sodium dodecyldiphenyletherdisulphonate (Dow Chemical Co., Midland, Mich., U.S.A.).
4. Armeen 12D, dodecylamine perchlorate (Armour Industrial Chemical Co., Chicago, Ill., U.S.A.).
5. Triton X-100, polyethyleneglycolether of monoisooctylphenol (Rohm and Haas Co., Philadelphia, U.S.A.).

One per cent stock solutions of the surfactants were prepared by simple dissolution of the commercial product in distilled water.

Results

Preliminary experiments showed that maxima on d.c. polarographic waves of

copper, lead, cadmium and zinc in 0.1 *M* potassium nitrate are easily suppressed by addition of 0.001–0.002% of any of the surfactants tested.

The effect of the surfactants on the height of the a.c. polarographic wave of $5 \cdot 10^{-4}$ *M* cadmium is shown in Fig. 1. No d.c. polarographic maximum is observed

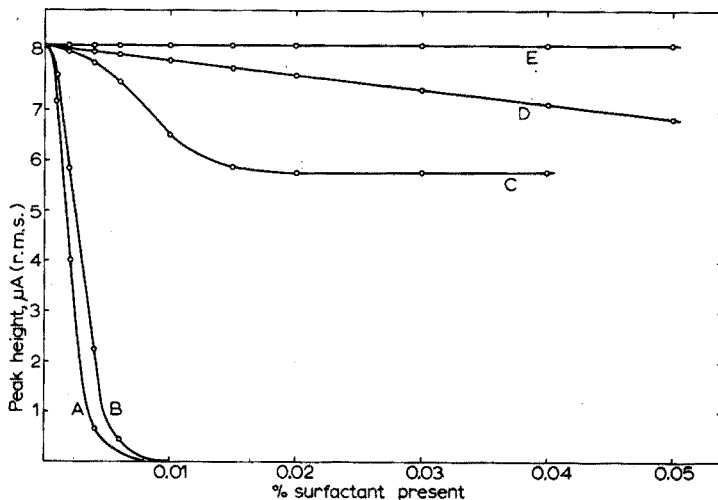


Fig. 1. Effect of various surfactants on the peak height of the a.c. polarographic wave of $5 \cdot 10^{-4}$ *M* cadmium in 0.1 *M* potassium nitrate containing 10^{-3} *M* nitric acid. (A) Triton X-100; (B) Armeen; (C) dodecylsulphate; (D) Aerosol AY; (E) Benax.

at this concentration and the a.c. polarographic wave is very well defined in the absence of surfactants. In the presence of 0.001% of the non-ionic substance Triton X-100 (curve A) or the cationic substance Armeen (curve B), the a.c. current is greatly decreased and upon increasing the concentration of any of these surfactants above 0.01%, the whole wave is omitted. Addition of dodecylsulphate to the electrolyte causes precipitation and the peak height of cadmium decreases (curve C). A small decrease in a.c. current is observed also in the presence of Aerosol AY (curve D), but the wave does not disappear even in the presence of large amounts of these anionic surfactants. However, the peak height of cadmium is constant and completely independent of the presence of the anionic substance Benax (curve E). Moreover, the summit potential coincides with the half-wave potential and the shape of the wave is not affected even on addition of 0.05% Benax to the electrolyte. Besides, the wave is symmetrical about the summit potential and the width of the wave at half-height, $\Delta E_{s/2}$, is 48 mV, which is very close to the theoretical value (46.6 mV) for a two-electron reduction².

Similar results were observed on addition of the surfactants to lead in the same supporting electrolyte. D.c. polarograms of $5 \cdot 10^{-4}$ *M* lead exhibit a small maximum which is depressed in the presence of 0.0005% of any of the surfactants and a well-defined a.c. polarographic wave is obtained. Upon increasing the concentration of Triton X-100 or Armeen above 0.001% the peak height is greatly decreased. A slight decrease in current and formation of a precipitate is observed in the presence of

dodecylsulphate, whereas the peak height of the lead wave is independent of the presence of Aerosol AY or Benax in the concentration range 0.001–0.05%. The width of the lead wave at half-height is 45 mV in the presence of 0.05% Benax and the wave is symmetrical about the summit potential which coincides with the half-wave potential.

The presence of Benax gives rise to two tensammetric waves with summit potentials at $E_T^+ = +0.25$ V and $E_T^- = -1.0$ V, respectively. As indicated in Fig. 2,

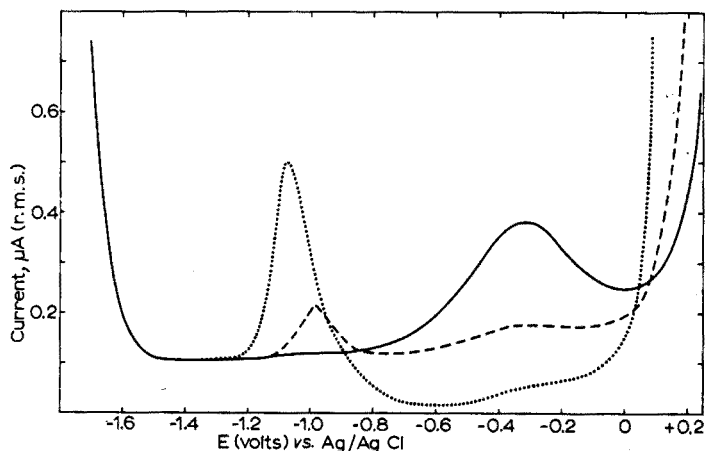


Fig. 2. Tensammetric waves of Benax. A.c. base current of 0.1 *M* potassium nitrate containing 10^{-3} *M* nitric acid (solid line) and in the presence of 0.002% Benax (dashed line), and 0.010% Benax (dotted line).

the base current is depressed between these potentials indicating a strong adsorption at the electrode. The tensammetric waves of Benax will interfere with a.c. polarographic waves appearing close to these potentials. Thus, a shoulder is observed on the a.c. polarographic wave of $5 \cdot 10^{-5}$ *M* zinc in 0.1 *M* potassium nitrate in the presence of 0.001 to 0.03% Benax. When the concentration of Benax is increased, the tensammetric peak is shifted to more negative potentials and at concentrations above 0.03% Benax the height of the zinc wave (at $E_s = -0.98$ V) can be measured without any interference from the tensammetric wave. The maximum on d.c. polarographic waves of $5 \cdot 10^{-4}$ *M* copper in 0.1 *M* potassium nitrate is depressed in the presence of 0.002% Benax and a well-defined a.c. polarographic wave with summit potential $E_s = +0.05$ V is obtained. However, when the concentration of Benax is increased, the positive tensammetric wave of Benax overlaps the copper wave. Hence, the application of Benax in a.c. polarography is restricted to the potential range 0 to -1.0 V vs. Ag/AgCl.

Conclusion

Although non-ionic surfactants like LEO and Triton X-100 and cationic surfactants like Armeen depress the peak height of a.c. polarographic waves of uncomplexed metal ions, the rate of the electron-transfer reaction is not affected by the presence of certain anionic surfactants. Benax appears to be the best maximum suppressor so far tested. This substance is very soluble in water and in the potential

range 0 to -1.0 V vs. Ag/AgCl, the height and the shape of the a.c. polarographic waves are not affected by the presence of even 0.05% Benax, which is a concentration about 50 times greater than necessary for depressing d.c. polarographic maxima.

Earlier experiments indicate that the electrode reaction of negatively charged complexes is inhibited in the presence of Benax⁸. Hence, Benax may also serve as a powerful electrochemical masking agent for anionic complexes. Work is now in progress to investigate the a.c. polarographic determination of cadmium in the presence of a large excess of indium using Benax as electrochemical masking agent.

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Determination of nitrate in sea water

Since nitrite can be sensitively and accurately determined by spectrophotometry after diazotization, almost all analytical methods for nitrate in sea water involve the reduction of nitrate to nitrite. Many methods for the reduction have been reported; recently, columns containing amalgamated cadmium¹ or copper-coated cadmium² have been proposed. Both methods seem to give good results for the determination of nitrate in sea water, but a simpler method with zinc powder is presented in this paper. HAGINO³, and CHOW AND JOHNSTONE⁴ have reported relatively high yields of nitrite by reduction with zinc powder in ammoniacal media, and the latter authors have applied the method to sea water. In acidic medium which is favorable for the following diazotization, however, the yield of nitrite had been as low as 10-50%⁵⁻⁷ and unreliable except for the recent works of MORIMOTO *et al.*⁸, and KOMATSU AND HAGINO⁹.

A fairly high yield of nitrite can be obtained at pH about 3 with the addition of ammonium chloride¹⁰. It is shown below that the method can be successfully applied to determination of nitrate in sea water.

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Reagents

Potassium chloride-hydrochloric acid buffer, pH 1.5. Add 50 ml of 0.2 M potassium chloride solution to 34 ml of 0.2 M hydrochloric acid, and dilute to 200 ml with water.

Zinc powder (400 mesh through). If it contains nitrite or nitrate, wash with 0.01 M hydrochloric acid and then with water. After drying, pass through a 400-mesh sieve.

Procedure

Pipet 25 ml of sea water into a 50-ml stoppered Erlenmeyer flask. Add 1 ml of aqueous 20% (w/v) ammonium chloride solution and 2 ml of buffer pH 1.5. The pH of the solution should be 3.1 to 3.5. Keeping the solution at 0–25°, add 0.2 g of zinc powder, and allow the flask to stand for 10 min with occasional (about 5 times) shaking for about 10 sec each time. Remove the zinc powder completely from the solution through a dry fine-grained filter paper. Add 1 ml of 1% (w/v) sulfanilamide solution in 0.8 M hydrochloric acid to 10 ml of the filtrate, followed by 1 ml of aqueous 0.1% (w/v) α -naphthylethylenediamine dihydrochloride solution after 2–8 min. After 10 min, measure the absorbance at 543 nm with 1-cm cells, water being used as the reference. A correction for the blank should be made.

A working curve is prepared by this procedure with known concentrations of nitrate added in artificial or natural sea water (Fig. 1). Since a sum of nitrate and nitrite in a sample ($\mu\text{g-at/l}$) is obtained by the working curve, the concentration of nitrate is

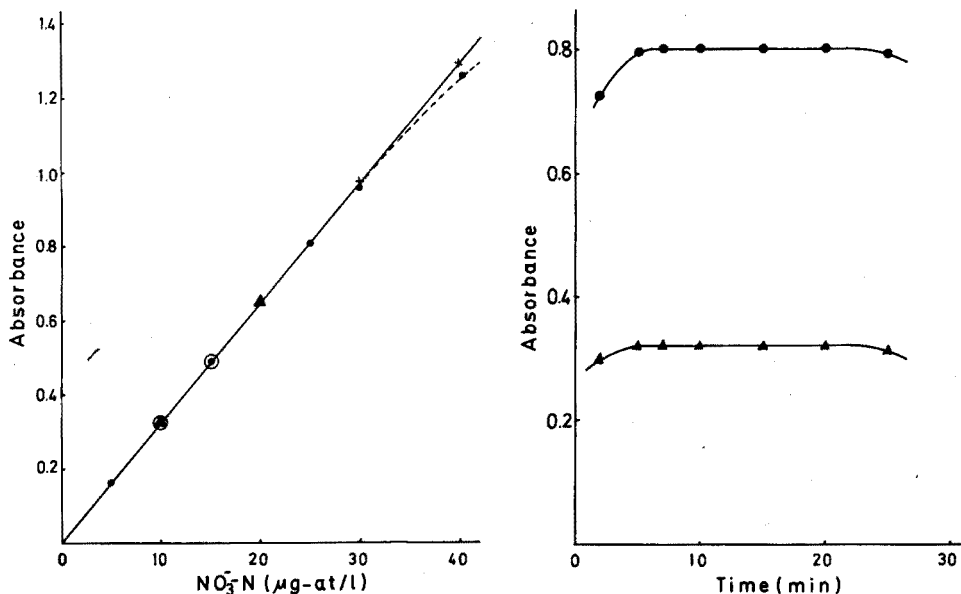


Fig. 1. Working curve for nitrate. ● Sea water, salinity 34‰, absorbance was measured directly; × sea water, salinity 34‰, absorbance measured with twice-diluted colored solution was doubled; ○ diluted sea water, salinity 17‰; ▲ artificial sea water, salinity 51‰.

Fig. 2. Time during the reduction. ● 25 $\mu\text{g-at/l}$ $\text{NO}_3\text{-N}$; ▲ 10 $\mu\text{g-at/l}$ $\text{NO}_3\text{-N}$.

given by the difference between the sum and the nitrite concentration ($\mu\text{g-at/l}$) determined separately by any method, e.g. BENDSCHNEIDER AND ROBINSON'S method¹¹.

Results and discussion

The conditions for the reduction were investigated previously¹⁰, with distilled water solutions of nitrate. In this paper, the conditions were re-examined with artificial sea water, and almost the same results were obtained as in the case of distilled water.

The effects of pH, time and temperature on the reduction were studied for solutions containing 10 or 25 $\mu\text{g-at NO}_3^- \text{-N/l}$. Constant values were obtained in the pH range 2.9–3.5 and in the temperature range 0–25°. The effect of time is shown in Fig. 2. The additions of 0.16–0.3 g of ammonium chloride and 0.12–0.25 g of zinc powder gave the same value for nitrate.

The yield of nitrite obtained by reduction of nitrate was nearly 80%; the recovery of nitrite was also found to be *ca.* 80% when a solution containing only

TABLE I

DETERMINATION OF NITRATE IN THE PRESENCE OF VARIOUS AMOUNTS OF NITRITE IN SEA WATER

Added ($\mu\text{g-at/l}$)		Found ($\mu\text{g-at/l}$)		
$\text{NO}_3^- \text{-N}$	$\text{NO}_2^- \text{-N}$	$\text{NO}_3^- \text{-N}$		
25.0	None	24.9	25.0	24.9
25.0	1.0	25.4	25.1	24.7
25.0	5.0	24.4	24.6	25.2
15.0	None	14.9	14.9	15.0
15.0	1.0	15.0	14.8	14.9
15.0	5.0	15.5	15.4	14.9
5.0	None	5.0	5.0	5.0
5.0	1.0	5.0	4.9	5.0
5.0	5.0	5.2	5.4	5.1

nitrite was treated with zinc powder. Hence, the working curve shown in Fig. 1 gives the total concentration of nitrate, and nitrite, if present originally.

SUGAWARA¹² has reported a salt effect on the color development of nitrite by BENDSCHNEIDER AND ROBINSON'S method¹¹. The authors also recognized the effect shown in Fig. 1 (broken line), but found that a straight line was obtained up to 40 $\mu\text{g-at/l}$ when the colored solution was diluted to twice the volume with water and its absorbance was doubled. Table I shows determinations of nitrate in the presence of various amounts of nitrite added to a sample of sea water which contained no nitrate and nitrite.

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Determination of traces of selenocyanate

In recent years, many selenocyanate complexes of transition metal ions¹⁻³ have been prepared and their properties studied. In a study of the conversion of elemental selenium to selenocyanate, it became necessary to determine traces of selenocyanate formed. A search of the literature showed a limited number of macro methods, based on conductometric and potentiometric titrations⁴ or iodometric titrations⁵, but there is no information on its determination when present in micro quantities. A colorimetric method for selenocyanate was therefore developed.

In the proposed method, the selenocyanate is reacted with bromine to form cyanogen bromide according to the following equation:



The cyanogen bromide is then allowed to react with pyridine-benzidine reagent to give a red color which is measured at 518 nm. A similar method has been employed by ALDRIDGE^{6,7} for the determination of cyanide and thiocyanate.

Reagents

Potassium selenocyanate (E. Merck reagent grade). This salt is very hygroscopic and was stored over phosphorus pentoxide in a desiccator. Since the selenium compounds are light-sensitive, the desiccator and the flask containing the selenocyanate solution were covered with tin foil. A stock solution was prepared by dissolving 33 mg of potassium selenocyanate in distilled water and diluting to 100 ml in a volumetric flask. A solution containing 2.4 μg SeCN^-/ml was prepared by suitable dilution with distilled water.

Pyridine-benzidine reagent. This was prepared as described by HIGSON AND BARK⁸. To 18 ml of freshly distilled pyridine (B.D.H.) were added 12 ml of distilled water and 3 ml of concentrated hydrochloric acid (A.R.); to this solution 10 ml of 1% benzidine (Extrapure, E. Merck quality) solution in 0.5 N hydrochloric acid was added.

A Spectronic-20 colorimeter/spectrophotometer (Bausch and Lomb) was used.

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Procedure

Place 1 ml of the selenocyanate solution in a test tube and pass bromine vapor (from A.R. bromine) until the solution shows a yellow color stable for at least 2 min. Then add 0.5 ml of aqueous 1% (w/v) phenol solution and shake well to remove the excess of bromine. Add 4 ml of the pyridine-benzidine reagent, shake well and set aside for 15 min. This time interval is essential for the maximum development of a stable red color and also for obtaining reproducible analytical results. Dilute the solution to 10 ml with water. Measure the transmission of the solution at 518 nm against a reagent blank.

Results

It can be seen from the results shown in Table I that the accuracy obtained was quite satisfactory. Beer's law was obeyed up to 0.5 $\mu\text{g SeCN}^-/\text{ml}$ in the final solution, but there were deviations above this concentration.

Cyanide^{6,8} and thiocyanate⁷ are also known to react with bromine and pyridine-benzidine reagent to give a red color, and must, therefore, be absent. Work is in progress to develop a method for the estimation of selenocyanate in presence of cyanide.

TABLE I
RESULTS OF ANALYSIS OF SELENOCYANATE

<i>SeCN</i> -taken ($\mu\text{g/ml}$)	<i>SeCN</i> -found ($\mu\text{g/ml}$)
0.180	0.179
	0.182
0.240	0.234
	0.242
0.300	0.298
	0.300
0.480	0.478
	0.482

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Rapid solvent extraction of titanium(IV) with tributyl phosphate

Several chelating agents have been used for the extraction of titanium. The diantipyrinylmethane-catechol complex¹ can be extracted into 1,2-dichloroethane or chloroform; the dioctylmethylene diphosphonate² complex can be extracted into octane. The complex with 2,3'-dipyridylsalicylic acid³ can be extracted at pH 4.6 with chloroform and then determined photometrically. The titanium-molybdophosphate complex⁴ can be extracted into a butanol-chloroform mixture, and the titanium peroxycomplex with diisopentyl hydrogen phosphate can be extracted into benzene⁵. Other possible extractants are 2-ethylhexyl dihydrogen phosphate⁶ and ethyl and pentyl acetates⁷.

Tributyl phosphate⁸ has been used to separate titanium from zirconium in 13.3 *M* sulphuric acid, the extraction being quantitative only at high acid concentrations. Thus the existing methods are time-consuming or need critical control of conditions. The method proposed in this communication is based on the use of magnesium chloride as salting-out agent: it is rapid, simple and adaptable for micro and macro work.

Apparatus and reagents

A Cambridge pH meter and a Model Φ_3 KH 57 filter photometer were used.

Titanium stock solution. Dissolve 0.407 g of titanium oxide in 10 ml of concentrated sulphuric acid, and dilute to 500 ml with water. Standardization of a solution with cupferron⁹ showed it to contain 251.5 μg Ti/ml.

Buffer solution. Dissolve 6.5 g of sodium acetate and 10.5 ml acetic acid in water and dilute to 1 l.

General procedure

To an aliquot of solution containing *ca.* 503 μg Ti, add enough magnesium chloride, hydrochloric acid and water to give concentrations of 4 *M* magnesium chloride and 5 *M* acid in a volume of 25 ml. Shake the solution for 5 min with 10 ml of 60% (v/v) TBP in xylene. Separate the layers and strip titanium from the organic phase with two 10-ml portions of distilled water. Add 20 ml of buffer solution and 5 ml of 20% sulphosalicylic acid to give a volume of 50 ml in a volumetric flask, and measure the characteristic yellow colored complex at 445 nm after 10 min¹⁰.

Effect of varying acid, TBP and salt concentrations

The concentration of hydrochloric acid was varied from 3 *M* to 6 *M* and the concentration of TBP from 25 to 100% (0.91 to 3.66 *M*) by dilution with xylene (Table I). In the absence of a salting-out agent it was possible to extract titanium quantitatively from 5 *M* hydrochloric acid with 75% or 100% TBP; 60% TBP could be used at this acidity only in the presence of 4 *M* magnesium chloride.

An attempt was made to determine the composition of the extractable titanium-TBP species by means of $\log D$ versus $\log [\text{TBP}]$ plots. The plots at 3 and 4 *M* hydrochloric acid showed slopes of 1.0 and 1.2 respectively, which indicates that the extractable species is most probably $\text{TiOCl}_2 \cdot 2\text{TBP}$. The optimum reagent concentration is 60% TBP in xylene, and the optimum acidity is 5 *M* containing 4 *M* magnesium chloride.

TABLE I

DISTRIBUTION RATIO AS A FUNCTION OF ACID CONCENTRATION

TBP concentration (%)	HCl (M) (initial)	Distribution ratio (D)
25 (0.91 M)	3	3.43
	4	4.91
	5	7.45
50 (1.83 M)	3	4.33
	4	10.68
	5	37.61
75 (2.74 M)	3	5.65
	4	21.64
	5	∞
100 (3.66 M)	3	5.65
	4	37.61
	5	∞
60 (1.89 M) in the presence of 4 M magnesium chloride	0.5	0.86
	1	1.52
	2	2.75
	3	5.65
	4	37.64
	5-6	∞

TABLE II

EFFECT OF DIVERSE IONS

(Ti(IV) = 503 µg; 5 M HCl + 4 M MgCl₂; 60% TBP-xylene)

Foreign ion	Added as	Tolerance limit (µg)	Foreign ion	Added as	Tolerance limit (µg)
Pb ²⁺	Pb(NO ₃) ₂ ·2H ₂ O	250	Ca ²⁺	CaCl ₂ ·2H ₂ O	5000
Hg ²⁺	HgCl ₂	5000	Sr ²⁺	SrCl ₂ ·2H ₂ O	500
Pd ²⁺	PdCl ₂	2500	Mg ²⁺	MgCl ₂	50000
Au ³⁺	HAuCl ₄	25	Mo ₇ O ₂₄ ⁶⁻	(NH ₄) ₆ Mo ₇ O ₂₄ ·12H ₂ O	5000
Ru ³⁺	RuCl ₃	250	VO ₃ ⁻	NH ₄ VO ₃	500
Cu ²⁺	CuSO ₄ ·5H ₂ O	500	SeO ₃ ²⁻	Na ₂ SeO ₃	5000
Cd ²⁺	3CdSO ₄ ·8H ₂ O	500	TeO ₃ ²⁻	Na ₂ TeO ₃	5000
Sb ³⁺	Sb ₂ (SO ₄) ₃	500	CrO ₄ ²⁻	K ₂ CrO ₄	1500
Bi ³⁺	Bi(NO ₃) ₃	500	WO ₄ ²⁻	Na ₂ WO ₄	1000
Sn ²⁺	SnCl ₂ ·2H ₂ O	5000	SCN ⁻	NH ₄ SCN	5000
			S ₂ O ₃ ²⁻	Na ₂ S ₂ O ₃ ·5H ₂ O	2500
Fe ³⁺	FeCl ₃	None	F ⁻	NaF	4000
Fe ²⁺	FeSO ₄	None	Br ⁻	NaBr	4000
Al ³⁺	Al(NO ₃) ₃ ·9H ₂ O	5000	PO ₄ ³⁻	Na ₂ HPO ₄ ·12H ₂ O	2500
Be ²⁺	Be(NO ₃) ₂	5000	ClO ₃ ⁻	KClO ₃	4000
Zr ⁴⁺	Zr(NO ₃) ₄ ·4H ₂ O	2500	Cit ³⁻	Citric acid	2500
Ce ⁴⁺	Ce(SO ₄) ₂	500	Tart ³⁻	Tartaric acid	5000
Th ⁴⁺	Th(NO ₃) ₄	1000	Ascorb ²⁻	Ascorbic acid	5000
U ⁶⁺	UO ₂ (NO ₃) ₂	2000	Acetate ⁻	Acetic acid	5000
Zn ²⁺	ZnSO ₄ ·7H ₂ O	5000	Malonate ²⁻	Malonic acid	5000
Mn ²⁺	MnSO ₄	500	Oxalate ²⁻	Oxalic acid	2500
Co ²⁺	Co(NO ₃) ₂ ·6H ₂ O	500	EDTA ⁴⁻	EDTA (disodium salt)	2500
Ni ²⁺	NiSO ₄ ·6H ₂ O	500			

The effect of varying concentrations of salting-out agents on the extraction of titanium with 60% TBP-xylene from 4–5 *M* acid solutions was studied. Concentrations of 4–11 *M* lithium chloride were tested; the distribution ratio increased as the salt concentration increased, quantitative extraction was obtained from 5 *M* hydrochloric acid containing 11 *M* lithium chloride. Aluminium chloride in 1–2 *M* concentrations gave low distribution ratios, as did 1–2 *M* magnesium chloride; 4 *M* magnesium chloride gave the optimal conditions for extraction.

Period of shaking

The period of shaking was varied from 1 to 20 min; the extent of extraction increased from 52.5% after 1 min to 100% after 5 min and then remained constant up to 20 min. The optimum period of equilibration was thus at least 5 min.

Effect of diverse ions

The various ions which are usually associated with titanium in alloys, etc., were tested for interference (Table II). The tolerance limit was set at the amount required to cause a 2% error in the titanium recovery. The results show that titanium can be extracted in the presence of 10-fold amounts of many different anions and cations. Ions such as zirconium, lead, palladium, phosphate, citrate and thiosulphate can be tolerated in 5-fold amounts. Only iron, gold, ruthenium and silver provide serious interferences, and these can be eliminated by appropriate masking.

The method is rapid, simple and selective, and permits the separation and determination of titanium at low levels. The average recovery of titanium was $98.8 \pm 1.2\%$. The standard deviation was $\pm 1.2\%$ in 10 determinations of 503 μg of titanium.

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Detection of halogen-substituted aldehydes

Various methods are available for the detection of aldehydes^{1,2}. However, it appears that chloral is much more difficult to detect than other aldehydes³. This may be due to the marked stability of chloral addition products relative to those of other aldehydes. As a result more vigorous conditions are required to drive chloral reactions to completion.

Chloral has been detected by techniques such as boiling the test sample in aqueous alkali containing pyridine². Another method involves saponifying chloral in the presence of phenol followed by condensation with hydrazine².

We have discovered a simple method of detecting chloral vapor. The vapor is passed through a detector tube containing silica gel impregnated with an amine. The tube is then heated at 110° to 120° to give a color change.

Detector tube

Aniline (0.1 g) was dissolved in 3 ml of ethyl ether. Silica gel (1.0 g) (28–200 mesh) was added and the mixture was allowed to dry in air. About 0.1 g of the gel was placed between organandy plugs in a glass tube of 2.5 mm diam.

Test procedure

After test vapors were drawn through the detector tube the tube was placed in an oven at 110–120° for 10 min. A discoloration of the tube was taken as a positive test. Sensitivity studies were performed with petroleum ether solutions of chloral according to a test procedure previously described⁴. In each case a blank containing only petroleum ether was used for comparison purposes. It is estimated that 100 ml of air containing the vapors from 10 μ l of petroleum ether were drawn through the detector tube.

Effect of aniline concentration

Strongest detection signals were obtained when 1 g of the gel contained 0.1 g of aniline. Weaker tests were obtained with less than 0.05 g or greater than 0.2 g of aniline. This comparison was made with *ca.* 5.0 mg of chloral.

Sensitivity and selectivity

Detector tubes were prepared with impure aniline (pale red in color) and freshly distilled aniline (colorless). Both tubes were equally effective in detecting chloral. The limit of detection was 15 μ g in tests that were carried out by drawing vapors from 10 μ l of a chloral-petroleum ether solution through the tube. The petroleum ether itself or air (100 ml) gave a very weak test. This interference prevented detection of chloral at concentrations lower than 15 μ g.

Detector tubes prepared with freshly distilled aniline provided better contrast between blanks and positive tests. However, there did not appear to be any major difference in selectivity. Of the eight compounds found to give a positive test (Table I) only dibromomethane did not respond with detector tubes prepared from impure aniline.

Effect of substrates

Various amines were tested on silica gel as detectors of chloral vapors. A

TABLE I
SELECTIVITY OF THE CHLORAL DETECTOR TUBE*

<i>Positive test</i>	<i>Negative test</i>
<i>Strong</i>	Glycolic acid
Chloral	Allyl ether
Dichloroacetaldehyde	Acetone
	Carbon tetrachloride
<i>Medium</i>	Trichloroacetic acid
Propionaldehyde	Methanol
	N,N-Dimethylacetamide
<i>Weak</i>	Ethyl acetate
Dibromomethane	Acetonitrile
Trimethylchlorosilane	Hexamethyldisilazane
Carbon tetrabromide	2-Carbomethoxy-1-methylvinyl-
<i>n</i> -Butyraldehyde	dimethylphosphate
2,2-Dichlorovinyl-dimethylphosphate	

* About 10 ml of air saturated with the test compound was drawn through the tube. The tube was then heated for 10 min at 120°.

TABLE II
AMINE SUBSTRATES IN THE DETECTION OF CHLORAL

<i>Amine</i>	<i>Color of the detection signal</i>
Aniline	Dark brown-green
N-Methylaniline	Green-blue
N,N-Dimethylaniline	Green-blue
2,5-Diethoxyaniline	Brown
<i>o</i> -Anisidine	Brown
<i>o</i> -Dianisidine · HCl	Light green
Diethylamine	Brown
Cyclohexylamine	Yellow
Dicyclohexylamine	Yellow
Tricyclohexylamine	Yellow
Pyridine	Yellow
3-Methyl-2-benzothiazolinone hydrazone · HCl	Yellow

comparison under similar conditions with about 5 mg of chloral indicated that aniline gave the strongest tests. However, it was interesting to find that a variety of amines (aliphatic, aromatic and heterocyclic) gave a test with chloral (Table II).

Effect of adsorbent

A number of solid adsorbents were tested with aniline for the detection of chloral vapors. Their relative rating in terms of producing the strongest detection signal is: silica gel (28-100 mesh) > alumina (anionic) = alumina (cationic) > silica gel (100 mesh) > alumina (neutral) > silica gel (powder) > anhydrous magnesium sulfate.

Mechanism

A mechanism of color formation is difficult to deduce without much additional research. The detection color differs depending on the material detected. For example, chloral gives a green-brown color (brown at lower concentrations), dichloroacetaldehyde gives a red-brown color, and trimethylchlorosilane gives a green color.

It may be pertinent to note that the chemical components required for the color formation, *i.e.*, amine and aldehyde, are each susceptible to autoxidation. The detection mechanism may be of the multicyclic catalytic type⁵ with halocarbon acting as a chain transfer agent.

A detector tube was designed in which the silica gel contained both dibromomethane and aniline (0.1 g of each component per 1.0 g of gel). In contrast to the tan color of the gel containing only aniline, this gel was colorless and produced much less blank color with air and/or petroleum ether. Actually the blank interfered so little that 5 μg of chloral could be detected easily, in contrast to the 15- μg limit established with the aniline gel. However, there did not seem to be any major increase in detection sensitivity towards butyraldehyde or propionaldehyde. The amount of dibromomethane is an important factor. Sampling dibromomethane in the absence of aldehyde gave a weak test (Table I); higher concentrations of the halocarbon inhibited decomposition of aniline.

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Anal. Chim. Acta, 45 (1969) 358-360

Oscillopolarographic determination of germanium

The oscillopolarographic behaviour of germanium has been studied before in ammoniacal buffer solutions¹, in mixtures of EDTA with ammonium chloride, magnesium sulfate, potassium chloride or borate solutions¹⁻³ and in mixtures of sodium perchlorate with oxalic acid⁴. With these supporting electrolytes, germanium(IV) gives a cathodic incision which is suitable for its detection and determination, and corresponds to the reduction of germanium(IV) to germanium(II). In this paper, the oscillopolarographic activity of germanium(IV) in concentrated acid solutions is described. The limit of detection is $1 \cdot 10^{-6}$ M, and determination of germanium in presence of many ions is possible in concentrated hydrochloric acid or hydrobromic acid solutions and in mixtures of concentrated perchloric acid with hydrochloric or hydrobromic acid or ammonium thiocyanate. The proposed method has been applied to the determination of germanium in ashes of Chilean coals.

Instrumentation and chemicals

A Polaroscope model P 576 (Křižik, Prague) was used.

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Germanium(IV) solution. A 10^{-2} M solution was prepared by dissolving 36.3 mg of finely powdered germanium metal (p.a., Merck) in 2 M sodium hydroxide in the presence of 30-vol. hydrogen peroxide. The excess of peroxide was destroyed by boiling and the solution was diluted to 100 ml with twice-distilled water. Other germanium(IV) solutions (10^{-3} and 10^{-4} M) were prepared by suitable dilution.

Supporting electrolytes. The supporting electrolytes used (Table I) were prepared from Merck p.a. reagents.

TABLE I

ACTIVITY OF GERMANIUM(IV) IN SOME SUPPORTING ELECTROLYTES

 $(E$ vs. SCE = -0.6 V)

Supporting electrolyte	Q	Sensitivity (M)
A. Hydrochloric acid ($d = 1.19$)	0.46	$1 \cdot 10^{-5}$
B. Hydrobromic acid ($d = 1.48$)	0.35	$1 \cdot 10^{-5}$
C. 10 M Perchloric acid + 0.5 M hydrochloric acid	0.53	$5 \cdot 10^{-6}$
D. 10 M Perchloric acid + 1.0 M hydrobromic acid	0.28	$5 \cdot 10^{-6}$
E. 10 M Perchloric acid + 1 M ammonium thiocyanate	0.26	$5 \cdot 10^{-6}$

Results and discussion

In the supporting electrolytes used (A-E, Table I) germanium(IV) gave reversible incisions, the cathodic one being much more sensitive than the anodic one. The results obtained in other acidic supporting electrolytes were as good as those obtained in the specified solutions. Table I shows the position of the incisions in the curve $dE/dt = f(E)$, and the sensitivities obtained. The best sensitivities were obtained with solutions C and D (Figs. 1 and 2); the oscillogram of supporting electrolyte D was very similar to that of electrolyte C.

Other ions also show oscillographic activity in the supporting electrolytes proposed (Table II). The following ions show no activity even at concentrations of 10^{-8} M: Zn(II), Cd(II), Cu(II), Ni(II), Co(II), Mn(II), Fe(III), Cr(III), Bi(III), In(III), La(III), Ti(IV), Zr(IV), Mo(VI), W(VI) and U(VI).

Lead(II) and tin(II) interfere with the detection of germanium in electrolyte C,

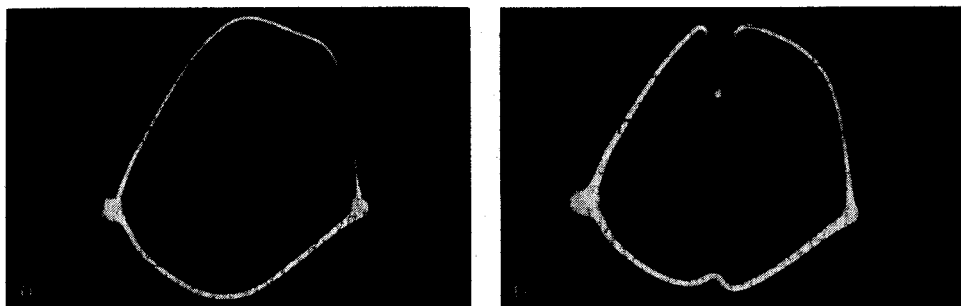


Fig. 1. (a) Oscillogram of supporting electrolyte C; (b) supporting electrolyte C with $4 \cdot 10^{-5}$ M germanium(IV).

because their incision potentials in this medium are the same. In electrolyte D the incision of germanium(IV) does not coincide with the incision of any other ion; the corresponding incisions of lead(II) and tin(II) appear at more negative potentials (Fig. 3).

The depth of the incision was found to be proportional to the concentration of germanium(IV). Calibration curves (Fig. 4) were drawn by plotting h -values *vs.* concentration in solutions C and D (h represents the distance between the extreme of the incision and the half-line of the curve).

TABLE II
ACTIVITY OF SOME IONS IN SUPPORTING ELECTROLYTES C AND D

Ion	Q Supporting electrolyte		Sensitivity (M)
	C	D	
As(III)	0.54	0.3	$1 \cdot 10^{-5}$
Sb(III)	0.54	0.3	$1 \cdot 10^{-5}$
Sn(II)	0.60	0.6	$5 \cdot 10^{-6}$
Pb(II)	0.60	0.46	$5 \cdot 10^{-6}$
Ga(III)	0.66	0.66	$1 \cdot 10^{-4}$

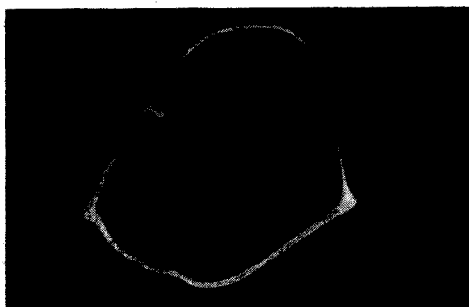


Fig. 2. Oscillopolarogram of supporting electrolyte D with $4 \cdot 10^{-5} M$ germanium(IV).

Fig. 3. Oscillopolarogram of germanium(IV) ($4 \cdot 10^{-5} M$) and lead(II) ($4 \cdot 10^{-5} M$) in supporting electrolyte D.

TABLE III
DETERMINATION OF GERMANIUM (%) IN ASHED COAL

Sample	Oscillopolarographic method	Spectrographic method ⁵
Pilpilco	0.0012	0.0014
Lota	0.00095	0.0012
Schwager	0.019	0.0212

Sn(II), Zn(II), Cd(II), Cu(II), Ni(II), Co(II), Mn(II), As(III), Sb(III), Cr(III), Ga(III), Fe(III), Bi(III), In(III), La(III), Ti(IV), Zr(IV), As(V), Sb(V), Mo(VI), W(VI) and U(VI) do not change the depth of the germanium(IV) incision in electrolyte D when their concentrations are less than 5-fold that of germanium. In electrolyte C, only lead(II) and tin(II) of the above-mentioned ions interfere.

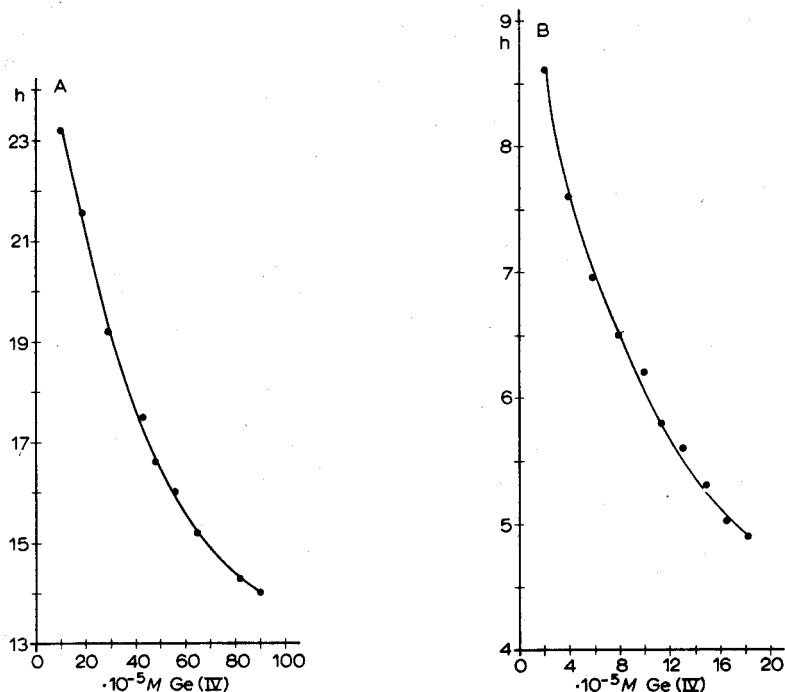


Fig. 4. (a) Calibration curve of germanium(IV) in supporting electrolyte C; (b) calibration curve of germanium(IV) in supporting electrolyte D.

Application

Supporting electrolyte D was used to determine germanium in Chilean coal ash. The samples were obtained from fume-hoods of industries that employ coals from the mines of Pilpilco, Lota and Schwager. Samples were fused with sodium carbonate or sodium peroxide, or digested with a mixture of nitric and sulfuric acids in the presence of hydrogen peroxide, to achieve dissolution. The results were compared with those obtained with a spectrographic method (Table III). Since the spectrographic method used is not very precise, the results obtained with the oscillographic method can be considered reasonable.

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ANNOUNCEMENT

A. A. BENEDETTI-PICHLER MEMORIAL AWARD

The American Microchemical Society has created a fund to commemorate the work of the late Dr. A. A. Benedetti-Pichler. The award will be made to an individual who has made outstanding contributions to the practice or teaching of microtechniques. The award will be given at regular intervals with the understanding that the recipient will give a lecture at a gathering of analytical chemists covering the field for which the award has been designed. A mutually agreeable location and occasion will be decided upon with the recipient.

Nominations are now being solicited and must be in the hands of the committee by May 1, 1969. A letter of 300 words or less, giving the name and address of the nominee and citing, in general, his work may be sent to the Chairman of the 1969 Committee, Mr. ERIK R. HOFFMANN, Ethicon, Inc., P. O. Box 151, Somerville, New Jersey 08876, U.S.A.

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ERRATUM

M. YANAGISAWA, M. SUZUKI AND T. TAKEUCHI, Extraction of manganese dithiocarbamate complexes for atomic absorption spectrophotometry, in *Anal. Chim. Acta*, 43 (1968) 500-502. The word "pyrrolidine" on the third line of p. 501 of the above paper should read "diethyl".

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