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# ANALYTICA CHIMICA ACTA

*International monthly devoted to all branches of analytical chemistry*  
*Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique*  
*Internationale Monatsschrift für alle Gebiete der analytischen Chemie*

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

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1. J. J. LINGANE AND A. M. HARTLEY, *Anal. Chim. Acta*, 11 (1954) 475.
  2. F. FEJFL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.
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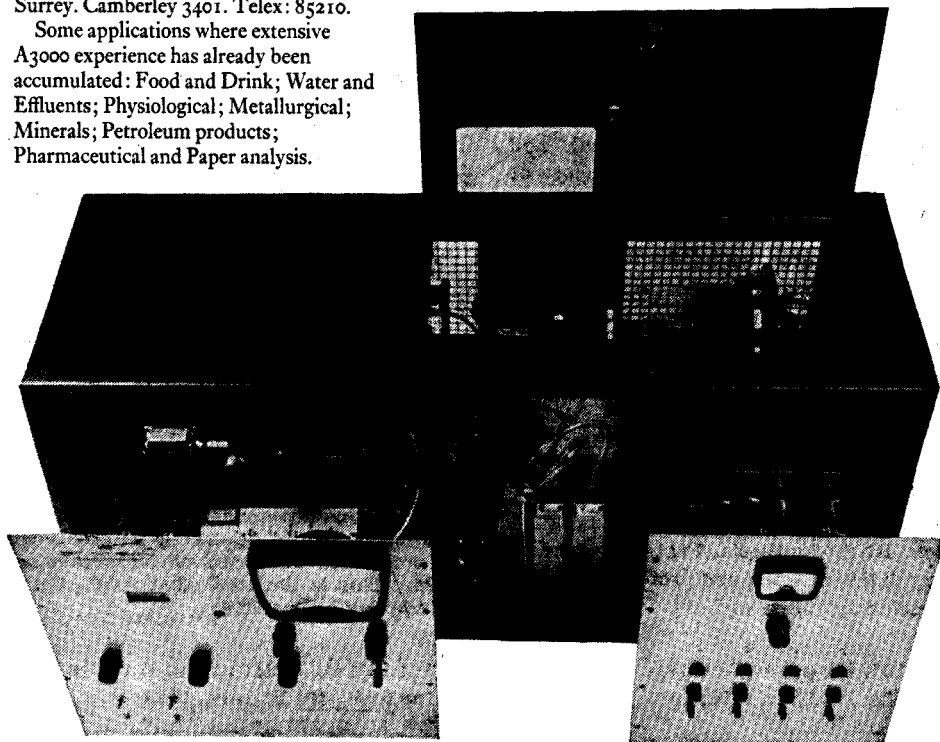
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Unsere Autoren sind als Diplom-Chemiker bei den Farbenfabriken Bayer AG tätig. Neben ihren Forschungsaufgaben im wissenschaftlichen Hauptlaboratorium beschäftigen sie sich mit Fragen der Ausbildung und erteilen mehrere Jahre Unterricht. Sie haben mit der Methode der programmierten Unterweisung Erfolge erzielt, die mit konventionellen Lehrbüchern nie zu erreichen gewesen wären.

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SUMMARIES OF PAPERS PUBLISHED IN  
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THE DETECTION OF IONS AND COMPOUNDS THAT CONSUME SULFIDE IONS

The colorless water-soluble alkali sulfomercurates behave in an alkaline milieu as sulfide-donors with simultaneous deposition of black mercury(II) sulfide. This permits the detection of inorganic and organic compounds that consume sulfide ions, either on the macro scale or within the bounds of the spot test technique. Among the inorganic compounds that consume sulfide are alkali hypohalogenites, cyanates, arsenites, arsenates, molybdates, tungstates, peroxides, and metal ions that are precipitated as sulfides in alkaline media. The following organic compounds have been found to be sulfide-consumers: alkali monochloroacetates and compounds which contain the  $\text{CH}_2$ -hal group; triketones; certain nitro compounds; ureides (barbituric acid and parabanic acid); purine compounds (uric acid, xanthine, theophylline, theobromine, caffeine, hydantoin, allantoin, uranil); oxamide and compounds that yield oxamide; dimethyl (diethyl) oxalate; strong organic oxidants (chloramine-T, chloramine-B, haloimides).

The behavior toward alkali sulfomercurate can be applied for the identification of malonic acid after its transformation to barbituric acid, and for the differentiation of *p*- and *o*-bromoacetophenone, 6- and 8-nitroquinoline, and cyanamide and dicyanamide.

F. FEIGL AND A. CALDAS,  
*Anal. Chim. Acta*, 49 (1970) 1-8

STUDIES WITH DITHIZONE

PART XX. ON THE NON-EXISTENCE OF SELENIUM DITHIZONATE

An organic-soluble yellow compound ( $\lambda_{\text{max}} \approx 420 \text{ nm}$ ) is formed when solutions of dithizone ( $\text{H}_2\text{Dz}$ ) in carbon tetrachloride are shaken with selenium(IV) in 6 *M* hydrochloric acid. STARÝ AND RŮŽIČKA ascribed the formula  $\text{Se}(\text{HDz})_4$ , showed that dithizone was regenerated on treatment with diethyldithiocarbamic acid (HDDC), and reported equilibrium constants for its "exchange reactions" with a number of metal complexes. The alleged selenium dithizonate does not exist. The yellow material is not a compound of selenium but an oxidation product of dithizone, viz. di-(1,5-diphenylformazyl-3)-disulphide which disproportionates on keeping (more rapidly in chloroform) to a mixture of dithizone and a sydnone, anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide. The disulphide can also be prepared stoichiometrically by oxidising dithizone with iodine and it is reduced back to dithizone by HDDC or hypophosphorous acid. These findings do not affect the procedures proposed for determining traces of selenium absorptiometrically, but STARÝ AND RŮŽIČKA's work is invalidated.

R. S. RAMAKRISHNA AND H. M. N. H. IRVING,  
*Anal. Chim. Acta*, 49 (1970) 9-17

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B. L. TWITTY AND M. W. BOBACK,  
*Anal. Chim. Acta*, 49 (1970) 19-24

## CHRONOPOTENTIOMETRY AND COULOMETRIC TITRATION OF N-SUBSTITUTED PHENOTHIAZINES

The electrochemical oxidation at a platinum anode of several N-substituted phenothiazines (levopromazine, chlorpromazine, miltorgan, profenamine, promethazine, diethazine, and thioproperazine) has been studied by the chronopotentiometric technique. A method has been developed for the coulometric titration of these substances with electrogenerated cerium(IV) ion. Quantities of 0.25-20 mg are determinable with an average error of less than  $\pm 1$  rel. %.

G. J. PATRIARCHE AND J. J. LINGANE,  
*Anal. Chim. Acta*, 49 (1970) 25-34

## TITRATION CURVES OF COMPLEXIMETRIC BACK-TITRATIONS

### PART I. MATHEMATICAL EXPRESSIONS

Formulae were calculated for the compleximetric back-titration of mixtures of metals, giving the relation between a titration parameter  $f$  and the concentration of the metals or the ligand. It is shown that the scope of these titrations is wider than has been realized.

U. HANNEMA AND G. DEN BOEF,  
*Anal. Chim. Acta*, 49 (1970) 35-42

## TITRATION CURVES OF COMPLEXIMETRIC BACK-TITRATIONS

### PART II. CONDITIONS FOR SHARP END-POINTS WITH INDICATION BY MEANS OF THE TITRANT

Conditions are derived for sharp end-points in compleximetric back-titrations of mixtures of metals with visual or potentiometric indication.

U. HANNEMA AND G. DEN BOEF,  
*Anal. Chim. Acta*, 49 (1970) 43-49

## THE MASS SPECTRA OF ORGANIC MOLECULES

by J. H. Beynon, R. A. Saunders and A. E. Williams, Research Department,  
Imperial Chemical Industries Ltd., Manchester, Great Britain

7 x 10", ix + 510 pages, 20 tables, 181 illus., 547 lit. refs., 1968, Dfl. 97.50

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## MASS SPECTROMETRIC ANALYSIS OF SOLIDS

edited by A. J. Ahearn, Member of Technical Staff, Bell Telephone Laboratories, Inc.,  
Murray Hill, New Jersey, U.S.A.

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

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## ATOMIC-ABSORPTION SPECTROSCOPY

and Analysis by Atomic-Absorption Flame Photometry

by J. Ramirez-Muñoz, Principal Applications Chemist at Beckman Instruments Inc. and Scientific  
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R. PIETSCH AND H. SINIC,  
*Anal. Chim. Acta*, 49 (1970) 51-56

## EXTRACTION OF TRACES OF CERIUM, EUROPIUM, TERBIUM AND LUTETIUM FROM URANIUM(VI) SOLUTIONS WITH DI-2-ETHYLHEXYL PHOSPHORIC ACID

Extraction measurements have been performed in order to explain the behaviour of rare-earth traces on an HDEHP-treated chromatographic column in the presence of milligram quantities of uranium(VI). Under column conditions the rare-earth separation factors are lowered, and this impairs the separation. A combined mechanism involving displacement reactions between UO<sub>2</sub><sup>2+</sup> and R.E.<sup>3+</sup>, and degradation of the uranium(VI) polymeric complex, is suggested to explain the retarded transfer of a rare-earth trace into the aqueous phase. It is shown that at HDEHP:uranium(VI) ratios above 6, the extraction of rare earths is not affected by the presence of uranium(VI), which makes possible the gradual separation of rare-earth traces from uranium(VI) solutions.

B. TOMAŽIČ,  
*Anal. Chim. Acta*, 49 (1970) 57-65

## SOLVENT EXTRACTION OF METALS BY ALKYL-SUBSTITUTED β-DIKETONES

The extractions of Pd<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup> and Cd<sup>2+</sup> by solutions of dipropionylmethane, diisobutyrylmethane, pivaloylacetylmethane and dipivaloylmethane in benzene, have been studied in relation to the pH values for extraction. The extraction constants and two-phase stability constants of the β-diketones were calculated. These can be used to establish the optimum conditions for the separation of the metals.

H. KOSHIMURA AND T. OKUBO,  
*Anal. Chim. Acta*, 49 (1970) 67-75

# 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                          |
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| 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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## A STUDY OF EQUILIBRIUM ISOTOPE EFFECTS OF TERTIARY AMINES BY NMR AND POTENTIOMETRY

A comparative study of solvent isotope effects on the dissociation constant of amine salts, by means of potentiometric and nuclear magnetic resonance techniques has been performed. Agreement of the results of the two techniques was generally good. The magnetic resonance technique offers an advantage in cases in which the amine is insoluble in neutral or basic solutions. An observed correlation between the isotopic shift of N-methyl proton chemical shift and the spin coupling between the methyl protons and the N-H proton is mentioned.

D. E. LEYDEN AND J. M. MCCALL,  
*Anal. Chim. Acta*, 49 (1970) 77-81

## ANODIC VOLTAMMETRIC DETERMINATION OF PLUTONIUM

### DIFFUSION COEFFICIENTS OF PLUTONIUM(III) IN MINERAL ACIDS

Plutonium(III) can be determined at the glassy carbon electrode by anodic voltammetry in the concentration range  $2.24 \cdot 10^{-4}$ – $4.48 \cdot 10^{-3}$  M in 0.5 M perchloric acid. Any oxidizing substance and iron(II) interfere. Hydrochloric, nitric and sulfuric acids also interfere at various concentrations. Diffusion coefficients were determined in 0.5 M perchloric, hydrochloric, nitric and sulfuric acids.

C. E. PLOCK,  
*Anal. Chim. Acta*, 49 (1970) 83-87

## THE SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM WITH ERIOCHROME BRILLIANT VIOLET B

Beryllium can be determined spectrophotometrically with eriochrome brilliant violet B (C.I. 43570). The complex shows maximum absorbance at pH 5.8–7.0; Beer's law is obeyed over the range 0.02–0.15 p.p.m. of beryllium at 560 nm. The molar absorptivity is 59500 and the sensitivity is 0.0002  $\mu$ g of beryllium per  $\text{cm}^2$ , corresponding  $\log I_0/I = 0.001$ . The mole ratio of beryllium and eriochrome brilliant violet B in the complex is estimated to be 1:2. Copper(II), cadmium, nickel, aluminum, iron(III), chromium(III), yttrium, scandium, and the rare earth elements interfere seriously; a method of separation is described.

K. UESUGI,  
*Anal. Chim. Acta*, 49 (1970) 89-95

## THE USE OF OXAZINES IN ANALYSIS

### PART II. THE SPECTROPHOTOMETRIC DETERMINATION OF IODIDE AND BROMIDE WITH NILE BLUE

(in German)

The determination of micro amounts of iodide or bromide with the oxazine dyestuff Nile Blue is described. The salt of the dye is extracted into chloroform and measured spectrophotometrically at 626 nm. Beer's law is obeyed over the range 0.5–3 p.p.m. for iodide and 1–6 p.p.m. for bromide. The methods are evaluated statistically and the effects of diverse ions are described.

W. LIKUSSAR, G. POKORNY AND H. ZECHMANN,  
*Anal. Chim. Acta*, 49 (1970) 97-102

# 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 first 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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## SPECTROPHOTOMETRIC STUDY OF THE REACTION OF NICKEL(II) WITH 4-(2-PYRIDYLAZO)-RESORCINOL IN ALKALINE MEDIA

Nickel(II) forms an orange complex with 4-(2-pyridylazo)-resorcinol in aqueous solutions at pH 8. Maximum absorbance is obtained at 495 nm and the metal/ligand ratio is 1 : 3. The molar absorptivity is  $76,400 \pm 300$  and the spectrophotometric sensitivity is  $0.00077 \mu\text{g Ni cm}^{-2}$  for  $A = 0.001$ . Beer's law is followed in the range  $0.024$ – $0.82 \mu\text{g Ni ml}^{-1}$ . Equilibrium constants have been calculated.

D. NONOVA AND B. EVTIMOVA,  
*Anal. Chim. Acta*, 49 (1970) 103–108

## DETERMINATION OF NIOBIUM IN ROCKS BY AN ISOTOPE DILUTION-SPECTROPHOTOMETRIC METHOD

Rocks and minerals are fused with sodium peroxide in the presence of carrier-free  $^{95}\text{Nb}$ . The fusion cake is leached with water and the precipitate dissolved in hydrofluoric-sulfuric acid mixture. Niobium is extracted into methyl isobutyl ketone and further purified by ion exchange. The amount of niobium is determined spectrophotometrically with 4-(2-pyridylazo)-resorcinol, and the chemical yield of the separations determined by counting  $^{95}\text{Nb}$ . This procedure is faster and less sensitive to interferences than previously proposed methods for determining niobium in rocks. The high purity of the separated niobium makes the method applicable to nearly all matrices.

L. P. GREENLAND AND E. Y. CAMPBELL,  
*Anal. Chim. Acta*, 49 (1970) 109–114

## THE ACIDITY OF METALLIC CATIONS IN ANHYDROUS ACETIC ACID SOLUTIONS

### VARIATION OF THE REDUCTION POTENTIAL OF METALS AND AMALGAMS WITH pH

(in French)

A study made principally by measuring equilibrium potentials has enabled determination of the nature and the formation constants of acetate complexes of the elements Bi(III), Cd(II), Pb(II), Zn(II), Sn(II), Ag(I), Cu(I), Hg(I) and Tl(I) in solution in anhydrous acetic acid (+  $0.5 M \text{LiClO}_4$ ); the complexes of indium(I) could not be established because of the irreversible behaviour of the electrode of this metal. The experimental results have been evaluated by computer techniques; the confidence intervals are given. The reducing power of these metals and their corresponding amalgams is represented on a potential-pH diagram.

J.-C. TOULLER AND B. TRÉMILLON,  
*Anal. Chim. Acta*, 49 (1970) 115–134

# SUBMICRO METHODS OF ORGANIC ANALYSIS

by R. BELCHER

Professor of Analytical Chemistry,  
The University of Birmingham, Great Britain

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

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

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

# TABLE OF META-STABLE TRANSITIONS FOR USE IN MASS SPECTROMETRY

by J. H. BEYNON, R. A. SAUNDERS AND A. E. WILLIAMS

Research Department, Imperial Chemical Industries Ltd.,  
Manchester, Great Britain

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

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

# STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Second International Symposium organized by the Chromatography  
Group of the Czechoslovak Chemical Society, at Liblice

by K. MACEK AND I.M.HAIS

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

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



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## AN ELECTROCHEMICAL STUDY OF IODINE IN ANHYDROUS ACETIC ACID SOLUTIONS

(in French)

A voltammetric study, with a platinum electrode, of the reduction of iodine in anhydrous acetic acid media and measurements of equilibrium potentials of iodine/iodide mixtures in 0.5 M NaClO<sub>4</sub> and 1 M NaOAc + 0.5 M NaClO<sub>4</sub> media, have allowed the determination of the formation constant of the iodine-iodide complex in acetic acid:

$\text{NaI} + \text{I}_2 \rightleftharpoons \text{NaI}_3$ ,  $\log \beta/\text{mole}^{-1} \text{l} = 5.24 \pm 0.12$ . This value is greater than that given by GUIDELLI AND PICCARDI (4.4).

The oxidation of iodine has been studied by voltammetry, constant potential coulometry and also with a ring-disk electrode. The observed phenomena can be explained as follows: iodine is oxidized to I<sup>+</sup> cations, which then react with the acetic acid to form mono-iodoacetic acid. This acid is then oxidized in the same way as for the KOLBE reaction with consumption of acetic acid and regeneration of iodoacetic acid.

G. DURAND AND B. TRÉMILLON,  
*Anal. Chim. Acta*, 49 (1970) 135-149

## TRACE ELEMENT ANALYSIS OF SOLUTIONS BY HOLLOW-CATHODE EXCITATION

Construction and operation of a shielded hollow-cathode tube for emission spectrometric trace element analysis of solutions is described. The demountable tube design also permits the tube to be used as a versatile line source in atomic absorption spectrometry. Quantitative analysis of solutions can be performed after evaporation of a small portion of the test solution containing a suitable carrier salt in the cavity of the hollow cathode. Both stainless steel and graphite have been studied as cathodes. The effects of cathode material, filler gas, lamp current, and carrier salt were investigated for solutions of lead, copper, boron, and tin. The precision attainable in quantitative analysis is of the order of  $\pm 3-5\%$ .

W. W. HARRISON AND N. J. PRAKASH,  
*Anal. Chim. Acta*, 49 (1970) 151-159

## ULTRAVIOLET EMISSION AND ABSORPTION SPECTRA PRODUCED BY ORGANIC COMPOUNDS IN OXYHYDROGEN FLAMES

### PART II. ABSORPTION SPECTRA. CONTINUOUS SOURCE

Ultraviolet absorption spectra produced by aspirating organic compounds into oxyhydrogen flames have been investigated. Spectra are presented and compared. The prominent bands observed are listed by wavelength and absorbing species. Flame absorption profiles for organic and inorganic fragments are presented. Maximum absorption by organic fragments occurred in the reaction zone of the flame. Absorption by OH fragments and by fragments containing phosphorus or sulfur was intense above and within the reaction zone of the flame. Absorption by whole solvent molecules in the flame was observed.

V. J. SMITH AND J. W. ROBINSON,  
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J. MATOUŠEK AND V. SYCHRA,  
*Anal. Chim. Acta*, 49 (1970) 175-181

## LOCATION METHOD FOR AMINO ACIDS AND SOME AMINES ON CHROMATOGRAMS AND ELECTROPHEROGRAMS

(*Short Communication*)

M. GUYER, JR. AND E. SAWICKI,  
*Anal. Chim. Acta*, 49 (1970) 182-184

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## A CAPILLARY TUBE SAMPLE HOLDER FOR DIFFERENTIAL SCANNING CALORIMETRY

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*(Short Communication)*

T. PANALAKS,

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A. CALDAS,

*Anal. Chim. Acta*, 49 (1970) 194

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G. F. ATKINSON AND I. J. ITZKOVITCH,

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## THE DETECTION OF IONS AND COMPOUNDS THAT CONSUME SULFIDE IONS

FRITZ FEIGL AND ALCIDES CALDAS

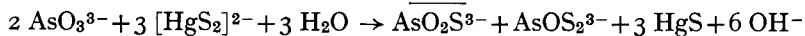
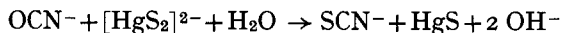
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The following equilibria are present in the colorless solution obtained by dissolving mercury(II) sulfide in sodium sulfide:

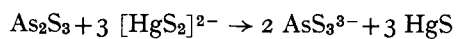


Obviously these equilibria can be disturbed, with simultaneous precipitation of black mercury(II) sulfide, not only by the action of hydrogen ions but also by the addition of ions or compounds that consume sulfide ions. *The occurrence of reactions that consume sulfide ions can be revealed in this way even in those cases in which the reactions with alkali sulfide are not directly visible.* This finding is well illustrated by the behavior of alkali cyanate and alkali arsenite, in alkaline media, toward sodium sulfide and sodium sulfomercurate ( $\text{Na}_2[\text{HgS}_2]$ ). No change is observed with sodium sulfide, whereas mercury(II) sulfide precipitates if sulfomercurate is used:



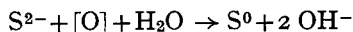
In line with expectations, solutions of alkali arsenate, molybdate and tungstate were found to behave like alkali arsenite with respect to partial O  $\rightarrow$  S exchange and simultaneous precipitation of mercury(II) sulfide. There appears to be no report in the literature describing the behavior of alkali cyanate as a sulfide consumer in wet reactions. An experimental confirmation of this finding was obtained by warming a solution of sodium sulfomercurate with excess of potassium cyanate, and then removing the precipitated mercury(II) sulfide by centrifuging; the addition of an acidic solution of iron(III) chloride to the clear liquid yielded immediately the familiar red iron(III) thiocyanate. The precipitation of mercury(II) sulfide by warming a mixture of the suspected cyanate with an alkali sulfomercurate may serve as a test for cyanate. However, this new test is not very sensitive; the detection limit, for example, was found to be 500  $\mu\text{g}$  of potassium cyanate.

The action of sulfomercurate as a sulfide-donor and the action of arsenic trisulfide as a sulfide-acceptor can be readily shown by warming a solution of an alkali sulfomercurate with an excess of arsenic trisulfide. Mercury(II) sulfide is precipitated. The reaction may be written:



This reaction permits the differentiation of the yellow arsenic(III) sulfide from the likewise yellow cadmium sulfide and uranyl sulfide, since the latter remain unaltered.

Some attention should be given here to the behavior of inorganic oxidants that react with sulfide in alkaline media. Pertinent oxidizing agents are alkali permanganate, hypohalogenite, hexacyanoferrate(III) and hydrogen peroxide. The underlying redox reaction is:



with production of mercury(II) sulfide if sodium sulfomercurate is used as sulfide-donor. However, the tests for inorganic oxidants based on this behavior were found to be of little use since they are not very sensitive. On the other hand, the action of sulfomercurates as sulfur-donors with accompanying deposition of mercury(II) sulfide may be applied as a sensitive preliminary spot test in qualitative inorganic analysis to reveal the presence of metal ions that produce insoluble sulfides in alkaline media.

The reactions with alkali sulfomercurates are not restricted to inorganic ions and compounds that consume sulfide ions. Organic preparative chemistry has frequently shown that alkali sulfide may be involved in redox and condensation reactions with suitable organic participants. The occurrence of pertinent reactions may be revealed through the precipitation of mercury(II) sulfide if an alkali sulfomercurate is used in place of alkali sulfide. The following pertinent reactions indicate that such changes can be of interest in qualitative organic analysis. The following tests and trials can be conducted within the spot test technique.

## EXPERIMENTAL

### *Procedure*

A small amount of the solid sample or a drop of the test solution is placed in a micro test tube or in a depression of a spot plate and made slightly alkaline, if need be, by adding a drop of sodium hydroxide solution. One or two drops of the reagent solution are added to the mixture. A positive response is indicated by the production of a black precipitate (HgS) at once or after a brief time.

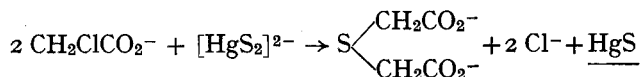
### *Sulfomercurate reagent*

Freshly prepared mercury(II) sulfide (1.5–2 g) is added to 50 ml of 2 M sodium or potassium hydroxide. A stream of hydrogen sulfide is passed through the suspension for 10 min. The latter is warmed and the excess of mercury(II) sulfide is removed by filtering. The clear solution will keep for several days in a closed container.

## DETECTION OF ORGANIC COMPOUNDS AND GROUPS

### *Behavior of alkali monochloroacetate and compounds containing a CH<sub>2</sub>-hal group*

KLASON AND CARLSON<sup>1</sup> found that neutral or alkaline solutions of alkali monochloroacetate react with alkali sulfide to yield alkali thioglycolate. It has now been observed that if sulfomercurate is used as the sulfide-donor, the reaction yields thiodiglycolate plus mercury(II) sulfide:



In alkaline media, this reaction occurs almost instantaneously and permits the detection of monochloroacetic acid (Ident. limit = 2  $\mu\text{g}$ ) and its differentiation from the corresponding di- and trichloroacetic acids, which do not react. This same behavior has been found to hold for the corresponding bromoacetic acids.

The release of halogen ions as shown in the preceding equation and also the formation of mercury(II) sulfide occur likewise with other compounds that contain a  $\text{CH}_2\text{Cl}$ -group. Ethylene chlorohydrin ( $\text{CH}_2\text{ClCH}_2\text{OH}$ ), epichlorohydrin ( $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{Cl}$ ), chloroacetamide ( $\text{CH}_2\text{ClCONH}_2$ ) and benzyl chloride ( $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ )

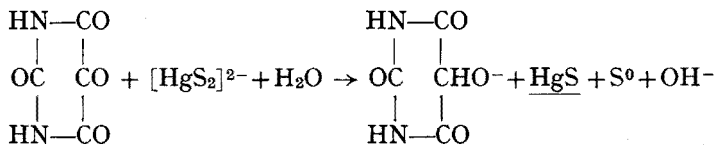
show this same behavior and it is likely that a test for the  $-\text{CH}_2\text{Cl}$  group will be developed with this behavior as its basis. This prediction is buttressed by the finding that  $\omega$ -bromoacetophenone reacts promptly with the sulfomercurate reagent whereas its isomer, which incidentally also has the melting point  $50^\circ$ , is inactive.



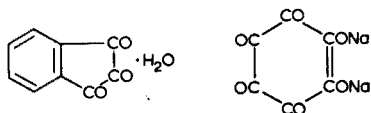
This difference in behavior presents an excellent example of the differentiation of two isomers by means of a simple spot test.

#### *Behavior of triketones*

Alloxan is reduced by alkali sulfide with production of the alkali salt of dialluric acid<sup>2</sup>. If alkali sulfomercurate is employed as the reductant, mercury(II) sulfide is precipitated:



It has been found that ninhydrin (triketohydrindene hydrate) and sodium rhodizonate, which have the structures



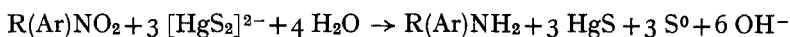
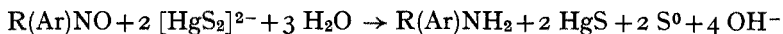
behave like alloxan. This behavior is probably due to the presence in these molecules of three vicinal CO groups and the centrally situated CO group is reduced to a CHOH group. 1,2-Diketones remain unchanged on treatment with sulfomercurate; for instance, diacetyl and benzil were found to be inactive in this regard.

#### *Behavior of nitroso and nitro compounds*

It was expected that nitro and nitroso compounds would be reduced by excess



sulfomercurate solution to yield the respective amines along with a deposition of mercury(II) sulfide:



However, trials with nitroso compounds have demonstrated that the nitroso group is not reduced by sulfomercurate. Negative results were obtained with *N*-nitrosodiphenylamine, and its isomer *p*-nitrosodiphenylamine, as well as with  $\alpha$ -nitroso- $\beta$ -naphthol, nitroso-R-salt, and *p*-nitrosodimethylaniline.

The behavior of nitro compounds toward sulfomercurate follows no uniform pattern. Some nitro compounds react immediately with deposition of mercury(II) sulfide while others remain unaffected. The first category includes, for instance, *o*-, *m*-, *p*-nitrophenol, *o*-nitrobenzaldehyde, dipicrylamine and 3,5-dinitrobenzoic acid. Among the nitro compounds that are resistant to the sulfomercurate reagent are nitronaphthalene, picric acid, dinitroresorcinol and 2,4-dinitrophenylhydrazine.

These findings regarding the behavior of nitroso and nitro compounds toward sulfomercurate are in accord with the literature dealing with the preparation of aliphatic and aromatic primary amines<sup>3</sup>. The spotting with sulfomercurate cannot be applied as general test for aliphatic and aromatic compounds.\*

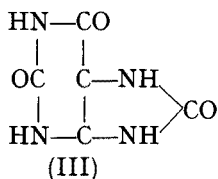
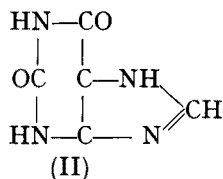
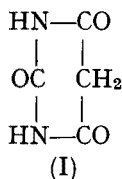
#### *Behavior of 6- and 8-nitroquinoline*

The behavior of nitro compounds toward sulfomercurate was described above and found to be not uniform; accordingly, attention was directed to the behavior of 6- and 8-nitroquinoline. When these positional isomers are treated with alkali sulfomercurate in alkaline medium, the 6-nitroquinoline reacts at once as indicated by an immediate deposition of mercury(II) sulfide. In contrast, 8-nitroquinoline remains unchanged even when warmed with this reagent. This again is a fine example of the use of spot tests for the differentiation of isomers.

The redox reaction with alkali sulfomercurate permits the detection of 10  $\mu\text{g}$  of 6-nitroquinoline in the presence of 1000 times as much of 8-nitroquinoline.

#### *Behavior of compounds that contain a cyclically bonded —N—CO—N— group*

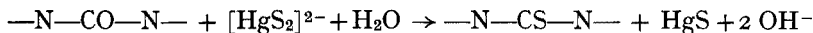
This category includes ureides and purine compounds as shown by the structures of barbituric acid (I), xanthine (II) and uric acid (III):



It was found that I, II and III as well as other compounds with a cyclically bound —N—CO—N— group react with alkali sulfomercurate readily and with immediate

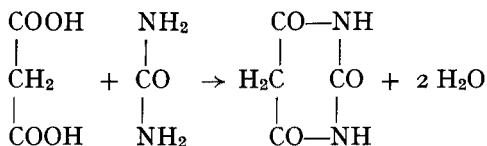
\* The best test for this purpose is based on the production of colored addition compounds by brief treatment with molten diphenylamine or tetrabase<sup>4</sup>.

deposition of mercury(II) sulfide. In all likelihood, there is an O → S exchange as shown in the following equation:



Positive results were obtained with 500- $\mu\text{g}$  amounts of barbituric acid, parabanic acid, uric acid, xanthine, theophylline, caffeine, hydantoin, allantoin and uranil.

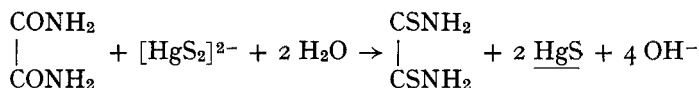
It may be noted that a test for malonic acid may be based on its reaction with fused (*ca.* 130°) urea:



followed by the test for the barbituric acid formed with sulfomercurate.

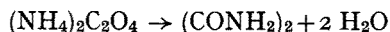
#### *Behavior of oxamide and dimethyl (ethyl) oxalate*

Contrary to expectations, these compounds behave as sulfide-consumers, as indicated by the precipitation of mercury(II) sulfide when they are treated with the sulfomercurate reagent. In contrast to this activity by non-electrolytes, alkali oxalates and, likewise, calcium oxalate, do not react. The underlying reaction in the case of oxamide yields dithiooxamide (rubeanic acid):



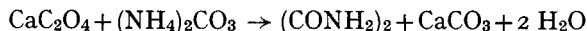
The occurrence of this hitherto unknown exchange of sulfur for oxygen was proved by the following experiment. A solution of sodium sulfomercurate was warmed with an excess of oxamide and then filtered. The filtrate was found to react with nickel(II) to give the violet nickel rubeanate which was first observed and then employed in analysis by RAY<sup>5</sup>. It is very likely that dimethyl (ethyl) oxalate undergoes the same type of reaction on treatment with sulfomercurate.

The action of oxamide as a sulfide-consumer with simultaneous precipitation of mercury(II) sulfide can be used not only as a means of detecting this amide but also for the detection of oxamide-formers. A good instance is the conversion of oxalic acid into oxamide. The successive necessary steps are: (1) formation of ammonium oxalate through evaporation of the test material with ammonium hydroxide or ammonium carbonate and (2) dry heating (200°) to convert the ammonium oxalate to oxamide:



If spot test techniques are used, this test permits the detection of 1  $\mu\text{g}$  of oxalic acid.

It has also been found that calcium oxalate yields oxamide by fuming with ammonium carbonate followed by dry heating to 200°. The underlying net reaction is:



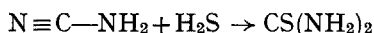
By carrying out this transformation and then spotting with the sulfomercurate

reagent, it is possible to detect calcium oxalate in mixtures with either water-soluble or water-insoluble inorganic or organic calcium salts.

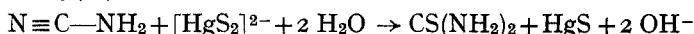
In this connection it should be pointed out that a color reaction for the detection of oxamide and also of compounds that can be converted into oxamide has been published<sup>6</sup>. The reagent suggested is thiobarbituric acid. Such compounds include esters of oxalic acid, alkyl oxamates, oxanilide, oxanilic acid, oxalic hydrazides, and nitriles and amides of carboxylic acids. Sulfomercurate reagent can be substituted for the thiobarbituric acid in these cases.

#### *Behavior of cyanamide and dicyanodiamide*

Thiourea is often prepared by adding hydrogen sulfide (or ammonium sulfide) to cyanamide<sup>7</sup>:

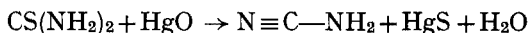


However, if sulfomercurate is used as the sulfide-donor, the products are thiourea and mercury(II) sulfide:



Cyanamide can be detected on the basis of this reaction and also differentiated from dicyanodiamide since the latter does not react with sulfomercurate.

The aqueous solution of cyanamide needed for this investigation was prepared<sup>8</sup> by treating a solution of thiourea with an excess of mercury(II) oxide and filtering:



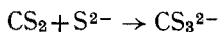
It should be noted that a new selective test for thiourea may be based on the above sulfuration followed by reaction of the resultant cyanamide with the sulfomercurate reagent. This test, whose essential steps are the decomposition and regeneration of thiourea, can be carried out on the macro scale or if preferred within the technique of spot test analysis.

#### *Behavior of haloimides*

Compounds of this class yield hypohalogenites on saponification and consequently in alkaline media are strong oxidants<sup>9</sup>. They are consumers of sulfide ions and hence react with the alkali sulfomercurate reagent. The following compounds were found to give a positive response, mercury(II) sulfide being deposited: N-chloro-(bromo)succinimide, chloramine-T, chloramine-B, 2,6-dibromoquinone-4-chlorimine and 2,6-dichloroquinone-4-chloroimine. No reaction was given by chloranil and benzoyl peroxide. However, these spot tests for haloimides involving alkali sulfomercurate are not sensitive\*.

#### *Behavior of carbon disulfide*

Carbon disulfide is well known to be a consumer of sulfide ions and produces trithiocarbonate:

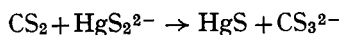


\* A good spot test for detecting organic oxidants that are active in alkaline solution is based on the formation of brown thallium (III) oxyhydrate:



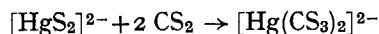
Microgram amounts of these oxidants may be detected in this way<sup>10</sup>.

Therefore it was logical to expect that on treatment with alkali sulfomercurate as sulfide-donor, mercury(II) sulfide would be formed along with alkali trithiocarbonate; in other words, the following reaction was expected:



However, actual trials showed that no mercury(II) sulfide is formed when a solution of alkali sulfomercurate is shaken with carbon disulfide or if the reagent is slightly warmed with a solution of carbon disulfide in alcohol. No precipitate appeared; instead the mixture turned orange.

A possible explanation is that the addition of carbon disulfide to a solution of sulfomercurate leads to the formation of a water-soluble orange alkali mercury trithiocarbonate:



This assumption is in accord with the finding by ROSENBLATT<sup>11</sup> that freshly prepared mercury(II) sulfide is readily soluble in alkali trithiocarbonate, probably owing to the formation of the complex anion shown above.

The authors are grateful to Mrs. E. Libergott for her assistance in the experimental work and to the Conselho Nacional de Pesquisas for its financial support of this investigation.

#### SUMMARY

The colorless water-soluble alkali sulfomercurates behave in an alkaline milieu as sulfide-donors with simultaneous deposition of black mercury(II) sulfide. This permits the detection of inorganic and organic compounds that consume sulfide ions, either on the macro scale or within the bounds of the spot test technique. Among the inorganic compounds that consume sulfide are alkali hypohalogenites, cyanates, arsenites, arsenates, molybdates, tungstates, peroxides, and metal ions that are precipitated as sulfides in alkaline media. The following organic compounds have been found to be sulfide-consumers: alkali monochloroacetates and compounds which contain the CH<sub>2</sub>-hal group; triketones; certain nitro compounds; ureides (barbituric acid and parabanic acid); purine compounds (uric acid, xanthine, theophylline, theobromine, caffeine, hydantoin, allantoin, uranil); oxamide and compounds that yield oxamide; dimethyl (diethyl) oxalate; strong organic oxidants (chloramine-T, chloramine-B, haloimides).

The behavior toward alkali sulfomercurate can be applied for the identification of malonic acid after its transformation to barbituric acid, and for the differentiation of *p*- and *ω*-bromoacetophenone, 6- and 8-nitroquinoline, and cyanamide and dicyanamide.

#### RÉSUMÉ

Les sulfomercurates alcalins incolores, solubles dans l'eau, se comportent en milieu basique comme donneurs d'ions sulfures avec formation simultanée de sulfure de mercure(II) noir. Ceci permet de déceler des composés inorganiques et organiques

qui consomment des ions sulfures. Parmi les composés inorganiques nous pouvons citer: les hypohalogénures alcalins, cyanates, arsénites, arséniates, molybdates, tungstates, peroxydes et ions métalliques précipitant comme sulfures; pour les composés organiques, nous avons: les monochloroacétates alcalins et composés renfermant le groupe  $\text{CH}_2\text{-hal}$ , les tricétones, certains nitrocomposés, les uréides, les dérivés de la purine, les oxamides, le diméthyl (ou diéthyl) oxalate et les oxydants organiques forts. Cette réaction peut servir également à identifier l'acide malonique après transformation en acide barbiturique et pour différencier divers composés.

#### ZUSAMMENFASSUNG

Die farblosen, wasserlöslichen Alkalisulfomercurate geben im alkalischen Milieu Schwefel ab unter gleichzeitiger Bildung von schwarzem Quecksilber(II)-sulfid. Dies ermöglicht den Nachweis von anorganischen oder organischen Verbindungen, die Sulfidionen aufnehmen, entweder im Makrobereich oder bei der Tüpfelanalyse. Anorganische Verbindungen, die Sulfidionen verbrauchen, sind Alkalihypohalogenite, Cyanate, Arsenite, Arsenate, Molybdate, Wolframate, Peroxide und Metallionen, die im alkalischen Medium als Sulfid gefällt werden können. Folgende organische Verbindungen verbrauchen Sulfidionen: Alkalimonochloroacetate und Verbindungen, die  $\text{CH}_2\text{Halogen}$ -Gruppen enthalten; Triketene; gewisse Nitroverbindungen; Ureide; Purine; Oxamide und Verbindungen die Oxamide bilden; Dimethyloxalat; starke organische Oxydationsmittel. Das Verhalten gegenüber Alkalisulfomercuraten kann verwendet werden zur Identifizierung von Maleinsäure nach ihrer Umlagerung zur Barbitursäure und zur Unterscheidung von *p*- und *b*-Bromoacetophenon, 6- und 8-Nitrochinolin und Cyanamid und Dicyanamid.

#### REFERENCES

- 1 P. KLASON AND T. CARLSON, *Ber.*, 39 (1906) 733.
- 2 V. GRIGNARD, *Précis de Chimie Organique*, 4me éd., Masson, Paris, 1958, p. 557.
- 3 Compare R. E. WAGNER AND H. D. ZOOK, *Synthetic Organic Chemistry*, J. Wiley Inc., New York, 1953, Chapter 23.
- 4 F. FEIGL, *Spot Tests in Organic Analysis*, 7th Edn., Elsevier, Amsterdam, 1966, p. 295.
- 5 P. RAY, *Z. anal. Chem.*, 79 (1929) 94.
- 6 F. FEIGL, *Spot Tests in Organic Analysis*, 7th Edn., Elsevier, Amsterdam, 1966, Chapters 2 and 5.
- 7 PAUL KARRER, *Lehrbuch der Organische Chemie*, 12th Edn., Stuttgart, 1959, p. 236.
- 8 Compare BEILSTEIN, *Handbuch der Organische Chemie*, vol. III (1921) p. 75.
- 9 J. TSCHERNIAC, *Ber.*, 34 (1901) 4209.
- 10 F. FEIGL AND R. A. ROSELL, *Z. anal. Chem.*, 159 (1958) 335.
- 11 TH. ROSENBLATT, *Z. anal. Chem.*, 26 (1886) 15.

## STUDIES WITH DITHIZONE

### PART XX. ON THE NON-EXISTENCE OF SELENIUM DITHIZONATE

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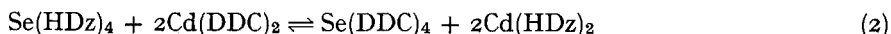
In 1963 MABUCHI AND NAKAHARA<sup>1</sup> reported the extraction of selenium(IV) from 6 *N* hydrochloric acid by a solution of dithizone (3-mercapto-1,5-diphenylformazan; H<sub>2</sub>Dz) in carbon tetrachloride. They described mono-colour and mixed colour procedures for the determination of traces of selenium at 420 and 410 nm respectively with sensitivities<sup>2</sup> of 0.001 and 0.002  $\mu\text{g}$  selenium per cm<sup>2</sup>, and noted the effect of interfering ions. The molecular extinction coefficient for the selenium-dithizone complex (whose composition was not determined) was given as  $70 \cdot 10^3$  at 420 nm: this would seem to be remarkably low for a complex containing four dithizone residues<sup>3</sup>.

SHCHERBOV *et al.*<sup>4</sup> made a critical survey of reagents proposed for the determination of selenium and reported that dithizone was the most sensitive. A procedure for liquid-liquid extraction from 6 *M* hydrochloric acid or 5.5 *M* sulphuric acid was worked up for the determination of selenium in raw minerals and ores after their wet oxidation. The coefficient of variance was less than 15% for samples containing  $10^{-3}$ – $10^{-4}\%$  of selenium.

More recently STARÝ AND RŮŽIČKA<sup>5</sup> prepared what they believed to be selenium(IV) dithizonate and deduced its composition as Se(HDz)<sub>4</sub> on the basis of the following experiment. First, selenium(IV) in 5 *M* hydrochloric acid was allowed to react with excess of dithizone dissolved in carbon tetrachloride and unreacted dithizone was stripped by shaking with dilute ammonia. The formation of the yellow "dithizonate" from 4.0  $\mu\text{mole}$  of selenium consumed 16.2 and 16.8  $\mu\text{mole}$  of dithizone. Secondly, on the addition of excess of diethyldithiocarbamic acid (HDDC), the amount of dithizone "liberated in a reversion reaction" was found to be 15.6 and 17.0  $\mu\text{mole}$  per 4.0  $\mu\text{mole}$  of selenium—leading to the ratio Se:H<sub>2</sub>Dz = 1:3.9–4.2. This last reaction was represented as



and attempts to measure the equilibrium constant "did not give reproducible results" although the value  $10^{6.27}$  was obtained indirectly from the exchange constant ( $10^{-0.78 \pm 0.10}$ ) for the reaction



and that for the reaction between Cd(HDz)<sub>2</sub> and HDDC ( $\log E_{\text{Cd}(\text{HDz})_2 - \text{HDDC}} = 3.53$ ).

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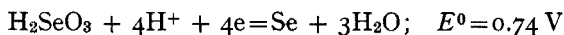
This result was confirmed by investigating the reaction



which gave an equilibrium constant  $\log E_{\text{Se}(\text{HDz})_4-\text{As}(\text{DDC})_3} = -9.2 \pm 0.2$  which when combined with the value  $\log E_{\text{As}(\text{DDC})_3-\text{H}_2\text{Dz}} = -7.93$  gave the value  $10^{6.67}$  for the equilibrium constant of eqn. (1). The agreement is remarkably good, especially in view of the fact that, as we shall now show, the species  $\text{Se}(\text{HDz})_4$  does not exist and the actual reaction between the yellow organic phase and excess HDDC is not reversible.

In none of these papers is there any direct evidence of the presence of selenium in the yellow organic solution ( $\lambda_{\text{max}}$  410–420) of the alleged "selenium dithizonate". It is noteworthy that MABUCHI AND NAKAHARA<sup>1</sup> mention making "several tests of selenium extraction with a dithizone solution using the radioactive isotope <sup>75</sup>Se as tracer" and they state that "for pH values higher than 2, only less than 1.5% of the total amount of selenium is extracted by a  $10^{-3}$  mol/l dithizone solution". Since the percentage of extraction of a metal dithizonate invariably decreases with increase in the acidity of the aqueous phase, this radiometric result would suggest that even less than 1.5% would be extracted from 6 N hydrochloric acid. The Russian authors<sup>4</sup> (Fig. 2 of that paper) found that the optical density of the "selenium dithizonate" extracted from mineral acid actually *increased* with acid concentration to a maximum at 6–7 M hydrochloric acid or 5.5–6 M sulphuric acid, but they too did not comment on this surprising feature.

Although both the earlier papers<sup>1,4</sup> refer to the interfering effects of ions and reagents that can also oxidise dithizone, the possibility that selenium(IV) was acting purely or partly as an oxidant seems to have been overlooked. This is surprising since the redox potential for the system



will be affected by the fourth power of the hydrogen ion activity: in concentrated acids selenium(IV) is a powerful oxidant.

#### *Absorbance spectra of dithizone extracts at different acidities with and without selenium*

Figure 1 shows the effect of shaking a solution of dithizone in carbon tetrachloride for a few minutes with equal volumes of hydrochloric acid of various strengths, all of which contained 200  $\mu\text{g}$  of selenium(IV). With increase in acid concentration the principal peak of dithizone at 620 nm (curve 1) falls progressively (curves 2–5) but there is no proportional decrease in the secondary maximum at 450 nm: on the contrary the absorption here becomes of comparable or even greater intensity and the maximum shifts hypsochromically. With 6 M hydrochloric acid (curve 5) the dithizone spectrum has been completely replaced by that of a yellow material whose spectrum shows a well developed maximum at 420 nm and a weak shoulder at *ca.* 570 nm. With still more concentrated acid (curves 6 and 7) the absorption at *ca.* 420 nm decreases and broad peaks begin to appear as shoulders at *ca.* 520 and *ca.* 570 nm.

Figure 1, curve 8 shows the spectrum of a solution of dithizone in carbon tetrachloride that has been equilibrated with 11 M hydrochloric acid in the entire absence of selenium(IV). The main effect here is the withdrawal of dithizone into the aqueous phase as its conjugate acid.

Whereas MABUCHI AND NAKAHARA<sup>1</sup> noted a progressive decrease in the optical

density at 410 nm if the yellow organic extract was allowed to remain in contact with the aqueous phase (6 M hydrochloric acid) after the reaction with selenium(IV), they reported no change over 30 min if the organic phase was separated from the aqueous phase immediately after equilibration. The Russian workers noted the effect of sunlight in reducing the optical density and recommended working in a darkened room or with feeble electric light<sup>4</sup>.

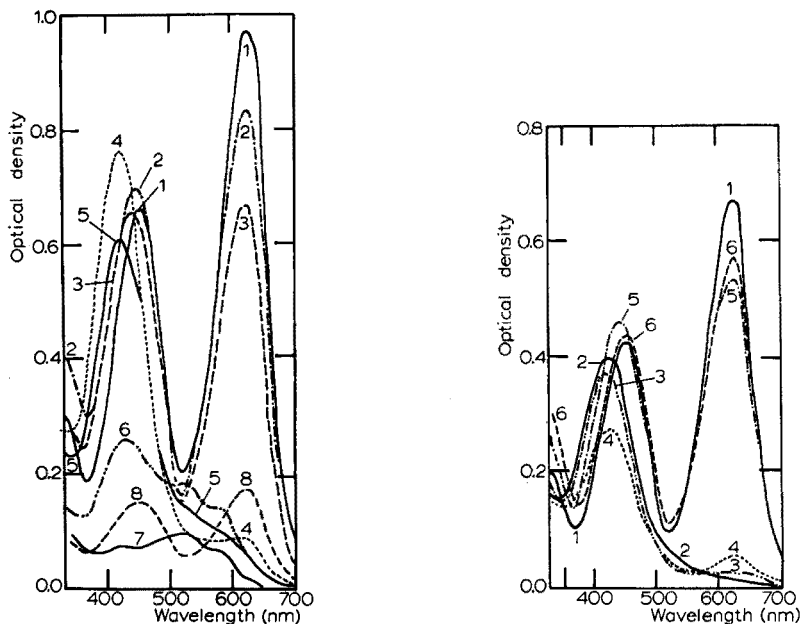


Fig. 1. The effect of selenium(IV) in various concentrations of hydrochloric acid on the absorption spectra of dithizone in carbon tetrachloride. (1)  $2.79 \cdot 10^{-5}$  M dithizone alone. (2-7)  $2.79 \cdot 10^{-5}$  M dithizone shaken with 200  $\mu$ g of selenium(IV) in 1, 2, 4, 6, 8 and 10 M hydrochloric acid, respectively. (8) Dithizone solution shaken with 11 M hydrochloric acid in the absence of selenium.

Fig. 2. The effect of time and of diethyldithiocarbamic acid on the spectrum of the selenium oxidation product of a solution of dithizone in carbon tetrachloride. (1)  $1.94 \cdot 10^{-5}$  M dithizone alone. (2-4) Spectrum of the yellow selenium oxidation product, taken immediately and after 1.5 and 24 h. (5, 6) Spectrum of the yellow oxidation after treatment with diethyldithiocarbamic acid, taken immediately and after 24 h.

Clearly 6 M hydrochloric acid represents optimum conditions for the reaction with dithizone, and Fig. 2 (curves 2-4) shows what is observed when the yellow organic layer is allowed to stand. As noted by the Russian workers the absorbance at 420 nm decreases, but the remarkable feature is the reappearance of a peak at 620 nm and indeed the slow return of the green colour typical of dithizone. This effect is markedly pronounced when the reaction is carried out in chloroform (Fig. 3, curves 2, 3 and 4) where the regeneration of dithizone is noticeably faster.

#### *The effect of diethyldithiocarbamic acid and other reducing agents*

If the yellow organic phases obtained by treatment with selenous acid are shaken with a solution of diethyldithiocarbamic acid in the same solvent, dithizone is



regenerated (Fig. 2, curves 5 and 6; Fig. 3, curves 5, 6 and 7). This confirms STARÝ's observations at least qualitatively. The additional feature of importance is that the regeneration of dithizone is not instantaneous *nor is it quantitative*. It is estimated that the recovery is *ca.* 85.6% in carbon tetrachloride and 88.6% in chloroform. The reason for this low recovery will be discussed below.

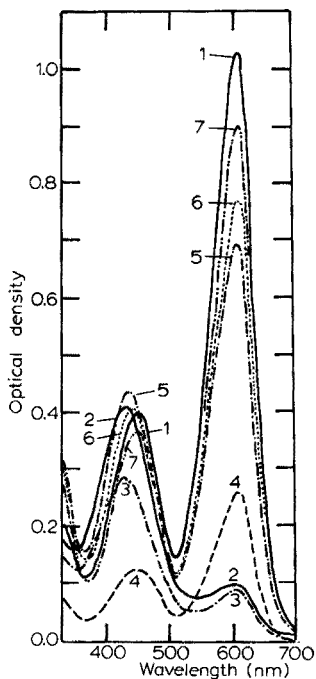


Fig. 3. The effect of time and of diethyldithiocarbamic acid on the spectrum of the selenium oxidation product of a solution of dithizone in chloroform. (1)  $2.46 \cdot 10^{-5}$  M dithizone alone. (2-4) Spectrum of the yellow selenium oxidation product, taken immediately and after 2 and 24 h. (5-7) Spectrum of the yellow oxidation product after treatment with diethyldithiocarbamic acid, taken immediately and after 2 and 6 h, respectively.

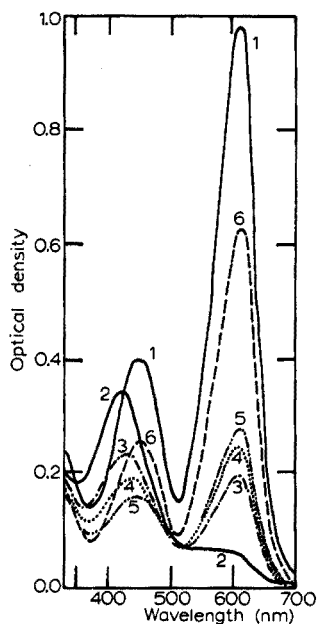


Fig. 4. The effect of iodine on a solution of dithizone in chloroform. (1)  $2.36 \cdot 10^{-5}$  M dithizone alone. (2-5) Spectrum of the yellow oxidation product taken immediately and after 0.5, 1.0 and 1.5 h. (6) Spectrum of the yellow oxidation product after treatment with diethyldithiocarbamic acid.

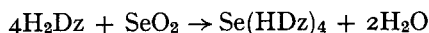
It is not necessary to use diethyldithiocarbamic acid to regenerate dithizone from the yellow "selenium dithizonate"; hypophosphorous acid is equally effective and a variety of other reducing agents can be used. Of great significance is that under no circumstance does red selenium separate. On the other hand when a solution of selenous acid in 6 M hydrochloric acid is treated with excess of dithizone and the yellow organic layer is separated—conditions hitherto assumed to be a means of transferring selenium quantitatively to the organic phase—selenium still remains in the aqueous layer and can be coagulated and collected as a red solid. Admittedly some does dissolve in the organic solvent and it is for this reason that any attempt to study the liquid-liquid extraction of the supposed "selenium dithizonate" by using, *e.g.*  $^{75}\text{Se}$  as a tracer must inevitably give misleading results.



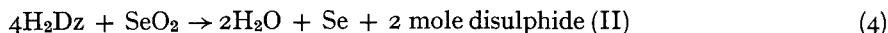
yellow-brown solid, m.p. 66–68°, can be isolated. This turns green on standing and it has not yet proved possible to obtain it analytically pure. Its solution in  $\text{CCl}_4$  and  $\text{CHCl}_3$  has  $\lambda_{\text{max}}$  420 nm and it is at least partially reduced to dithizone by sulphurous acid, hypophosphorous acid or HDDC. The infrared spectra showed no characteristic absorption for  $>\text{C}=\text{S}$ .

If the role of selenium(IV) must now be relegated to that of an oxidant, the role of the diethyldithiocarbamic acid can scarcely be other than that of a reductant and there is abundant experimental evidence of the ease with which it is oxidised. (In passing it should be pointed out that HDDC now proves to be as effective as hypophosphorous acid in preparing "selenazone" by reduction of the diselenide<sup>11</sup>.)

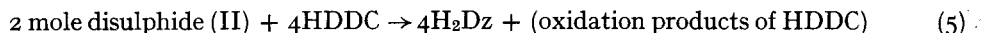
The previous experimental evidence for the existence and formula of selenium dithizonate<sup>5</sup> is now seen to rest on a series of misinterpretations of experimental observations. The first part of the experiment (page 9) should now be formulated not as



but as



and the previous data confirm this stoichiometry. The second part, on the other hand, must be restated as



Since the primary experimental data from which STARÝ AND RŮŽIČKA calculated equilibrium constants for reactions represented by eqns. (2) and (3) are not given in their paper<sup>5</sup>, it is impossible to see how they could have obtained two values in such satisfactory agreement for the equilibrium constant of what we must now consider to be an irreversible reaction (5).

The non-existence of selenium dithizonate does not, of course, invalidate the absorptometric methods for determining trace quantities of selenium<sup>1,4</sup> in terms of the yellow oxidation product of dithizone. However, the further reaction of this material (see above) to give dithizone and the sydnone (III), and the fact that other oxidants will give the same result show that scrupulous care must be taken over formulating and maintaining the experimental procedure.

## EXPERIMENTAL

### Reagents

A solution of dithizone in carbon tetrachloride was purified by published methods<sup>12</sup> until the peak ratio (the ratio of the absorbancy at 622 nm to that at 452 nm) did not increase on further cycles of extraction with 1:100 isopiestic ammonia and back-extraction on acidification. Solutions of pure dithizone in chloroform were prepared similarly.

Stock solutions of selenium(IV) were prepared by dissolving A.R. selenium powder (0.2 g) in concentrated nitric acid, evaporating to dryness, dissolving the selenium dioxide in the minimum volume of concentrated hydrochloric acid and making up to 1 l.

A solution of diethyldithiocarbamic acid (HDDC) was prepared by adding 0.5

*M* sulphuric acid dropwise to a mixture of carbon tetrachloride (50 ml) and an equal volume of a *ca.*  $10^{-3}$  *M* aqueous solution of its sodium salt (B.D.H., AnalaR), shaken in a separatory funnel, until the pH lay between 2 and 3. The organic layer was then separated, dried over anhydrous sodium sulphate, and placed in the dark. This solution was freshly prepared immediately before use.

*The reaction of selenium(IV) in hydrochloric acid of various concentrations on a solution of dithizone in carbon tetrachloride*

Aliquot portions (10 ml) of a  $2.79 \cdot 10^{-5}$  *M* solution of dithizone in carbon tetrachloride were severally shaken for a few minutes with aqueous phases prepared from 1 ml of stock selenium(IV), *x* (0, 1, 2, 4, 6 and 8) ml of 11 *M* hydrochloric acid and (10 - *x*) ml of distilled water. Each organic layer was then removed and centrifuged to remove droplets of water and its spectrum recorded with a Unicam SP 700 spectrophotometer in matched 1-cm silica cells (Fig. 1).

When treated with sulphurous acid or hypophosphorous acid the (separated) aqueous phase from experiment 5 (6 *M* hydrochloric acid) soon deposited finely divided red selenium. Treatment of the (separated) organic phase under the same conditions produced no deposit or colloidal suspension of selenium, whilst the green colour and spectrum of dithizone reappeared.

*The effect of diethyldithiocarbamic acid on the product of oxidising a solution of dithizone with selenium(IV)*

*In carbon tetrachloride.* A  $1.94 \cdot 10^{-5}$  *M* solution of purified dithizone in carbon tetrachloride (40 ml) was diluted to 46 ml and shaken for 5 min with an equal volume of selenium(IV) in 6 *M* hydrochloric acid of concentration  $3.24 \cdot 10^{-4}$  mole  $l^{-1}$ . The organic phase was then separated and freed from water droplets by centrifugation and divided into two equal portions (23 ml). One portion was diluted with pure carbon tetrachloride (2 ml) and its spectrum recorded immediately and after 1.5 and 24 h (Fig. 2, curves 2, 3 and 4). The second portion of 23 ml was mixed with a *ca.*  $10^{-3}$  *M* solution of HDDC (2 ml) and its spectrum recorded immediately and after 12 h when no further change appeared to be taking place (Fig. 2, curves 5 and 6).

*In chloroform.* Essentially the same series of experiments were carried out with a  $2.46 \cdot 10^{-5}$  *M* solution of dithizone in chloroform. Figure 3, curves 2, 3 and 4, show changes in the yellow oxidation product on being kept and curves 5, 6 and 7 the progress of its reduction by HDDC after various intervals of time.

*The reducing effect of diethyldithiocarbamic acid on the diselenide.*

A solution of di-(1,5-diphenylformazyl-3)-diselenide<sup>11</sup> in chloroform (1.2 g/l) was treated with excess HDDC. The spectrum of selenazone ( $\lambda_{\max}$  450 and 622,  $\lambda_{\min}$  368, 560) appeared at once and the absorbance increased by less than 2% during the course of 1 h after which no further change occurred. The peak ratio ( $A_{622}/A_{450}$ ) changed from 0.404 to 0.417.

*The action of iodine on a solution of dithizone in chloroform.*

A  $2.36 \cdot 10^{-5}$  *M* solution of purified dithizone in chloroform (20 ml) was shaken with pure chloroform (2 ml),  $1.603 \cdot 10^{-4}$  *M* iodine in chloroform (3 ml) and water (25 ml). The green colour of dithizone was immediately replaced by yellow. The organic

phase was separated and centrifuged to remove water droplets and the spectrum recorded after various intervals of time (Fig. 4). On treating a sample of the oxidation compound with excess HDDC the spectrum of dithizone reappeared (Fig. 4, curve 6).

One of us (R.S.R.) wishes to thank the Department of Inorganic and Structural Chemistry for a Research Fellowship.

#### SUMMARY

An organic-soluble yellow compound ( $\lambda_{\max} \approx 420$  nm) is formed when solutions of dithizone ( $H_2Dz$ ) in carbon tetrachloride are shaken with selenium(IV) in 6 *M* hydrochloric acid. STARÝ AND RŮŽIČKA ascribed the formula  $Se(HDz)_4$ , showed that dithizone was regenerated on treatment with diethyldithiocarbamic acid (HDDC), and reported equilibrium constants for its "exchange reactions" with a number of metal complexes. The alleged selenium dithizonate does not exist. The yellow material is not a compound of selenium but an oxidation product of dithizone, *viz.* di-(1,5-diphenylformazyl-3)-disulphide which disproportionates on keeping (more rapidly in chloroform) to a mixture of dithizone and a sydnone, anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide. The disulphide can also be prepared stoichiometrically by oxidising dithizone with iodine and it is reduced back to dithizone by HDDC or hypophosphorous acid. These findings do not affect the procedures proposed for determining traces of selenium absorptiometrically, but STARÝ AND RŮŽIČKA's work is invalidated.

#### RÉSUMÉ

Le sélénium(IV) donne avec la dithizone ( $H_2Dz$ ) dans le tétrachlorure de carbone un composé jaune soluble dans le solvant organique ( $\lambda_{\max} \approx 420$  nm), en milieu acide chlorhydrique 6 *M*. STARÝ ET RŮŽIČKA ont admis la formule  $Se(HDz)_4$ ; cependant, le dithizonate de sélénium n'existe pas. La substance jaune n'est pas un composé sélénium, mais le produit d'oxydation de la dithizone. Cette découverte ne diminue pas l'intérêt du procédé proposé pour le dosage absorptiométrique de traces de sélénium.

#### ZUSAMMENFASSUNG

Es wird eine gelbe Verbindung ( $\lambda_{\max} \approx 420$  nm) gebildet, wenn Lösungen von Dithizon ( $H_2Dz$ ) in Tetrachlorkohlenstoff mit Selen(IV) in 6 *M* Salzsäure geschüttelt werden. STARÝ UND RŮŽIČKA geben die Formel  $Se(HDz)_4$  an und zeigen, dass Dithizon durch Behandlung mit Diäthylthiocarbaminsäure (HDDC) regeneriert wird. Sie geben die Gleichgewichtskonstanten dieser Austauschreaktion für eine Anzahl von Metallkomplexen an. Die angeführten Selendithizonate existieren nicht. Der gelbe Stoff ist nicht eine Verbindung des Selens sondern ein Oxydationsprodukt des Dithizons, Di-(1,5-diphenylformazyl-3)-disulphid, welches zu einer Mischung von Dithizon und einem Sydnon, Anhydro-5-mercapto-2,3-diphenyltetraazoliumhydroxyd, disproportioniert. Das Disulfid kann auch in stöchiometrischer Zusammensetzung durch Oxydation von Dithizon mit Jod und anschliessender Rückreduktion zum Dithizon durch HDDC oder Hypophosphorsäure hergestellt werden. Diese Erkennt-

nisse beeinflussen nicht das Verfahren, welches für die Bestimmung von Spuren Selen vorgeschlagen wurde.

## REFERENCES

- 1 H. MABUCHI AND H. NAKAHARA, *Bull. Chem. Soc. Japan*, 36 (1963) 151.
- 2 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 2nd Edn., Interscience, New York, 1959.
- 3 H. IRVING AND J. J. COX, *J. Chem. Soc.*, 1470 (1961).
- 4 D. P. SHCHERBOV, A. I. IVANKOVA AND G. P. GLADSHEVA, *Zavodsk. Lab.*, 33 (1967) 683.
- 5 J. STARÝ AND J. RŮŽIČKA, *Talanta*, 15 (1968) 505.
- 6 E. FISCHER, *Ann.*, 190 (1878) 118; 212 (1882) 316.
- 7 W. S. McDONALD, H. M. N. H. IRVING, G. RAPER AND D. C. RUPAINWAR, *Chem. Commun.*, 392 (1969).
- 8 H. M. N. H. IRVING AND D. C. RUPAINWAR, *Anal. Chim. Acta*, 45 (1969) 249.
- 9 H. M. N. H. IRVING AND D. C. RUPAINWAR, *Anal. Chim. Acta*, paper submitted (Part XIX).
- 10 S. S. SAHOTA, *Ph. D. Thesis*, Leeds, 1964.
- 11 H. M. N. H. IRVING AND R. S. RAMAKRISHNA, *Anal. Chim. Acta*, 48 (1969) 251.
- 12 H. M. N. H. IRVING AND A. M. KIWAN, *Anal. Chim. Acta*, 45 (1969) 243.

*Anal. Chim. Acta*, 49 (1970) 9-17

## RAPID DETERMINATION OF THORIUM IN URINE BY THERMAL NEUTRON ACTIVATION ANALYSIS\*

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In the nuclear industries, one of the most widely-used methods of assessing inhalation exposures is the analysis of urine for the element or particular nuclide of interest. The usefulness of this technique depends, in part, on the solubility of the inhaled particles in body fluids and on the sensitivity of the detection method. In order to interpret the urinalysis data, there must be some known correlation between the nuclide concentration in the urine and the amount of that nuclide deposited in the body. This correlation is obtained from animal experiments or pooled human exposure experience.

Urinalysis has not been widely used to assess routine thorium exposures because most forms of thorium encountered in industrial operations are considered insoluble when deposited in the lungs<sup>1</sup>. Therefore, exposure control is usually based on measurement of thorium in the air, or on whole-body measurements<sup>2</sup>. Although methods are available for the determination of thorium in the urine, there is a lack of data to show that the techniques are capable of detecting changes in thorium concentration which match changes in the degree of exposure to airborne thorium dusts. Exposure assessment methods, other than urinalysis, also have disadvantages when considered for routine use. Gross air analysis alone does not provide a measurement of material deposited in the body. Deposition depends on the size and density of airborne particles, and these parameters must be measured or estimated. Fecal analysis is useful for identifying exposed persons, but it does not provide a measure of how much airborne dust was deposited in the body.

Whole-body, or *in vivo*, counting is an excellent technique but few production facilities have these counters available. Furthermore, a person should have no exposure to thorium for several days preceding an *in vivo* count so that out-of-equilibrium daughter products can decay. If a facility does not have its own counter, the need for an exposure-free period, plus the time and expense of transporting employees to a counter, may make this type of measurement impractical for routine use with large numbers of employees. However, counting of a limited number of exposed persons plus an analysis of their urine for thorium might establish a correlation between thorium deposited and thorium excreted. If this correlation were established, urinalysis could be used in a routine program of exposure control, identifying exposure cases where *in*

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*in vivo* counts would be warranted. However, a sensitive method for thorium determination would be required. These considerations led to the development of neutron activation techniques for the determination of thorium in urine samples.

## EXPERIMENTAL

### *Apparatus*

All irradiations, post-irradiation sample treatment, and counting, were performed at the Nuclear Engineering Test Facility, Air Force Institute of Technology, Wright-Patterson Air Force Base, Fairborne, Ohio. The Facility's 10-MW reactor provided a thermal flux of about  $10^{12}$  n cm<sup>-2</sup> sec<sup>-1</sup>. Samples were transferred by a pneumatic tube system between the insertion port and the core face. After post-irradiation treatment, the samples were counted with a 3 × 3 in NaI(Tl) crystal mounted in a Heath Chamber, and a RIDL 12-B 400-channel pulse-height analyzer.

### *Reagents*

*Thorium standard.* Prepare a stock thorium solution and standardize by evaporating aliquots in platinum dishes, igniting, and weighing as ThO<sub>2</sub>. Dilute aliquots of the stock with 1 M nitric acid to obtain a standard containing 10<sup>-11</sup> g Th/ml. Prepare the dilute standard as needed.

*Lanthanum carrier.* Dissolve 12.5 g of lanthanum nitrate hexahydrate in 100 ml of 1 M hydrochloric acid.

*Sodium chloride solution.* Dissolve 50 g of sodium chloride in 500 ml of 1 M hydrochloric acid.

### *Procedure*

Transfer 30 ml of urine to two 100-ml beakers. To one beaker add 3 ml of thorium standard (10<sup>-11</sup> g Th/ml). Add 5 ml of concentrated nitric acid and heat for 1 h. Cool, add concentrated ammonium hydroxide until the precipitation is complete, and heat the solution for 1 h. Centrifuge, discard the supernate, and wash the precipitate with 10 ml of distilled water. Dissolve the precipitate with concentrated nitric acid and transfer to 8-ml plastic activation vials. Use enough rinsing water to bring the final volume to 5 ml. Heat-seal both vials and place them together in a container (rabbit) for transfer in the pneumatic tube system. Irradiate for 15 min at a thermal flux of  $10^{12}$  n cm<sup>-2</sup> sec<sup>-1</sup>. After irradiation, immediately transfer the vial contents to 40-ml heavy-wall centrifuge tubes. Add 1 ml of lanthanum carrier and 5 ml of sodium chloride solution. Add an excess of concentrated ammonium hydroxide. Centrifuge and discard the supernate. Dissolve the precipitate with concentrated nitric acid, add 5 ml of sodium chloride solution and repeat the precipitation. Centrifuge, discard the supernate, and dissolve the precipitate with 2 ml of concentrated nitric acid. Transfer to a counting vial, and use 5 ml of rinse water to obtain a standard final volume of 7 ml.

### *Calculations*

All vials were counted 1 inch from the face of a 3 × 3 in NaI(Tl) scintillation crystal mounted in a Heath chamber. Each vial was counted in turn for 3 min; the delay time between activation and counting, 20–30 min, was recorded. The activity under the <sup>233</sup>Th peak was corrected for background activity by averaging the Comp-



ton continuum on each side of the peak. Each count was corrected for decay to a common time-point. This was necessary since only one vial could be counted at a time.

The thorium concentration of the sample was calculated from  $S = R \cdot K / (1 - R)$  where  $S$  is the unknown thorium concentration in the samples,  $K$  is the known thorium spike concentration, and  $R$  is the ratio of the counting activities of the unspiked to the spiked aliquots, respectively.

As an alternative means of processing the data, magnetic tape spectrum stripping was also used successfully. After each count the sample and spiked reference spectra were recorded on tape. Then the thorium peak of one spectrum was subtracted, or stripped, from the other until only a Compton continuum was left in the thorium peak area. The stripping factor (fractional strips required) is the ratio of the count of one sample to the other. This ratio was corrected for the difference in decay times between the two countings. The corrected ratio ( $R$ ) was then used directly in the calculation of the thorium concentration. This method was faster than, and as precise as, that based on typed readout data.

## RESULTS

After the reagent blank had been determined and the experimental procedures had been optimized, the precision of the method was evaluated on two urine samples. The first sample was a composite from four employees not occupationally exposed to thorium. The second sample was from an employee who was at the time working in areas which had moderate concentrations of airborne thorium. Ten years previously he had worked for about 1 year in an area where the concentration was higher. Eight individual determinations were made on each of the two urine samples. The average

TABLE I  
COUNT DATA

| Urine sample <sup>a</sup> | Gross count<br>in Th channels<br>( $\cdot 10^3$ ) | Net count<br>in Th channels<br>( $\cdot 10^3$ ) | Stripping<br>factor <sup>b</sup> | Time<br>correction | Calculated<br>thorium<br>concentration<br>( $\cdot 10^{-8}$ g/l) |
|---------------------------|---|---|----------------------------------|--------------------|--|
| I                         | 163   | 83  | 6.38                             | 0.136              | 6.60   |
| I                         | 74  | 46  | 3.70                             | 0.230              | 5.66   |
| I                         | 72  | 48  | 3.01                             | 0.283              | 5.69   |
| I                         | 76  | 39  | 3.15                             | 0.275              | 6.42   |
| I                         | 112   | 57  | 2.34                             | 0.368              | 6.14   |
| I                         | 87  | 41  | 2.24                             | 0.379              | 5.61   |
| II                        | 67  | 16  | 0.490                            | 0.246              | 0.137  |
| II                        | 121   | 7   | 0.304                            | 0.383              | 0.132  |
| II                        | 75  | 14  | 0.197                            | 0.567              | 0.126  |
| II                        | 52  | 3   | 0.240                            | 0.472              | 0.128  |
| II                        | 49  | 9   | 0.357                            | 0.335              | 0.136  |
| III                       | 51  | 2   | 0.246                            | 0.560              | 0.159  |
| IV                        | 32  | 7   | 0.529                            | 0.378              | 0.251  |
| V                         | 75  | 9   | 0.565                            | 0.532              | 0.430  |

<sup>a</sup> (I) Composite urine from thorium worker. (II) Composite of urine from unexposed persons. (III, IV, V) Single urine voidings from unexposed persons.

<sup>b</sup> Stripping factor is multiplied by time correction to obtain  $R$  in the equation given in the text. Reference spectrum used in stripping was obtained from a spike of  $10^{-8}$  g Th/l.

thorium concentration found was  $0.126 \cdot 10^{-8}$  g/l (relative standard deviation 3.7%) for the composite sample from the unexposed employees and  $6.02 \cdot 10^{-8}$  g/l (relative standard deviation 7.1%) for the sample from the exposed employee. The thorium spike used was  $1 \cdot 10^{-8}$  g/l. Other urine samples from several unexposed persons were analyzed and yielded values of 0.25, 0.43, and 0.16 ( $\cdot 10^{-8}$  g/l) for thorium. Table I shows the precision data.

## DISCUSSION

Neutron bombardment of  $^{232}\text{Th}$  produces the isotope  $^{233}\text{Th}$ , a  $\beta$ ,  $\gamma$ -emitter with a half-life of 23.3 min. Thorium-233 decays to  $^{233}\text{Pa}$ , a  $\beta$ ,  $\gamma$ -emitter with a half-life of 27.4 d. With suitable standards, the  $\gamma$ -activity from either nuclide may be used to calculate the original concentration of  $^{232}\text{Th}$ . The  $\gamma$ -activity from  $^{233}\text{Pa}$  is generally used<sup>3</sup>, because the longer half-life allows more time for the chemical separations needed to remove interferences.

Thorium-233 was selected for this work because of its higher specific activity and because the analyses were performed at a facility which was distant from the normal work site. If  $^{233}\text{Pa}$  were used, a delay of several hours would be required for ingrowth before counting. Of course, this delay time could be used to make chemical separations; however, it was found that interferences could be adequately removed by short, simple separation techniques immediately after irradiation.

Urine, when activated, yields high activities from iron, chlorine, and especially sodium. The activation and decay properties of these elements are shown in Table II. The major constituents, by virtue of their relatively high  $\gamma$ -energies, produce a very large Compton continuum in the energy regions where the thorium products,  $^{233}\text{Th}$  and  $^{233}\text{Pa}$ , are measured, hence chemical separations were required.

TABLE II  
ACTIVATION AND DECAY PROPERTIES

| Activated isotope | Product isotope   | Half-life | $\gamma$ -Energies (keV) and abundance        |
|-------------------|-------------------|-----------|---|
| $^{232}\text{Th}$ | $^{233}\text{Th}$ | 23 min    | 86.9 (2.7%), decays to 27-d $^{233}\text{Pa}$ |
|                   | $^{233}\text{Pa}$ | 27 d      | 313 (80%)                                     |
| $^{23}\text{Na}$  | $^{24}\text{Na}$  | 15 h      | 1,368 (100%); 2,754 (100%)                    |
| $^{37}\text{Cl}$  | $^{38}\text{Cl}$  | 37 min    | 1,150 (47%); 1,600 (31%)                      |
| $^{58}\text{Fe}$  | $^{59}\text{Fe}$  | 45 d      | 1,098 (57%); 1,289 (43%)                      |
| $^{56}\text{Fe}$  | $^{56}\text{Mn}$  | 2.6 h     | 845 (50%); 1,810 (30%); 2,130 (20%)           |

The pre-irradiation treatment concentrated the thorium in a small volume and reduced the sodium and chloride content. Approximately 99.9% of the sodium originally present was removed in these separations. However, post-irradiation separations by hydroxide precipitation and the use of sodium chloride hold-back carrier were needed to improve the resolution of the thorium peaks. The effects of using one and two precipitation steps after irradiation can be seen in Fig. 1. With a single precipitation, the  $^{233}\text{Th}$  peak was not significantly resolved above the Compton background. With a double precipitation the  $^{233}\text{Th}$  activity obtained was *ca.* 2.5 the Compton background. The activities from  $^{59}\text{Fe}$  and  $^{56}\text{Mn}$  were not removed by these separa-

tions. In some urine samples, these activities were of the same order of magnitude as the thorium activity. It was found that coprecipitation of thorium with lanthanum fluoride would reduce the  $^{59}\text{Fe}$  and  $^{56}\text{Mn}$  activities by two orders of magnitude.

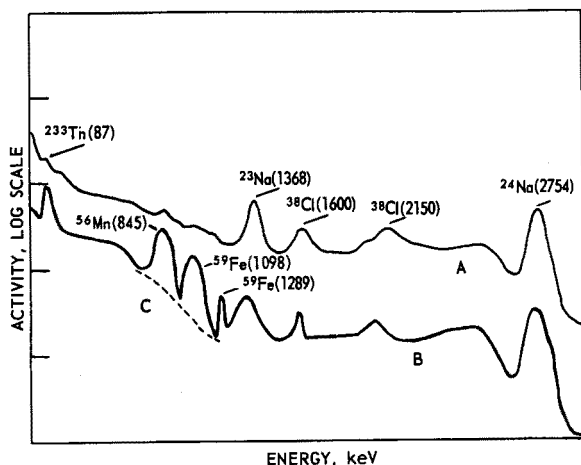


Fig. 1.  $\gamma$ -Spectra of activated urine after post-irradiation treatment. (A) One  $\text{La}(\text{OH})_3$  coprecipitation. (B) Two  $\text{La}(\text{OH})_3$  coprecipitations. (C) Two  $\text{La}(\text{OH})_3$  coprecipitations and one  $\text{LaF}_3$  coprecipitation.

The use of the known thorium spike in a second aliquot yields good precision accompanied by high sensitivity. The spiked aliquot serves as an excellent flux monitor since it has exactly the same characteristics as the sample being analyzed. This is especially important since the composition of urine can vary greatly from sample to sample. Assuming identical parameters during the simultaneous separation of the two aliquots, this technique inherently corrects for variations in the completeness of thorium separation. The counting efficiency is also inherently adjusted, so that no absolute calibration is required. This technique requires, for good precision, that the thorium concentration of the spike be near that of the sample, as can be seen from the calculation equation. Since the level of thorium in urine was not previously known for this work, a urine sample was run to estimate the concentration of spike that would be required.

The method described here is capable of high sensitivity. It could be used at an order of magnitude lower than the  $10^{-9}$  g/l range encountered. This sensitivity has permitted the establishment of a general thorium level for persons who are not occupationally exposed; this level, however, is only tentative because of the small population surveyed. The precision obtained (standard deviations of better than 10%) are considered excellent for polytypical samples of such extremely low thorium levels. About 45 min is required at the reactor site for a single analysis or 20 min per sample for multiple analyses by two technicians.

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## SUMMARY

The determination of subnanogram quantities of thorium in human urine is described. A urine sample is split into two aliquots, one of which is spiked with a known concentration of thorium; the aliquots are processed simultaneously. Simple pre- and post-irradiation separations are used to minimize  $^{24}\text{Na}$  and  $^{38}\text{Cl}$  Compton interferences, after 15-min activations at about  $10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ .  $^{233}\text{Th}$  is counted as quickly as possible after irradiation. The sensitivity of the method is  $10^{-10} \text{ g Th/l}$ , and processing requires only 45 min. A urine sample from a thorium worker averaged  $6.02 \cdot 10^{-8} \text{ g Th/l}$ . A composite sample from four unexposed persons averaged  $0.13 \cdot 10^{-8} \text{ g Th/l}$ . Other samples from unexposed persons contained 0.16, 0.25, and  $0.43 (\cdot 10^{-8}) \text{ g Th/l}$ .

## RÉSUMÉ

On décrit un dosage de thorium dans l'urine humaine, à l'échelle du subnanogramme. L'échantillon d'urine est divisé en deux parties aliquotes; l'une est additionnée d'une quantité connue de thorium. Les deux parties aliquotes sont traitées simultanément. De simples séparations pré- et post-irradiation sont effectuées pour minimiser les interférences Compton de  $^{24}\text{Na}$  et  $^{38}\text{Cl}$ . Après 15 min d'activation à  $10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ ,  $^{233}\text{Th}$  est compté aussi rapidement que possible. La sensibilité est de  $10^{-10} \text{ g Th/l}$ . La durée d'un dosage est de 45 min.

## ZUSAMMENFASSUNG

Es wird die neutronenaktivierungsanalytische Bestimmung von Subnanogrammen Thorium in menschlichen Urin beschrieben. Eine von zwei aliquoten Teilen der Probe wird mit einer bekannten Konzentration Thorium versetzt; beide werden dann gleichzeitig behandelt. Einfache Trennungen vor und nach der Bestrahlung werden verwendet, um Störungen durch Comptonstrahlung von  $^{24}\text{Na}$  und  $^{38}\text{Cl}$  zu verringern. Nach einer Aktivierung von 15 Minuten bei  $10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$  wird das  $^{233}\text{Th}$  so schnell wie möglich gezählt. Die Empfindlichkeit der Methode beträgt bei einer Arbeitszeit von 45 Minuten  $10^{-10} \text{ g Th/l}$ . Die Urinprobe eines Thoriumarbeiters enthält etwa  $6 \cdot 10^{-8} \text{ g Th/l}$  und liegt damit etwa 20 bis 40 mal höher als normal.

## REFERENCES

- 1 R. G. THOMAS, *AEC Report UR-480*, Rochester University, New York, Dec. 1956.
- 2 L. M. SCOTT, *Health Phys.*, 12 (1966) 101.
- 3 L. KOSTA AND G. B. COOK, *Talanta*, 12 (1965) 977.

*Anal. Chim. Acta*, 49 (1970) 19-24

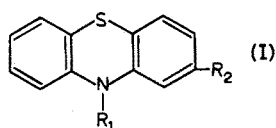
## CHRONOPOTENTIOMETRY AND COULOMETRIC TITRATION OF N-SUBSTITUTED PHENOTHIAZINES

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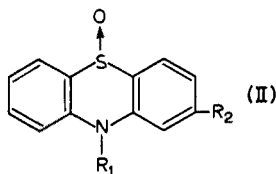
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Several N-substituted phenothiazines, of the general formula I, are commonly employed in medicine, and therefore their determination in pharmaceutical preparations is of considerable importance. Previously proposed determinative methods



include spectrophotometric determination via the colored complexes of these compounds with certain heavy metal ions<sup>1,2</sup>, gravimetric determination by precipitation with silicotungstic acid<sup>3</sup>, and acidimetric titration in non-aqueous media<sup>4</sup>. ZUMAN<sup>5</sup> also mentions a polarographic method based on the decrease of the diffusion current of silicotungstic acid owing to its precipitation by the compound.

A common property of all the N-substituted phenothiazines is that they are easily oxidized, either chemically or electrolytically, and thus they are amenable to determination by electroanalytical techniques. MERKLE AND DISCHER<sup>6</sup> demonstrated that electrolytic oxidation at a platinum anode in aqueous sulfuric acid media proceeds in two 1-electron stages. The first stage, resulting simply from the loss of an electron from the parent compound, produces the corresponding cation free radical (usually intensely reddish colored). The second stage is a further 1-electron oxidation of the free radical to the colorless sulfoxide(II).



At a relatively low acidity (0.5 M sulfuric acid) the free radical disproportionates quite rapidly into the parent compound and the sulfoxide, but it is quite stable at sulfuric acid concentrations above 3 M. Consequently, in 3 M or larger concentrations of sulfuric acid, the two stages of oxidation at a platinum anode are separated by several tenths of a volt. MERKLE AND DISCHER demonstrated that the free radical

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can be produced with nearly 100% current efficiency in 4.5 *M* sulfuric acid by controlled potential oxidation of the original *N*-substituted phenothiazine at a platinum anode whose potential is held constant just below the value required for the second oxidation stage.

Polarograms obtained by MERKLE AND DISCHER with a rotated platinum microelectrode indicate that the first stage of oxidation of the *N*-substituted phenothiazines (formation of the free radical) proceeds reversibly. In the present study this was confirmed by chronopotentiometric measurements.

The chief purpose of the present study was to investigate the feasibility of determining various pharmaceutically important *N*-substituted phenothiazines by coulometric titration with electrogenerated cerium(IV). This has proved to be a convenient, accurate method for their determination.

## EXPERIMENTAL

### *Compounds studied*

The compounds studied are listed in Table I in terms of the substituent groups  $R_1$  and  $R_2$  on the parent phenothiazine (I), and also by their trivial names. Hereinafter they are identified by the trivial names. They were all obtained gratuitously in a pure state from Société Parisienne d'Expansion Chimique, Rhône Poulenc, Paris.

TABLE I  
FORMULAE AND TRIVIAL NAMES OF THE COMPOUNDS STUDIED

| <i>Trivial name</i> | $R_1$   | $R_2$                                  |
|---------------------|---|--|
| Levomepromazine     | $-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{N}(\text{CH}_3)_2$                        | $-\text{OCH}_3$                        |
| Chlorpromazine      | $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$  | $-\text{Cl}$                           |
| Multergan           | $-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{SO}_4\text{CH}_3}{\text{N}}(\text{CH}_3)_3$ | —                                      |
| Promethazine        | $-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{N}(\text{CH}_3)_2$                                    | —                                      |
| Profenamine         | $-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{N}(\text{C}_2\text{H}_5)_2$                           | —                                      |
| Diethazine          | $-\text{CH}_2-\text{CH}_2-\text{N}(\text{C}_2\text{H}_5)_2$   | —                                      |
| Thiopropazine       | $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N} \langle \text{hexagon} \rangle \text{N}-\text{CH}_3$         | $-\text{SO}_2-\text{N}(\text{CH}_3)_2$ |

### *Procedures*

The coulometric titrations were performed in an H-type glass cell, with a fine sintered glass disk in the cross arm. The solution level in the auxiliary electrode compartment was kept above that in the working electrode compartment to prevent

backflow of sample. The volume of test solution was 75 to 100 cm<sup>3</sup>, and rapid magnetic stirring was employed.

As discussed in detail by LINGANE *et al.*<sup>7,8</sup>, the current efficiency for the oxidation of cerium(III) to cerium(IV) ion at a platinum anode approaches more closely to 100%, the greater the concentrations of both cerium(III) ion and sulfuric acid. However, because the solubility of cerium(III) sulfate is not very large and decreases with increasing concentration of sulfuric acid a compromise is necessary. An optimum compromise is 3 *F* sulfuric acid and 0.05 *F* Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O, and this supporting electrolyte was used in most of the titrations. This same supporting electrolyte was used in the auxiliary electrode compartment.

It was found that some lots of commercial Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O were contaminated by a rather large amount of an organic, reducing impurity. This was easily destroyed by heating the salt with concentrated sulfuric acid to strong fuming for about 15 min before diluting to volume. A supporting electrolyte prepared in this way showed a negligibly small titration blank.

Since a generating current between 10 and 15 mA was most convenient for the sample sizes used, and because the current efficiency for generation of cerium(IV) rapidly decays below 100% when the current density is smaller than about 1 mA/cm<sup>2</sup>, a platinum foil generator anode with an area of 5 cm<sup>2</sup> (total of both sides) was used to provide a current density of 2–3 mA/cm<sup>2</sup>. A coiled platinum wire served as auxiliary electrode and its area was not critical.

The electrolysis current was supplied from a conventional line-operated power supply. Since the current was only approximately constant ( $\pm 1\%$ ), the Ether Ltd. (formerly Electro Methods Ltd.) integrator previously described<sup>8,9</sup> was used to measure precisely ( $\pm 0.1\%$ ) the number of coulombs passed during the coulometric titrations.

The same cell and electrodes were used for the chronopotentiometric measurements, with the addition of a silver–silver chloride reference electrode against which the potential of the platinum working electrode was measured as a function of time. The chronopotentiograms were recorded with a strip-chart potentiometer recorder, with a quiescent solution.

## RESULTS AND DISCUSSION

### *Chronopotentiometry of N-substituted phenothiazines*

The electrochemical characteristics of a typical N-substituted phenothiazine (multergan) are illustrated by the chronopotentiograms in Fig. 1. As shown by curve 1 in Fig. 1, two oxidation stages are clearly delineated. As expected for successive 1-electron oxidations, the individual transition time of the second wave is three times that of the first. In the 3 *M* sulfuric acid used as supporting electrolyte, the quarter-wave potential,  $E_{1/4}$ , of the first wave is 0.664 V *vs.* Ag/AgCl, KCl(s), and that of the second wave is 0.968 V (0.861 V and 1.165 V *vs.* N.H.E.).

That the first oxidation step (production of the free radical) proceeds reversibly is indicated by the fact that a plot of  $E$  *vs.*  $\log t^{1/2}/(\tau^{1/2} - t^{1/2})$  produces a straight line whose slope (0.062 V) is very close to the theoretical value (0.059 V) for a 1-electron oxidation (see Ref. 8, p. 624). This reversibility is further confirmed by curve 2 in Fig. 1, which is a reversed current chronopotentiogram obtained by suddenly reversing

the polarity of the current when the first transition time was just reached, and which shows a cathodic wave for the reduction of the free radical at the same potential as the original anodic wave. The transition time for the reversed current cathodic wave is one-third that of the original anodic wave, as expected when both transition times are diffusion-controlled.

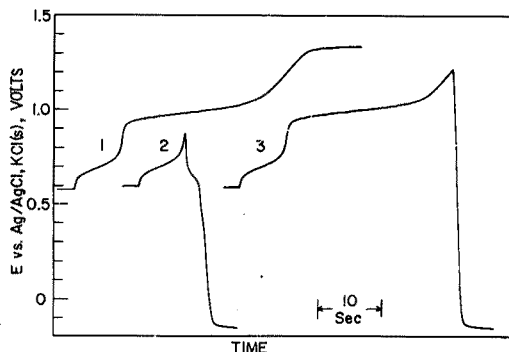


Fig. 1. Chronopotentiograms of 0.017 *M* multergan in 3 *M* sulfuric acid. Platinum anode. Constant current density 0.75 mA/cm<sup>2</sup>. (1) Complete chronopotentiogram, (2) current reversed at first transition time, (3) current reversed at second transition time.

The oxidation of the free radical to the sulfoxide does not proceed reversibly. This is indicated by the fact that the slope of the second wave of curve 1 in Fig. 1 is about twice the theoretical value. It is confirmed by the reverse current chronopotentiogram, shown as curve 3 in Fig. 1, obtained by suddenly reversing the current when the second transition time was reached. Curve 3 shows no reversed current cathodic wave; the potential falls abruptly to the value at which reduction of hydrogen ion occurs. To be sure, MERKLE AND DISCHER demonstrated that the sulfoxide can be reduced at a mercury cathode, but the potential required ( $-0.95$  V *vs.* S.C.E.) is nearly 2 V more negative than the potential at which the sulfoxide is formed by oxidation of the free radical; *i.e.*, the reduction overpotential is nearly 2 V. Furthermore, reduction under these conditions is to the original *N*-substituted phenothiazine rather than to the free radical.

The observed chronopotentiometric quarter-wave potentials,  $E_{\frac{1}{4}}$ , of the first and second waves of several of the *N*-substituted phenothiazines are listed in Table II.

TABLE II  
CHRONOPOTENTIOMETRIC QUARTER-WAVE POTENTIALS

| Substance      | $E_{\frac{1}{4}}(V)$ |             |
|----------------|----------------------|-------------|
|                | First wave           | Second wave |
| Chlorpromazine | 0.570                | 0.950       |
| Diethazine     | 0.610                | 0.990       |
| Promethazine   | 0.640                | 0.955       |
| Multergan      | 0.664                | 0.968       |
| Thiopropazine  | 0.680                | 1.040       |



Because the first wave is reversible, its  $E_{1/2}$  value is very nearly equal to the formal potential of the reaction.

The chronopotentiograms of all these compounds also show a definite but rather attenuated third wave, which evidently corresponds to further oxidation. The ratios of the individual transition times of this third wave to that of the first varied from about 8 to 27, depending on the compound. This variability suggests that this third reaction probably involves oxidation of the side chains, rather than oxidation of the sulfoxide to the sulfone. This further oxidation was of no concern in the present study because it requires a potential above 1.3 V vs. Ag/AgCl, KCl(s) (or 1.5 V vs. N.H.E.). Since this is somewhat above (more oxidizing than) the formal potential of the cerium(IV)-cerium(III) couple in dilute sulfuric acid media, this further oxidation does not occur during titrations of the N-substituted phenothiazines with cerium(IV) ion, and a sharp, stoichiometric end-point results after the 2-electron oxidation to the sulfoxide.

#### *Coulometric titrations of N-substituted phenothiazines*

The end-points of the coulometric titrations can be detected either potentiometrically with a platinum indicator electrode or amperometrically. The end-point is also signalled by the disappearance of the reddish color of the intermediate free radical, so that spectrophotometric end-point detection probably could also be employed.

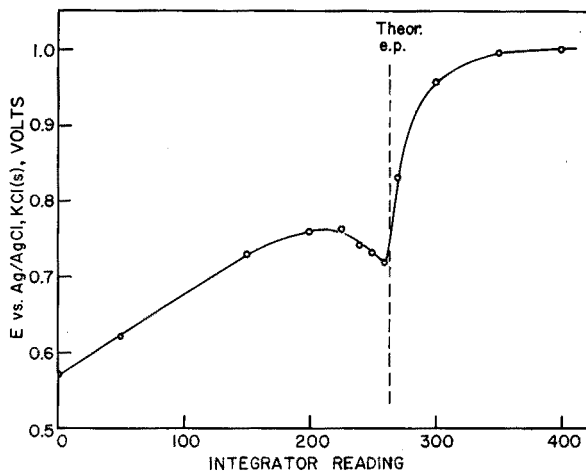


Fig. 2. Typical potentiometric titration curve of 2.05 mg of multergan in 100 cm<sup>3</sup> of 3 M sulfuric acid. The potential of a platinum indicator electrode was measured against an Ag/AgCl, KCl(s) reference electrode. The abscissa is the reading of the integrator in series with the coulometric titration cell. The theoretical 2-electron equivalence point is indicated by the vertical dashed line.

A typical potentiometric titration curve is shown in Fig. 2. An abnormal characteristic (which was reproducible) is that the potential *decreases* sharply just before its large increase at the 2-electron equivalence point. Beyond suggesting that it probably is related to the irreversibility (in a thermodynamic sense) of the second stage of oxidation of the free radical to sulfoxide, we cannot offer a plausible expla-

nation of this phenomenon. Fortunately, it does not interfere with recognizing the large increase in potential at the equivalence point.

Amperometric end-point detection was performed in the usual manner<sup>8</sup> by measuring the current that flowed between two small platinum wire electrodes (area 0.35 cm<sup>2</sup> each) across which a constant voltage (500 mV) was impressed. With this applied voltage, the plot of current *vs.* quantity of electricity passed was V-shaped in the immediate vicinity of the equivalence point, and the latter was determined by extrapolating the two branches to their point of intersection.

TABLE III

## RESULTS OF DIRECT COULOMETRIC TITRATION WITH ELECTROGENERATED CERIUM(IV) ION

(In all cases the supporting electrolyte was 0.05 *F* Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in 3 *M* sulfuric acid, and the solution volume was 75–100 cm<sup>3</sup>. Amperometric end-point detection)

| Substance      | Taken<br>(mg) | Found<br>(mg) | Diff.<br>(mg) |
|----------------|---------------|---------------|---------------|
| Miltorgan      | 0.250         | 0.261         | + 0.011       |
|                | 0.500         | 0.489         | – 0.011       |
|                | 1.000         | 1.008         | + 0.008       |
|                | 2.00          | 1.99          | – 0.01        |
|                | 5.05          | 5.08          | + 0.03        |
|                | 5.00          | 5.06          | + 0.06        |
| Levopromazine  | 1.000         | 1.002         | + 0.002       |
|                | 1.026         | 1.030         | + 0.004       |
|                | 2.05          | 2.06          | + 0.01        |
|                | 3.00          | 3.10          | + 0.10        |
|                | 5.00          | 5.68          | + 0.68        |
| Chlorpromazine | 0.300         | 0.300         | 0.00          |
|                | 0.500         | 0.501         | + 0.001       |
|                | 1.007         | 1.010         | + 0.003       |
|                | 3.02          | 3.03          | + 0.01        |
|                | 5.00          | 10.02         | + 5.02        |
| Profenamine    | 1.004         | 1.032         | + 0.028       |
|                | 2.00          | 2.00          | 0.00          |
| Promethazine   | 1.000         | 0.997         | – 0.003       |
|                | 2.00          | 2.01          | + 0.01        |
|                | 3.00          | 3.11          | + 0.11        |
|                | 5.00          | 5.83          | + 0.83        |
|                | 11.10         | 19.05         | + 7.95        |
|                | 14.50         | 100.9         | + 86.4        |
| Diethazine     | 1.000         | 0.999         | – 0.001       |
|                | 2.02          | 2.03          | + 0.01        |
|                | 2.02          | 2.05          | + 0.02        |
|                | 5.00          | 5.83          | + 0.83        |

Table III summarizes results obtained by direct coulometric titration with electrogenerated cerium(IV) ion, *i.e.*, the sample was present right from the start of the titration. Amperometric end-point detection was used, and the quantity of substance found was computed on the basis of a 2-electron oxidation.

With regard to Table III, it should be noted that when the sample size was

smaller than about 3 mg, the titration yielded accurate results with all of the compounds. However, as the sample size was increased, a rapidly increasing positive error ensued. For example, with a 5-mg sample of chlorpromazine the positive error was 100% relative, and with a 14.5-mg sample of promethazine the quantity of electricity passed before the amperometric end-point was observed was seven times the theoretical value! Such behaviour is most unusual, because the relative error in a coulometric titration ordinarily decreases as the sample size is increased.

In searching for the cause of this exceptional phenomenon, it was found that the large positive error disappeared when about 95% of the requisite quantity of cerium(IV) ion was pre-generated in the supporting electrolyte *before the sample was added*. As shown in Table IV, this pre-generation technique yields accurate results even with samples as large as 20 mg.

TABLE IV

## RESULTS BY PRE-GENERATION

(Supporting electrolyte was 0.05  $F$   $Ce_2(SO_4)_3 \cdot 8 H_2O$  in 3  $M$  sulfuric acid. About 95% of the requisite cerium(IV) ion was pre-generated before addition of sample. Amperometric end-point detection)

| Substance      | Taken<br>(mg) | Found<br>(mg) | Diff.<br>(mg) |
|----------------|---------------|---------------|---------------|
| Levopromazine  | 5.13          | 5.26          | +0.13         |
|                | 10.26         | 10.39         | +0.13         |
| Chlorpromazine | 5.03          | 5.03          | 0.00          |
|                | 10.07         | 10.06         | -0.01         |
| Profenamine    | 10.00         | 10.03         | +0.03         |
|                | 20.00         | 19.67         | -0.33         |
|                | 20.10         | 20.14         | +0.04         |
| Promethazine   | 8.06          | 8.05          | -0.01         |
|                | 10.00         | 10.13         | +0.13         |
|                | 20.16         | 20.31         | +0.15         |
| Diethazine     | 6.00          | 6.02          | +0.02         |
|                | 6.00          | 6.00          | 0.00          |
|                | 10.00         | 10.07         | +0.07         |
|                | 20.00         | 20.05         | +0.05         |

The very large positive errors by direct titration (Table III) could not have been due to further oxidation beyond the 2-electron stage by cerium(IV) *in the bulk of the solution* because this would have been favored even more under the pre-generation conditions of Table IV. The correct results by the pre-generation technique suggested an abnormality at the platinum generator anode itself during the direct titrations. This was confirmed by measuring the potential of the platinum generator anode during the generation of cerium(IV) both without and with the N-substituted phenothiazine present.

Typical results of such measurements are shown in Fig. 3. With the supporting electrolyte alone (curve 1), the potential attains a value of only 1.45 V *vs.* Ag/AgCl, KCl(s), which is the expected value corresponding to the formal potential of the cerium(IV)–cerium(III) couple in 3  $M$  sulfuric acid. However, when an N-substituted phenothiazine is present (curve 2), the potential during the generation is abnormally large (1.88 V *vs.* Ag/AgCl, KCl(s) or 2.08 V *vs.* N.H.E.). This is even larger than the

potential ordinarily observed during the oxidation of water in 3 *M* sulfuric acid alone. This remarkably large overpotential of about 0.4 V has not been reported in any previous coulometric titrations with cerium(IV) ion.

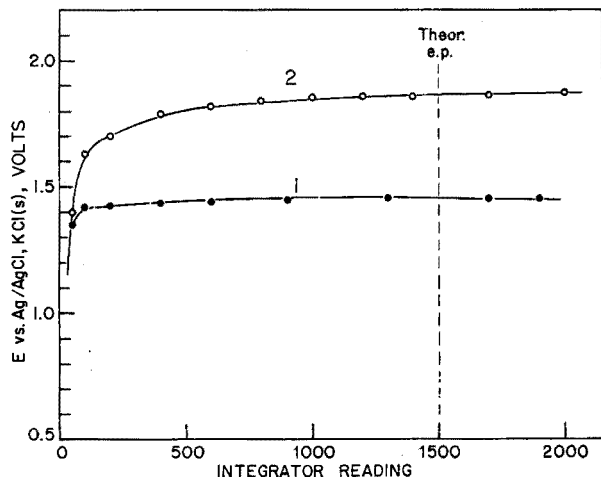


Fig. 3. Potentials of platinum working anode during generation of cerium(IV) ion. (1) 0.05 *F*  $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  in 3 *M* sulfuric acid without sample, (2) the same solution with 10 mg of chlorpromazine.

Evidently, this large overpotential is the cause of the large positive errors observed in the direct titrations (Table III). The potential of 1.88 V *vs.* Ag/AgCl, KCl(s) attained during the direct titrations is large enough to cause some oxidation of water, and therefore, the current efficiency for cerium(IV) ion generation is drastically decreased. Furthermore, at this potential the third stage of oxidation observed in the chronopotentiometric measurements can occur, which, of course, would also contribute to a positive error.

Evidently, the potential of the electrode rises to an abnormally large value because something occurs at its surface to inhibit the oxidation of cerium(III) to cerium(IV) ion. The most likely occurrence is the formation of an insulating film, produced either by adsorption of the oxidation product or by the electrostatic precipitation of an insoluble compound of cerium(IV) ion and the oxidation product. The latter interpretation is more probable, because it seems unlikely that adsorption could produce a film capable of causing an overpotential of 0.4 V. It was observed in test tube experiments that when excess of cerium(IV) ion is added to a solution of an *N*-substituted phenothiazine, a brown colloidal precipitate forms. This colloidal precipitate, if negatively charged, could be attracted to, and discharged at, the electrode to form an insulating film which inhibits access of cerium(III) ion to the electrode surface.

The overpotential phenomenon does not occur when the concentration of the *N*-substituted phenothiazine is smaller than about 3 mg/100 cm<sup>3</sup>, which accounts for the correct results obtained with samples smaller than this by the direct titration method (Table III). This is also the reason why the pre-generation technique yields correct results even with samples as large as 20 mg (Table IV), because when about

95% of the cerium(IV) ion is generated before the sample is added, only about 1 mg of the original compound remains to be finished by the final direct titration.

It should be easily possible to determine considerably less than 1 mg of these compounds simply by employing a smaller volume of supporting electrolyte in an appropriately smaller cell. This would be desirable, for example, after separation of small amounts of the compounds from interfering substances by thin-layer chromatography.

The present method is, of course, not specific, but this is not a serious limitation because one usually is concerned with determining these compounds under conditions where they occur singly. When necessary, mixtures of them can first be resolved by thin-layer chromatography. In the analysis of pharmaceutical products it will also be necessary to perform a prior separation from other compounds that are oxidizable by cerium(IV) ion, and this can be done by methods that are already familiar to practitioners of pharmaceutical analysis.

We are grateful to La Fondation Nationale de la Recherche Scientifique (Belgium) and to the NATO organization which provided fellowships to G.J.P.

#### SUMMARY

The electrochemical oxidation at a platinum anode of several N-substituted phenothiazines (levopromazine, chlorpromazine, multergan, profenamine, promethazine, diethazine, and thioproperazine) has been studied by the chronopotentiometric technique. A method has been developed for the coulometric titration of these substances with electrogenerated cerium(IV). Quantities of 0.25–20 mg are determinable with an average error of less than  $\pm 1$  rel. %.

#### RÉSUMÉ

Les propriétés électrochimiques de diverses phénothiazines substituées à l'azote (lévopromazine, chlorpromazine, multergan, profénamine, prométhazine, diéthazine, et thiopropérazine) sont examinées par chronopotentiométrie. La titration coulométrique de ces constituants est développée à l'aide de l'ion cérique électrogénéré sur des quantités comprises entre 0.25 et 20 mg avec une bonne précision ( $\pm 1\%$  d'erreur relative).

#### ZUSAMMENFASSUNG

Es wurde chronopotentiometrisch die elektrochemische Oxydation von N-substituierten Phenothiazinen untersucht. Dabei wurde eine Methode zur coulometrischen Titration dieser Substanzen mit elektroerzeugten Cer(IV)-Ionen entwickelt. Mengen von etwa 0.25 bis 20 mg sind mit einem durchschnittlichen Fehler von weniger als  $\pm 1\%$  zu bestimmen.

#### REFERENCES

- 1 P. DUBOST AND S. PASCAL, *Ann. Pharm. Franc.*, 11 (1953) 615.
- 2 J. A. RYAN, *J. Am. Pharm. Assoc.*, 48 (1959) 240.

- 3 *Notes Techniques, SPECIA*, Rhône Poulenc, Paris.
- 4 J. B. MILNE AND L. G. CHATTEN, *J. Pharm. Pharmacol.*, 9 (1957) 686.
- 5 P. ZUMAN, *Organic Polarographic Analysis*, Pergamon Press, Oxford, 1964, p. 159.
- 6 F. H. MERKLE AND C. A. DISCHER, *J. Pharm. Sci.*, 53 (1964) 620; *Anal. Chem.*, 36 (1964) 1639.
- 7 J. J. LINGANE, C. H. LANGFORD AND F. C. ANSON, *Anal. Chim. Acta*, 16 (1957) 165.
- 8 J. J. LINGANE, *Electroanalytical Chemistry*, 2nd Edn., Interscience, New York, 1958, p. 494.
- 9 J. J. LINGANE, *Anal. Chim. Acta*, 44 (1969) 199.

*Anal. Chim. Acta*, 49 (1970) 25-34

## TITRATION CURVES OF COMPLEXIMETRIC BACK-TITRATIONS

### PART I. MATHEMATICAL EXPRESSIONS

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In previous papers, some mathematical expressions for the titration curves of compleximetric titrations of mixtures of metals with one ligand were discussed<sup>1</sup> and conditions were derived<sup>2</sup> for the possibility of sharp end-point indication by means of metallochromic indicators or potentiometry.

In the present paper mathematical expressions are derived for back-titrations of mixtures of metals. In subsequent papers conditions will be derived for sharp end-point indication, involving indication either by means of the titrant, or by means of an indicator ion.

#### *Terminology and symbols*

The symbols used in this paper (see Table I) are in accordance with present practice in this field<sup>3</sup>, with the exception that concentrations and stability constants are not primed, because only conditional constants and concentrations are being used. Stability constants used for the computation of conditional stability constants were taken from the tables by RINGBOM<sup>3</sup> and by SILLÉN AND MARTELL<sup>4</sup>.

TABLE I  
SYMBOLS USED

|  |  |
|--|--|
| [M], [N], [P]                                    | Concentration of the metals in any form, except the chelates MY, NY and PY in any form.                  |
| [Y]  | Concentration of the ligand Y in any form, except the chelates MY, NY and PY in any form.                |
| [MY], [NY], [PY]                                 | Concentration of the chelates MY, NY and PY in any form.   |
| $c_Y$  | Concentration of added ligand Y in any form.   |
| $c_M$  | Concentration of titrant M in any form.  |
| $c_N, c_P$                                       | Concentration of the metals to be titrated, N and P, in any form.  |
| $K_{MY}, K_{NY}, K_{PY}$                         | Conditional stability constant of MY, NY and PY.   |
| $f = c_M/c_Y$                                    | Titration parameter = $\frac{\text{amount of titrant in moles}}{\text{total amount of ligand in moles}}$ |
| $f_{ep}$   | Value of the titration parameter at an equivalence point.  |
| $f_c, f_M, f_N, f_P, f_c^*, f_M^*, f_N^*, f_P^*$ | Parts of the mathematical expressions for the titration curves.  |
| $[Y]_+, [M]_+, f_+$                              | Values of [Y], [M] and $f$ 1% after an equivalence point.  |
| $[Y]_-, [M]_-, f_-$                              | Values of [Y], [M] and $f$ 1% before an equivalence point.   |
| $\alpha_{Hg}$                                    | Side-reaction coefficient of mercury(II), used in the conversion of pHg to mV.                           |

## MATHEMATICAL EXPRESSIONS

It is assumed that only 1:1 complexes are formed and that changes in volume may be neglected. It is also assumed that the reactions are sufficiently rapid. The titration curves for the back-titration of a mixture of metals N and P, to which an excess of ligand Y has been added, with the titrant M may then be derived from the following equations, which hold during the whole titration:

$$[M] + [MY] = c_M \quad (1)$$

$$[N] + [NY] = c_N \quad (2)$$

$$[P] + [PY] = c_P \quad (3)$$

$$[Y] + [MY] + [NY] + [PY] = c_Y \quad (4)$$

$$K_{MY} = [MY]/[M][Y] \quad (5)$$

$$K_{NY} = [NY]/[N][Y] \quad (6)$$

$$K_{PY} = [PY]/[P][Y] \quad (7)$$

A suitable definition for the titration parameter  $f$  is

$$f = c_M/c_Y \quad (8)$$

Two indication methods are of importance in the potentiometric back-titration of a metal N to which ligand is added in excess: (1) indication by means of the concentration of the titrant M; and (2) indication by means of an indicator metal ion P added to the titration solution in an amount which in general is small with respect to the amount of N.

Indication by means of the concentration of the metal ion to be determined, N, is unimportant from the analytical point of view, as in that case a direct titration will be possible as well. Accordingly, the relations between  $f$  and  $[M]$  and between  $f$  and  $[P]$  should be calculated. The relation between  $f$  and  $[M]$  cannot be easily expressed explicitly, but the  $f$ - $[M]$  curve may be obtained from the relationships between  $f$  and  $[Y]$  and between  $[M]$  and  $[Y]$ .

The relation between  $f$  and  $[Y]$  may also serve as a starting point in the derivation of all the other titration curves of back-titrations and is therefore derived first.

From eqns. (1) and (5) are found

$$[M] = c_M/(1 + [Y]K_{MY}) \quad (9)$$

and

$$[MY] = [Y]c_MK_{MY}/(1 + [Y]K_{MY}) \quad (10)$$

In the same way, equations may be found for  $[N]$ ,  $[NY]$ ,  $[P]$  and  $[PY]$ :

$$[N] = c_N/(1 + [Y]K_{NY}) \quad (11)$$

$$[NY] = [Y]c_NK_{NY}/(1 + [Y]K_{NY}) \quad (12)$$

$$[P] = c_P/(1 + [Y]K_{PY}) \quad (13)$$

$$[PY] = [Y]c_PK_{PY}/(1 + [Y]K_{PY}) \quad (14)$$

Substituting eqns. (10), (12) and (14) into (4) leads to

$$c_Y = [Y] + \frac{[Y]c_MK_{MY}}{1 + [Y]K_{MY}} + \frac{[Y]c_NK_{NY}}{1 + [Y]K_{NY}} + \frac{[Y]c_PK_{PY}}{1 + [Y]K_{PY}} \quad (15)$$



In this equation,  $c_M$  may be eliminated by introducing the titration parameter  $f$ , cf. eqn. (8). A formula for the titration curve  $f$ -[Y] is then obtained after rearrangement:

$$f = \left( I + \frac{I}{[Y]K_{MY}} \right) \left( I - \frac{[Y]}{c_Y} - \frac{c_N}{c_Y} \frac{[Y]K_{NY}}{I + [Y]K_{NY}} - \frac{c_P}{c_Y} \frac{[Y]K_{PY}}{I + [Y]K_{PY}} \right) \quad (16)$$

By means of the equation

$$[Y] = \frac{c_P - [P]}{[P]K_{PY}} \quad (17)$$

which is derived from eqn. (13), eqn. (16) may be transformed to a relation between  $f$  and [P]:

$$f = \left( I + \frac{[P]}{c_P - [P]} \frac{K_{PY}}{K_{MY}} \right) \left( I - \frac{c_N}{c_Y} \frac{I}{\frac{[P]}{c_P - [P]} \frac{K_{PY}}{K_{NY}} + I} - \frac{c_P}{c_Y} \frac{I + [P]K_{PY}}{[P]K_{PY}} \frac{c_P - [P]}{c_P} \right) \quad (18)$$

The relationships between  $f$  and [PY], [N] and [NY] may be derived analogously.

The titration curves  $f$ -[M] and  $f$ -[MY] can best be derived from the  $f$ -[Y] curve by means of eqns. (9a) and (10a):

$$[M] = f c_Y / (I + [Y]K_{MY}) \quad (9a)$$

$$[MY] = f[Y]c_Y K_{MY} / (I + [Y]K_{MY}) \quad (10a)$$

These curves are calculated as follows: selected values of [Y] are substituted in eqn. (16), giving values of  $f$ . The same values of [Y], together with the calculated values of  $f$  are then substituted in either eqn. (9a) or eqn. (10a), thus leading to the relation between  $f$  and [M] or between  $f$  and [MY].

#### GRAPHICAL REPRESENTATION

In the previous papers<sup>1,2</sup>, it has been shown that for the discussion of titration curves, it is convenient to divide the mathematical expression for  $f$  into several parts,  $f_1, f_2$ , etc. An analogous procedure may be applied to the mathematical relationships in back-titrations. There is, however, one difference: in back-titrations it is advantageous to use a product instead of a sum of terms.

For potentiometric indication logarithmic plots of the titration curves are most useful and as a consequence only logarithmic plots will be used in this paper. Linear plots, which are important for other indication methods, will be discussed at a later date.

#### Indication by means of the titrant M

The relation between  $f$  and [Y], cf. eqn. (16), is written as

$$f = f_M (I + f_c + f_N + f_P)$$

in which the abbreviations have the following meaning:

$$f_M = I + \frac{I}{[Y]K_{MY}}$$

$$f_c = -\frac{[Y]}{c_Y}$$

$$f_N = -\frac{c_N}{c_Y} \frac{[Y]K_{NY}}{1 + [Y]K_{NY}}$$

and

$$f_P = -\frac{c_P}{c_Y} \frac{[Y]K_{PY}}{1 + [Y]K_{PY}}$$

These parts  $f_M$ ,  $f_c$ ,  $f_N$  and  $f_P$  are plotted separately;  $1$ ,  $f_c$ ,  $f_N$  and  $f_P$  are added, and finally this sum is multiplied by  $f_M$ .

The terms  $f_M$  and  $(1 + f_c)$  are the same as in the titration of a ligand  $Y$  with a metal  $M$ . Consequently, the  $f$ - $pY$  curve for back-titrations may be regarded as the curve of the titration of  $Y$  with  $M$ . The shape of the curve, however, is changed by the terms  $f_N$  and  $f_P$ , resulting from the presence of the metals  $N$  and  $P$ . A few examples will illustrate this procedure.

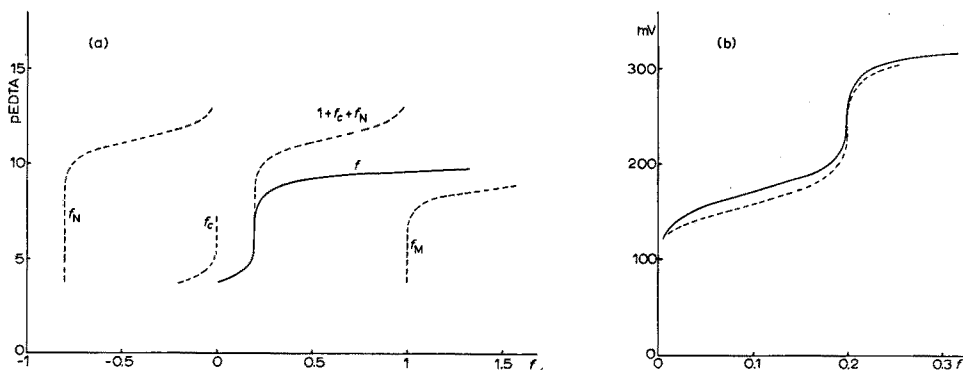


Fig. 1a. Construction of the theoretical  $f$ - $pEDTA$  curve for the back-titration with mercury(II) of 0.0008  $M$  copper(II) and 0.001  $M$  EDTA in 0.1  $M$  acetate buffer, pH 5;  $f = f_M(1 + f_c + f_N)$ ;  $\log K_{HgEDTA} = 9.0$ ;  $\log K_{CuEDTA} = 11.3$ .

Fig. 1b. Titration curves  $f$ -mV (mercury electrode vs. S.C.E.). (—) Theoretical curve, calculated from Fig. 1a by means of eqn. (9a) and with  $\log \alpha_{Hg} = 6.2$ ; (- - - -) experimental curve.

$M$  forms a weaker complex than  $N$ . Figure 1a shows the construction of the  $f$ - $pY$  curve for the back-titration with mercury (II) of excess of EDTA after reaction with copper(II). The composition of the solution to be titrated was 0.0008  $M$  copper(II), 0.001  $M$  EDTA and 0.1  $M$  acetate buffer, pH 5. The stability constants used in the calculation were  $\log K_{CuEDTA} = 11.3$  and  $\log K_{HgEDTA} = 9.0$ . In Fig. 1b the corresponding  $f$ -mV (mercury electrode vs. S.C.E.) curve is plotted. In order to obtain this curve, first the  $f$ - $pHg$  curve was calculated from the  $f$ - $pEDTA$  curve, and then the  $f$ - $pHg$  curve was converted to the  $f$ -mV curve by means of the Nernst equation. The side-reaction coefficient,  $\log \alpha_{Hg} = 6.2$ , was used to convert the conditional concentration of mercury to its actual concentration. In the same Fig. 1b, the experimental curve is plotted. This experimental curve was recorded with a Radiometer automatic titrator, provided with a mercury electrode and a S.C.E. Full experimental details will be given in a later paper.

*M forms stronger complexes than N.* An example of the back-titration with a metal forming a more stable complex with the ligand than the metal to be titrated is given in Figs. 2a and 2b. A solution containing 0.0008 *M* lead(II), 0.001 *M* DTPA and 0.02 *M* acetate buffer, pH 5, was titrated with mercury(II). Figure 2a shows the construction of the *f*-pY curve, and Fig. 2b the calculated and the experimental *f*-mV curves. In this example two pY jumps and two potential jumps are found, the first jump occurring when the excess of ligand has been complexed, and the second when the total amount of Y is present as the complex MY.

*A mixture of metals N and P.* Figure 3a shows the construction of the *f*-pY curve for the back-titration of a mixture of metals. A solution containing 0.0003 *M* lead(II), 0.0005 *M* iron(III), 0.001 *M* DTPA and 0.02 *M* acetate buffer, pH 5, was titrated with Hg(II). Figure 3b gives the calculated and the experimental *f*-mV curves.

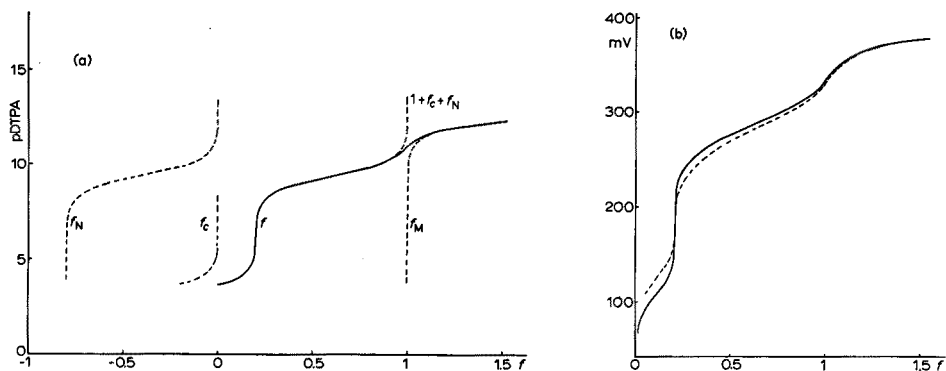


Fig. 2a. Construction of the theoretical *f*-pDTPA curve for the back-titration with mercury(II) of 0.0008 *M* lead(II) and 0.001 *M* DTPA in 0.02 *M* acetate buffer, pH 5;  $\log K_{\text{HgDTPA}} = 12.6$ ;  $\log K_{\text{PbDTPA}} = 9.3$ .

Fig. 2b. Titration curves *f*-mV (mercury electrode vs. S.C.E.). (—) Theoretical curve, calculated from Fig. 2a by means of eqn. (9a) and with  $\log \alpha_{\text{Hg}} = 4.9$ ; (----) experimental curve.

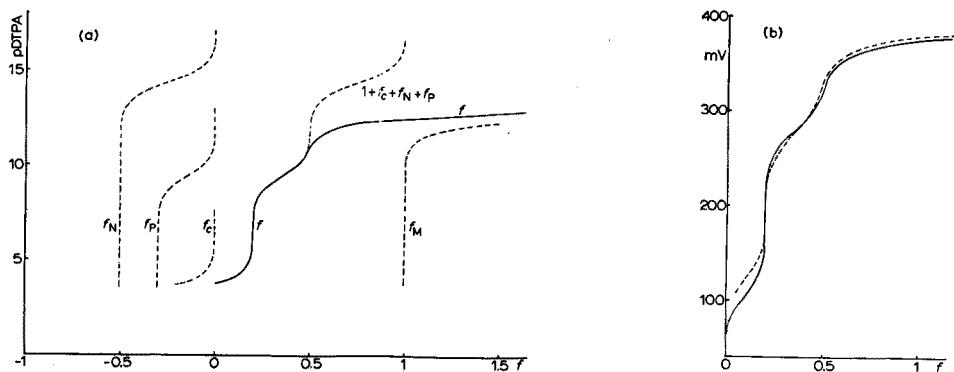


Fig. 3a. Construction of the theoretical *f*-pDTPA curve for the back-titration with mercury(II) of 0.0003 *M* lead(II), 0.0005 *M* iron(III) and 0.001 *M* DTPA in 0.02 *M* acetate buffer, pH 5;  $f = f_{\text{M}}(1 + f_{\text{c}} + f_{\text{N}} + f_{\text{P}})$ ;  $\log K_{\text{HgDTPA}} = 12.6$ ;  $\log K_{\text{PbDTPA}} = 9.3$ ;  $\log K_{\text{FeDTPA}} = 14.4$ .

Fig. 3b. Titration curves *f*-mV (mercury electrode vs. S.C.E.). (—) Theoretical curve, calculated from Fig. 3a by means of eqn. (9a) and with  $\log \alpha_{\text{Hg}} = 4.9$ ; (----) experimental curve.

The following stability constants were used for the calculations of Figs. 2 and 3:  $\log K_{\text{HgDTPA}}=12.6$ ,  $\log K_{\text{PbDTPA}}=9.4$  and  $\log K_{\text{FeDTPA}}=14.4$ . The side-reaction coefficient was  $\log \alpha_{\text{Hg}}=4.9$ .

*Indication by means of an indicator ion P*

The indication of the back-titration of N with M by means of an indicator P may be treated by means of the relationship between  $f$  and  $[P]$  given in eqn. (18). For this purpose

$$f = \left( I + \frac{[P]}{c_P - [P]} \frac{K_{PY}}{K_{MY}} \right) \left( I - \frac{c_N}{c_Y} \frac{I}{\frac{[P]}{c_P - [P]} \frac{K_{PY}}{K_{NY}} + I} - \frac{c_P}{c_Y} \frac{I + [P]K_{PY}}{[P]K_{PY}} \frac{c_P - [P]}{c_P} \right) \quad (18)$$

may be written as

$$f = f_M^*(I + f_N^* + f_P^*).$$

In this case the abbreviations  $f_M^*$ ,  $f_N^*$  and  $f_P^*$  stand for:

$$f_M^* = I + \frac{[P]}{c_P - [P]} \frac{K_{PY}}{K_{MY}}$$

$$f_N^* = - \frac{c_N}{c_Y} \frac{I}{\frac{[P]}{c_P - [P]} \frac{K_{PY}}{K_{NY}} + I}$$

and

$$f_P^* = - \frac{c_P}{c_Y} \frac{I + [P]K_{PY}}{[P]K_{PY}} \frac{c_P - [P]}{c_P}$$

$f_M^*$ ,  $f_N^*$  and  $f_P^*$  are again plotted separately,  $f_N^*$ ,  $f_P^*$  and  $I$  are added, and finally this sum is multiplied by  $f_M^*$ .

*Complex of indicator ion PY weaker than MY and NY.* Figure 4a shows the

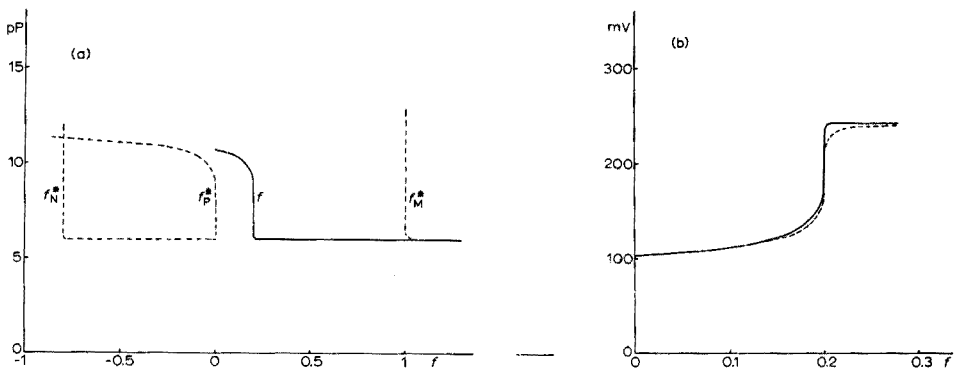


Fig. 4a. Construction of the theoretical  $f$ -pH curve for the back-titration with copper(II) of  $0.0008 M$  iron(III) and  $0.001 M$  EDTA in  $0.2 M$  acetate buffer, pH 5, indicated by means of  $10^{-6} M$  mercury(II).  $f = f_M^*(I + f_N^* + f_P^*)$ ;  $\log K_{\text{CuEDTA}} = 10.9$ ;  $\log K_{\text{FeEDTA}} = 12.4$ ;  $\log K_{\text{HgEDTA}} = 8.4$ .

Fig. 4b. Titration curves  $f$ -mV (mercury electrode vs. S.C.E.). (—) Theoretical curve, calculated from Fig. 4a with  $\log \alpha_{\text{Hg}} = 6.8$ ; (----) experimental curve.

construction of the theoretical titration curve  $f$ -pHg for the back-titration with copper(II) of 0.0008  $M$  iron(III),  $10^{-6}$   $M$  mercury(II) and 0.001  $M$  EDTA in 0.2  $M$  acetate buffer, pH 5. The constants used are:  $\log K_{\text{CuEDTA}} = 10.9$ ,  $\log K_{\text{FeEDTA}} = 12.4$  and  $\log K_{\text{HgEDTA}} = 8.4$ . Figure 4b gives both the theoretical  $f$ -mV curve, calculated with  $\log \alpha_{\text{Hg}} = 6.8$ , and the experimental  $f$ -mV curve.

*Complex of indicator ion PY weaker than MY but stronger than NY.* Titration curves having two equivalence points are shown in Figs. 5 and 6, which show the titration with copper(II) solution of a mixture of calcium(II) and mercury(II) to which EDTA has been added in excess. In Fig. 5 the concentrations of calcium(II) and mercury(II) are equal, whereas in Fig. 6 only a small amount of mercury(II) is present as an indicator ion.

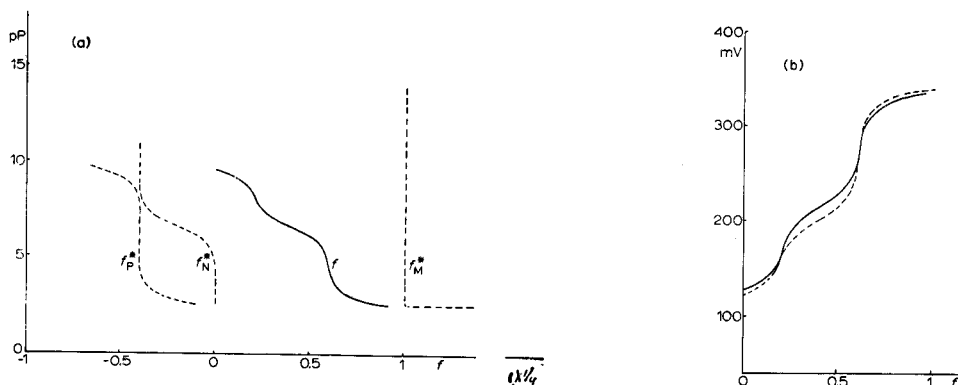


Fig. 5a. Construction of the theoretical  $f$ -pHg curve for the back-titration with copper(II) of 0.004  $M$  calcium(II), 0.004  $M$  mercury(II) and 0.01  $M$  EDTA in 0.2  $M$  acetate buffer, pH 6;  $\log K_{\text{CuEDTA}} = 12.4$ ;  $\log K_{\text{CaEDTA}} = 5.7$ ;  $\log K_{\text{HgEDTA}} = 9.9$ .

Fig. 5b. Titration curves  $f$ -mV (mercury electrode vs. S.C.E.). (—) Theoretical curve, calculated from Fig. 5a with  $\log \alpha_{\text{Hg}} = 7.1$ ; (----) experimental curve (pH 6.0  $\rightarrow$  5.8).

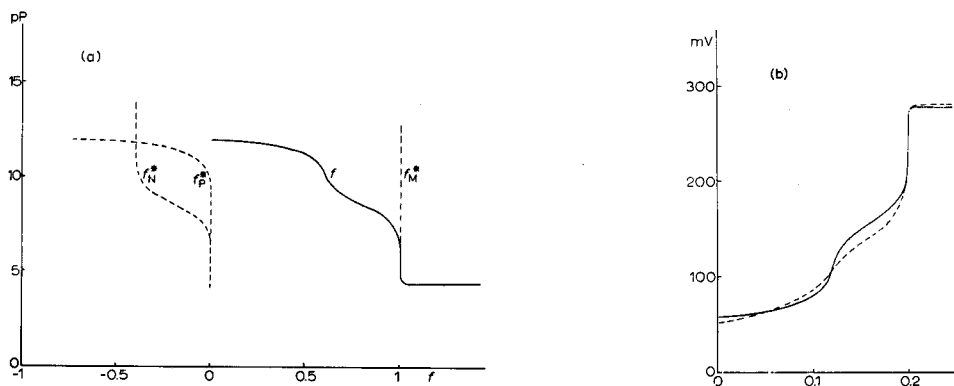


Fig. 6a. Construction of the theoretical  $f$ -pHg curve for the back-titration with copper(II) of 0.004  $M$  calcium and 0.01  $M$  EDTA in 0.2  $M$  acetate buffer, pH 6, indicated by means of  $4 \cdot 10^{-5}$   $M$  mercury(II);  $\log K_{\text{CuEDTA}} = 12.4$ ;  $\log K_{\text{CaEDTA}} = 5.7$ ;  $\log K_{\text{HgEDTA}} = 9.9$ .

Fig. 6b. Titration curves  $f$ -mV (mercury electrode vs. S.C.E.). (—) Theoretical curve, calculated from Fig. 6a with  $\log \alpha_{\text{Hg}} = 7.1$ ; (----) experimental curve (pH 6.0  $\rightarrow$  5.7).

Figure 5a shows the construction of the theoretical curve  $f$ -pHg for the titration of  $4 \cdot 10^{-3} M$  calcium(II),  $4 \cdot 10^{-3} M$  mercury(II) and  $10^{-2} M$  EDTA in  $0.2 M$  acetate buffer, pH 6, with copper(II). Figure 5b shows the theoretical and the experimental  $f$ -mV curves.

Figures 6a and 6b show the titration curves for the corresponding titration of  $4 \cdot 10^{-3} M$  calcium(II), indicated by means of  $4 \cdot 10^{-5} M$  mercury(II).

The constants used in the computation of Figs. 5 and 6 are:  $\log K_{CuEDTA} = 12.4$ ,  $\log K_{CaEDTA} = 5.7$ ,  $\log K_{HgEDTA} = 9.9$  and  $\log \alpha_{Hg} = 7.1$ .

#### DISCUSSION

The calculations and the experimental verification demonstrate that the scope of these back-titrations is larger than has previously been thought. Especially the fact that the stability constant of the complex of the metal used as back-titrant may be stronger than the complex of the metal to be determined, has often been overlooked.

#### SUMMARY

Formulae were calculated for the compleximetric back-titration of mixtures of metals, giving the relation between a titration parameter  $f$  and the concentration of the metals or the ligand. It is shown that the scope of these titrations is wider than has been realized.

#### RÉSUMÉ

Des expressions mathématiques ont été établies pour les courbes de titrage complexométriques en retour. Les expressions permettent une représentation graphique simple de ces courbes de titrage. Quelques exemples illustrent l'efficacité de ces expressions.

#### ZUSAMMENFASSUNG

Für die Titrationskurven komplexometrischer Rücktitrationen von Metallgemischen werden theoretische Ausdrücke abgeleitet. Die Ausdrücke ermöglichen eine einfache graphische Wiedergabe dieser Titrationskurven. An einigen Beispielen wird die Brauchbarkeit der Formeln erläutert.

#### REFERENCES

- 1 U. HANNEMA AND G. DEN BOEF, *Anal. Chim. Acta*, 39 (1967) 167.
- 2 U. HANNEMA AND G. DEN BOEF, *Anal. Chim. Acta*, 39 (1967) 479.
- 3 A. RINGBOM, *Complexation in Analytical Chemistry*, Interscience, New York, 1963.
- 4 L. G. SILLÉN AND A. E. MARTELL, *Stability Constants of Metal Ion Complexes*, The Chemical Society, London, 1964.

## TITRATION CURVES OF COMPLEXIMETRIC BACK-TITRATIONS

### PART II. CONDITIONS FOR SHARP END-POINTS WITH INDICATION BY MEANS OF THE TITRANT

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Some mathematical expressions for the titration curves of compleximetric back-titrations have been derived in a previous paper<sup>1</sup>. In the same paper the graphical representation of these equations was discussed for the case of logarithmic plots, which are of importance for potentiometric end-point indication and for visual end-point indication by means of metallochromic indicators.

In the present paper conditions for sharp end-points in these logarithmic representations will be calculated. The terminology and symbols are the same as in the previous paper<sup>1</sup>.

In general, it is accepted that a pM jump of 2 pM units in the interval of 1% before and 1% after an equivalence point ( $f_-$ - $f_+$ ) will always give a potential jump sufficiently large for an accurate potentiometric end-point determination. The same pM jump is adequate for visual indication provided that an indicator is available which changes colour in just this pM interval.

In the case of potentiometric back-titrations, a slight modification of the  $f$ -interval in which a jump of 2 pM units occurs is to be preferred. It is more appropriate to relate the values of  $f_+$  and  $f_-$  to the concentrations which are derived from the equivalence point under consideration than to the value of  $f$  itself. Consequently, for an equivalence point at, for example,  $f = 1 - [(c_N + c_P)/c_Y]$  corresponding to the titration of the excess ligand, the  $f$ -interval should be  $f = 1 - [(c_N + c_P)/c_Y] \pm 10^{-2} (c_N + c_P)/c_Y$ , as this equivalence point yields the concentration  $c_N + c_P$ . Other equivalence points are dealt with in a similar fashion.

#### CONDITIONS FOR SHARP END-POINTS; pY INDICATION

Since no simple explicit relationship is to be found between  $f$  and the concentration of the titrant M, it is necessary to derive the conditions for sharp pM indication in an indirect way. It appeared to be suitable in the first place to derive the conditions for sharp pY end-points and then to transform these conditions into the conditions for sharp pM end-points.

For the back-titration with a metal ion M of a mixture of two metal ions N and P to which a ligand Y has been added in excess, the conditions for sharp pY end-points may be found from the equation

$$f = \left( 1 + \frac{1}{[Y]K_{MY}} \right) \left( 1 - \frac{[Y]}{c_Y} - \frac{c_N}{c_Y} \frac{[Y]K_{NY}}{1 + [Y]K_{NY}} - \frac{c_P}{c_Y} \frac{[Y]K_{PY}}{1 + [Y]K_{NY}} \right) \quad (1)$$

which was derived in the previous paper<sup>1</sup>. This equation is more conveniently written as

$$f = f_M(I + f_c + f_N + f_P) \quad (2)$$

The concentrations  $c_Y$ ,  $c_N$  and  $c_P$  are assumed to be of the same order of magnitude. The metal ion N is assumed to form more stable complexes with Y than those formed by P. When  $K_{NY}$  and  $K_{PY}$  are of the same order of magnitude the system behaves as though only one metal were present. As a consequence only the extreme case  $K_{NY} \gg K_{PY}$  will be considered. Depending on the value of  $K_{MY}$  with respect to  $K_{NY}$  and  $K_{PY}$ , three important cases can be distinguished, *viz.*

1.  $K_{MY} \ll K_{PY} \ll K_{NY}$
2.  $K_{PY} \ll K_{MY} \ll K_{NY}$
3.  $K_{PY} \ll K_{NY} \ll K_{MY}$

These three cases will be discussed separately.

#### $K_{MY} \ll K_{PY} \ll K_{NY}$

In Fig. 1 an example of this case is given. Only one pY jump occurs in this case. At this equivalence point, the excess of the ligand  $c_Y - c_N - c_P$  has reacted with M. No other equivalence points are to be found because M cannot displace N or P from their complexes.

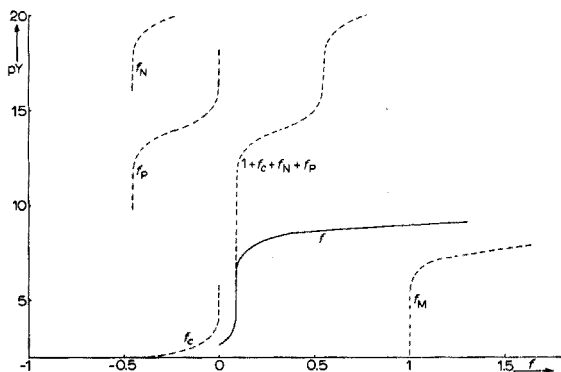


Fig. 1. Construction of the theoretical titration curve  $f$ -pY for the back-titration with the metal M of a solution in which the molarity of the metals N and P is 0.01 and that of the ligand Y is 0.022;  $f = f_M(I + f_c + f_N + f_P)$ ;  $\log K_{MY} = 8$ ;  $\log K_{NY} = 20$ ;  $\log K_{PY} = 14$ .

The value of  $pY_-$ , the lower limit of this pY jump can be determined as follows.

$$f_- = I - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} - 10^{-2} \left( \frac{c_N + c_P}{c_Y} \right) = f_M (I + f_c + f_N + f_P)$$

In those cases leading to suitable titration curves,  $f_M = 1$  at this lower limit. With regard to  $f_N$  and  $f_P$ , it can be stated that they have the value  $-c_N/c_Y$  and  $-c_P/c_Y$  during the whole titration. We therefore may write:

$$I - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} - 10^{-2} \left( \frac{c_N + c_P}{c_Y} \right) = I - \frac{[Y]_-}{c_Y} - \frac{c_N}{c_Y} - \frac{c_P}{c_Y}$$



This leads to:

$$[Y]_- = 10^{-2} (c_N + c_P)$$

or

$$pY_- = -\log(c_N + c_P) + 2 \quad (3)$$

With regard to the value of  $pY_+$ , the upper limit of the  $pY$  jump, it can be stated that at this value  $f_c = 0$ .

Consequently,

$$f_+ = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} + 10^{-2} \frac{c_N + c_P}{c_Y} = f_M \left( 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} \right)$$

This leads to:

$$f_M = 1 + \frac{1}{[Y]_+ K_{MY}} = 1 + 10^{-2} \frac{c_N + c_P}{c_Y - c_N - c_P}$$

or

$$[Y]_+ K_{MY} = 10^{-2} \frac{c_Y - c_N - c_P}{c_N + c_P}$$

In practical back-titrations  $(c_Y - c_N - c_P)/(c_N + c_P)$  generally will not differ much from unity and hence

$$[Y]_+ K_{MY} = 10^2$$

or

$$pY_+ = \log K_{MY} - 2 \quad (4)$$

As the condition for a sharp end-point is:

$$pY_+ - pY_- = 2,$$

the eqns. (3) and (4) lead to:

$$(c_N + c_P) K_{MY} = 10^6 \quad (5)$$

$$K_{PY} \ll K_{MY} \ll K_{NY}$$

Figure 2 shows the situation in which the stability constant of MY lies between

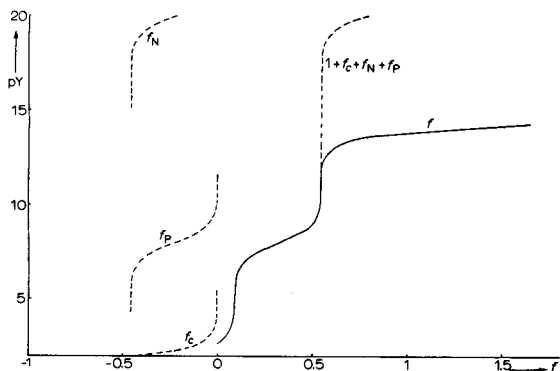


Fig. 2. Construction of the theoretical titration curve  $f$ - $pY$  for the back-titration with the metal M of a solution in which the molarity of the metals N and P is 0.01 and that of the ligand Y is 0.022;  $f = f_M(1 + f_c + f_N + f_P)$ ;  $\log K_{MY} = 14$ ;  $\log K_{NY} = 20$ ;  $\log K_{PY} = 8$ .

the values of the stability constants of PY and NY. If the stability constant of PY, the weakest complex, is large enough, two pY jumps occur in the curve. The first is at

$$f = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y},$$

where the excess of the ligand has reacted with M. The second equivalence point is at  $f = 1 - c_N/c_Y$  where the metal ion P has been totally displaced from its complex PY by the titrant M. As M cannot replace N from NY no further pY jump is to be found.

It is obvious that in this case not only the sum of the concentrations  $c_N + c_P$ , but also the values of  $c_N$  and  $c_P$  can be determined. For both equivalence points, conditions for sharp end-points can be derived.

As the equivalence point at

$$f = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y}$$

not only serves for the determination of the sum of N and P, but also for the determination of P, the  $f$ -interval at this equivalence point will be used:

$$f = 1 - \frac{c_N + c_P}{c_Y} \pm 10^{-2} \frac{c_P}{c_Y}$$

The lower limit is again determined by  $f_c$  and consequently a relationship similar to eqn. (3) is found for  $pY_-$ , *i.e.*

$$pY_- = -\log c_P + 2 \quad (3a)$$

It can be seen from Fig. 2 that the upper limit at this equivalence point depends on  $f_P$ .

$$f_+ = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} + 10^{-2} \frac{c_P}{c_Y} = f_M(1 + f_e + f_N + f_P)$$

At this upper limit,  $f_M = 1$ ,  $f_c = 0$  and  $f_N = -c_N/c_Y$ .

This leads to:

$$1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} + 10^{-2} \frac{c_P}{c_Y} = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} \frac{[Y]_+ + K_{PY}}{1 + [Y]_+ + K_{PY}}$$

resulting in:

$$pY_+ = \log K_{PY} - 2 \quad (6)$$

Combination of eqns. (3a) and (6) leads to the condition for a pY jump of 2 pY units at the first equivalence point.

$$K_{PY} c_P = 10^6 \quad (7)$$

The second pY jump at  $f = 1 - c_N/c_Y$  in this case depends on  $f_P$  and  $f_M$ .

As this equivalence point can be used for the determination of P, the  $f$ -interval is taken as:

$$f = 1 - \frac{c_N}{c_Y} \pm 10^{-2} \frac{c_P}{c_Y}$$

The lower limit depends on  $f_P$

$$f_- = 1 - \frac{c_N}{c_Y} - 10^{-2} \frac{c_P}{c_Y} = f_M(1 + f_c + f_N + f_P)$$

Proceeding in the same way as before, we find:

$$1 - \frac{c_N}{c_Y} - 10^{-2} \frac{c_P}{c_Y} = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} \frac{[Y] - K_{PY}}{1 + [Y] - K_{PY}}$$

which leads to:

$$pY_- = \log K_{PY} + 2 \quad (8)$$

The upper limit depends on  $f_M$ :

$$f_+ = 1 - \frac{c_N}{c_Y} + 10^{-2} \frac{c_P}{c_Y} = f_M(1 + f_c + f_N + f_P)$$

At this upper limit not only  $f_c$  but also  $f_P$  equals 0. The value of  $f_N$  still is  $-c_N/c_Y$ , which leads to:

$$1 - \frac{c_N}{c_Y} + 10^{-2} \frac{c_P}{c_Y} = f_M \left( 1 - \frac{c_N}{c_Y} \right)$$

Rearrangement gives:

$$[Y]_+ K_{MY} = 10^{+2} \frac{c_Y - c_N}{c_P}$$

When the excess of ligand is not large with respect to  $c_P$ , this approximately leads to:

$$pY_+ = \log K_{MY} - 2 \quad (4)$$

Combination of eqns. (4) and (8) then leads to the condition for a pY jump of 2 pY units at the second equivalence point

$$\frac{K_{MY}}{K_{PY}} = 10^6 \quad (9)$$

$K_{PY} \ll K_{NY} \ll K_{MY}$

Figure 3 shows the situation in which the stability constant of MY is larger

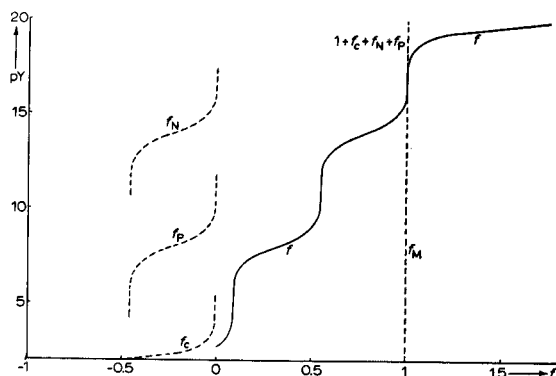


Fig. 3. Construction of the theoretical titration curve  $f$ - $pY$  for the back-titration with the metal M of a solution in which the molarity of the metals N and P is 0.01 and that of the ligand Y is 0.022;  $f = f_M(1 + f_c + f_N + f_P)$ ;  $\log K_{MY} = 20$ ;  $\log K_{NY} = 14$ ;  $\log K_{PY} = 8$ .

than both PY and NY. If the stability constant of PY is large enough, three pY jumps occur in the curve. The first and second jumps occur at the same values of  $f$  as in the previous case. The third jump corresponds to the replacement of N from NY by M. As a matter of fact, this third jump has only slight analytical significance.

The condition for a sharp end-point at  $f = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y}$  is the same as in case 2,

cf. eqn. (7).

The pY jump at  $f = 1 - c_N/c_Y$  depends on  $f_N$  and  $f_P$ . The value of pY<sub>-</sub> is again given by eqn. (8). The upper limit depends on  $f_N$ .

$$f_+ = 1 - \frac{c_N}{c_Y} + 10^{-2} \frac{c_P}{c_Y} = f_M(1 + f_c + f_N + f_P)$$

At this upper limit,  $f_c = 0$ ,  $f_P = 0$  and  $f_M = 1$ , which leads to:

$$1 - \frac{c_N}{c_Y} + 10^{-2} \frac{c_P}{c_Y} = 1 - \frac{c_N}{c_Y} \frac{[Y]_+ + K_{NY}}{1 + [Y]_+ + K_{NY}}$$

$$[Y]_+ + K_{NY} = 10^2 \frac{c_N}{c_P} - 1$$

When  $c_N$  and  $c_P$  are of the same order of magnitude, this leads to:

$$pY_+ = \log K_{NY} - 2 \quad (10)$$

Combination of eqns. (8) and (10) then leads to the condition for a pY jump of 2 pY units at the second equivalence point

$$\frac{K_{NY}}{K_{PY}} = 10^6$$

When  $c_P$  is small with respect to  $c_N$ , this ratio should be larger.

The third jump is of no practical significance. It can easily be found that

$$\frac{K_{MY}}{K_{NY}} = 10^6$$

is the condition for a pY jump of 2 pY units at this third equivalence point.

#### CONDITIONS FOR SHARP pM END-POINTS

As the change in  $f$  in any of the pY jumps mentioned previously is necessarily very small, the concentration of the complex [MY] at any of the equivalence points is nearly constant. It then can be concluded from  $K_{MY} = [MY]/[M][Y]$ , the stability constant of the complex MY, that at the equivalence points the product [M][Y] is constant. This means that a pY jump of 2 pY units at an equivalence point is directly coupled with a pM jump of also 2 pM units. It may therefore be concluded, that the conditions for sharp pM end-points are the same as for the pY end-points.

#### EXPERIMENTAL VERIFICATION

Figures 1, 2 and 3 of the previous paper on compleximetric back-titrations<sup>1</sup> may serve as theoretical and experimental examples.

Figure 1 of Part I shows that a sharp end-point is found in the back-titration of 0.0008 *M* copper(II) and 0.001 *M* EDTA in 0.1 *M* acetate buffer, pH 5, with mercury(II) solution. The product  $c_{\text{Cu}}K_{\text{HgEDTA}} = 10^{5.7}$  appears to be adequate, cf. eqn. (5). Only one pM jump is found since  $K_{\text{HgEDTA}} < K_{\text{CuEDTA}}$ .

Figure 2 of Part I shows the titration curves for the back-titration of 0.0008 *M* lead(II) and 0.001 *M* DTPA in 0.02 *M* acetate buffer, pH 5, with mercury(II) solution. The product  $c_{\text{Pb}}K_{\text{PbDTPA}} = 10^{6.2}$  results in a value high enough for a sharp end-point at  $f=0.2$ , cf. eqn. (7). Another jump occurs at  $f=1$ , but this jump is not well developed because the ratio  $K_{\text{HgDTPA}}/K_{\text{PbDTPA}}$  is too small.

In Fig. 3 the titration curves are plotted for the back-titration of 0.0003 *M* lead(II), 0.0005 *M* iron(III) and 0.001 *M* DTPA in 0.02 *M* acetate buffer, pH 5, with mercury(II) solution. The first end-point at  $f=0.2$  is sharp, as is to be expected, since  $c_{\text{Pb}}K_{\text{PbDTPA}} = 10^{6.2}$ , cf. eqn. (7). The second end-point at  $f=0.5$  is not sharp because the value of  $K_{\text{HgDTPA}}/K_{\text{PbDTPA}}$  is only  $10^{3.1}$ , cf. eqn. (9). A third jump is not to be expected since  $K_{\text{HgDTPA}} < K_{\text{FeDTPA}}$ .

#### DISCUSSION

Back-titrations may be important in those cases where a direct titration fails, e.g. because of a slow reaction of one of the metal ions involved with the ligand. Another advantage may be the determination of a metal P in the presence of another metal N that forms stronger complexes with the ligand than P. Back-titration with a metal M giving stronger complexes than P may make it possible to determine P. An example has been given above in the case of the determination of lead in the presence of iron(III) by means of the addition of DTPA in excess and back-titration with mercury(II) solution.

#### SUMMARY

Conditions are derived for sharp end-points in compleximetric back-titrations of mixtures of metals with visual or potentiometric indication.

#### RÉSUMÉ

On a examiné les conditions pour le titrage compleximétrique en retour de mélanges de métaux, avec indication précise du point final par potentiométrie ou visuellement.

#### ZUSAMMENFASSUNG

Es werden Bedingungen festgestellt für die kompleximetrische Rücktitration von Gemischen von Metallen, unter besonderer Berücksichtigung der potentiometrischen und visuellen Endpunktsanzeige.

#### REFERENCE

- 1 U. HANNEMA AND G. DEN BOEF, *Anal. Chim. Acta*, 49 (1970) 35.

## UNTERSUCHUNGEN ÜBER DIE EXTRAHIERBARKEIT VON METALLIONEN MIT HOMOLOGEN ALIPHATISCHEN CARBONSÄUREN

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Die Eigenschaften der Carbonsäuren zur extraktiven Verwendung in der analytischen Chemie sind bisher relativ wenig bearbeitet worden. Wie Vorversuche ergaben, sind aliphatische langkettige Carbonsäuren in der Lage, mit Metallionen Verbindungen einzugehen, die sich in organischen Lösungsmitteln, im besonderen in Chloroform, gut extrahieren lassen.

JOHNSON<sup>1</sup> extrahierte die Benzoate einiger Metalle. Caprinsäure haben WEST *et al.*<sup>2</sup> als Extraktionsmittel für Kupfer, Mangan und Eisen verwendet. Nähere Untersuchungen über die Struktur von Capraten, die in Benzol extrahiert wurden, machten TANAKA und seine Mitarbeiter<sup>3,4</sup>. Auch die Buttersäure wurde verschiedentlich bereits zu Extraktionen herangezogen<sup>5-8</sup>, wobei neben Chloroform auch Äthyläther und Benzol als organisches Lösungsmittel zur Anwendung gelangten. MILLS UND WHETSEL<sup>9</sup> arbeiteten mit Perfluorbuttersäure. BIFFIN<sup>10</sup> extrahierte Calciumstearat mit Trichlorbenzol als Lösungsmittel.

Aus dieser Übersicht der wichtigsten Untersuchungen geht hervor, dass noch keine systematische Bearbeitung der Extraktion von Metallionen mit Carbonsäuren durchgeführt worden ist. Für die homologe Reihe primärer aliphatischer Carbonsäuren soll dies in der vorliegenden Arbeit geschehen.

### EXPERIMENTELLER TEIL

Für die Untersuchungen wurden die folgenden Carbonsäuren verwendet: Propionsäure (Propansäure), Buttersäure (Butansäure), Valeriansäure (Pentansäure), Capronsäure (Hexansäure), Önanthsäure (Heptansäure), Caprylsäure (Octansäure), Pelargonsäure (Nonansäure) und Caprinsäure (Decansäure).

Zur Bearbeitung gelangten die nachstehenden Metallionen: Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Ce<sup>4+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>, Th<sup>4+</sup>, Cr<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Al<sup>3+</sup>, Pb<sup>2+</sup>, und Bi<sup>3+</sup>.

Vorversuche ergaben, dass sich Chloroform als Lösungsmittel am besten eignet, weshalb es auch ausschliesslich als organische Phase der Extraktionen verwendet wurde.

### *Arbeitsvorschrift*

Die im folgenden angegebene Vorschrift ist bei sämtlichen Versuchen streng eingehalten worden, um eine gute Vergleichbarkeit derselben zu erhalten. Es wurde eine Metallsalzlösung, die rund 0.4 Milligramm-Atom Metall enthielt, in einen Schüttel-

trichter gegeben und mit Wasser auf 80 ml verdünnt. Hierauf erfolgte die Zugabe von 2 mMol Säure, gelöst in 20 ml Chloroform. Nach gutem Durchschütteln zur Gleichgewichtseinstellung konnte das gewünschte pH der im Schütteltrichter oben stehenden wässrigen Phase mit verdünntem Ammoniak oder verdünnter Salz- bzw. Salpetersäure gegen Spezialindikatorpapier Merck eingestellt werden. Nach neuerlichem guten Durchschütteln zur Extraktion blieb der Scheidetrichter zur Phasentrennung eine Viertelstunde stehen. Die untere Chloroformphase wurde hierauf in einen trockenen Titrierkolben abgelassen und gleichzeitig durch ein Weissbandfilter filtriert, um Verfälschungen der Extraktionswerte durch eventuelle Trübungen der organischen Phase zu vermeiden. Unmittelbar nach Ablassen der Chloroformphase erfolgte die Messung des bei der Extraktion vorgelegenen genauen pH-Wertes der wässrigen Phase mit einem pH-Meter. Auf diese Weise sind je Metall jeweils mindestens 6 Ansätze im pH-Gebiet zwischen 2 und 10 bearbeitet worden.

Anschliessend wurde das Chloroform in einer geeigneten Apparatur vollkommen verdampft, der verbleibende trockene Rückstand mit wenig verdünnter Salzsäure oder Salpetersäure kurz aufgekocht und das darin enthaltene Metall quantitativ bestimmt. Dies geschah in den meisten Fällen durch Titration mit einer 0.1 M Lösung des Dinatriumsalzes der Äthylendiamintetraessigsäure. Wo dies nicht möglich war, erfolgte in der Siedehitze eine Fällung mit Ammoniak mit nachfolgendem Verglühen des gefällten Hydroxydes in Platin- oder Porzellantiegeln bis zur Gewichtskonstanz.

#### EXTRAKTIONSERGEBNISSE

Die Extraktionsergebnisse der einzelnen Metallionen mit den verschiedenen Carbonsäuren werden in den Abbildungen 1–6 einander gegenübergestellt. Der Ordinatenabstand zwischen zwei Metallionen in den Abbildungen beträgt jeweils 100% Extraktion. Nicht extrahierte Metallionen scheinen in den Abbildungen nicht auf. Die Ergebnisse mit einzelnen, besonders interessanten Metallionen werden auch im folgenden näher besprochen.

##### *Propionsäure*

Bei den Versuchen mit Propionsäure zeigten sich erwartungsgemäss keine nennenswerten Extraktionen der Metallionen. Im schwach sauren bzw. alkalischen Gebiet fielen durchwegs die Hydroxyde der Metalle aus und sammelten sich in der Chloroformphase an. Nur von Thorium fanden sich bei pH 4.5 im Extrakt 8% des Metalles wieder.

##### *Buttersäure*

Von allen untersuchten Metallen wurde nur Thorium zwischen pH 3 und pH 6 extrahiert. Um die Maximalextraktion zu erreichen, war es notwendig, den pH der wässrigen Lösung genau auf 4.2 bis 5.2 einzustellen, da bei Verschiebung um nur eine pH-Einheit der Extraktionswert von 98% auf 15–20% absank. Die vor der Extraktion erfolgende pH-Einstellung konnte mit Spezialindikatorpapier Merck genügend genau vorgenommen werden.

##### *Valeriansäure*

Mit Valeriansäure (Abb. 1) konnten wesentlich mehr Metallionen extrahiert

werden, als dies mit Buttersäure der Fall war. Wie aus der Abbildung ersichtlich ist, zeigten die besten Extraktionsergebnisse Eisen mit 91%, Thorium mit 86% und Blei mit 70%. Geringere Extraktionswerte ergaben Aluminium, Cer, Kupfer, Beryllium und Zirkon. Bei den restlichen zwölf Metallen (Mg, Ca, Ba, Ti, Cr, U, Mn, Co, Ni, Zn, Cd, Bi) konnte keine Extrahierbarkeit festgestellt werden.

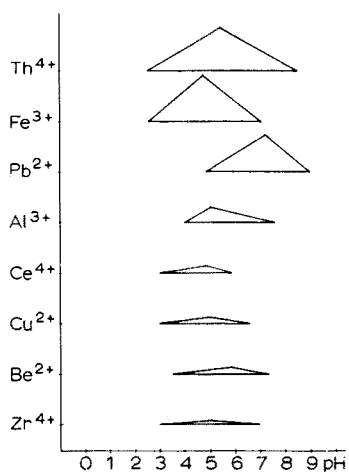


Abb. 1. Extraktion mit Valeriansäure.

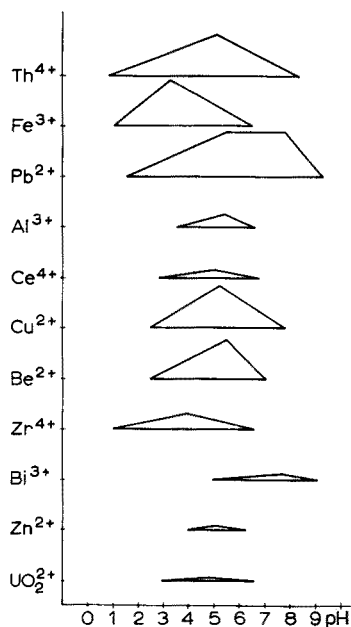


Abb. 2. Extraktion mit Capronsäure.

### Capronsäure

Mit Capronsäure waren über die Hälfte der untersuchten Metalle extrahierbar (Abb. 2). Die höchsten Extrahierbarkeiten lagen bei Thorium, Eisen, Blei, Kupfer und Beryllium mit 80%–90% vor. Aber auch die Extraktionen einiger anderer Ionen waren gegenüber Valeriansäure angestiegen. Die Metalle Wismut, Zink und Uran wurden zum ersten Mal extrahierbar. Bei neun untersuchten Metallionen (Mg, Ca, Ba, Ti, Cr, Mn, Co, Ni, Cd) war keine Extrahierbarkeit vorhanden.

### Önanthsäure

Die vereinfachte graphische Darstellung der Extraktionsergebnisse zeigt die Abb. 3. Abgesehen von der guten Extrahierbarkeit von Thorium mit 83%, Eisen mit 86%, Blei mit 90% und Kupfer mit 89%, war erstmals eine höhere Extrahierbarkeit von Cer mit 70% gegeben. Die Extraktion von Uran als Uranylion stieg auf 41%, und jene von Zink auf 23% an. Die Berylliumextraktion blieb gegenüber Capronsäure gleich. Weiters traten die Metalle Cadmium, Mangan, Nickel und Kobalt in den Kreis der extrahierbaren Metalle ein. Keine Extraktion zeigten Calcium, Barium, Magnesium, Chrom und Titan.

### Caprylsäure

Mit Caprylsäure liessen sich fünfzehn der insgesamt zwanzig untersuchten



Metalle extrahieren (Abb. 4). Neben guten Extraktionsergebnissen von Thorium, Eisen, Blei und Kupfer mit über 90% wurde Cer zu 80% extrahiert, was ein Ansteigen seiner Extrahierbarkeit gegenüber der vorhergehenden Säure zeigte. Auch eine Anzahl anderer Metallionen zeigte gegenüber der Önanthsäure eine Zunahme der Extraktion, oder erschien erstmals extrahierbar. Die Extraktionswerte von Beryllium mit 60%, Uranylion mit 29% waren stark abgesunken, die Extraktion von Zink überhaupt nicht mehr durchführbar. Weiters zeigten auch die Metallionen von Calcium, Barium, Magnesium und Chrom keine Extraktion.

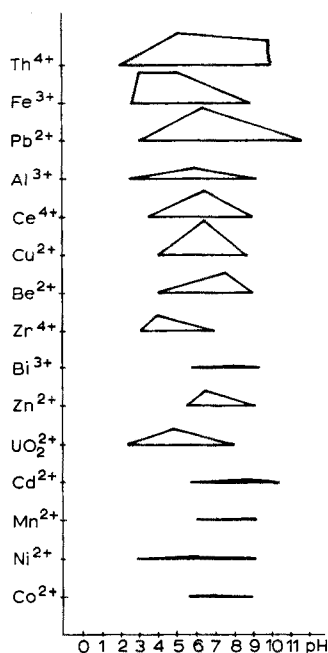


Abb. 3. Extraktion mit Önanthsäure.

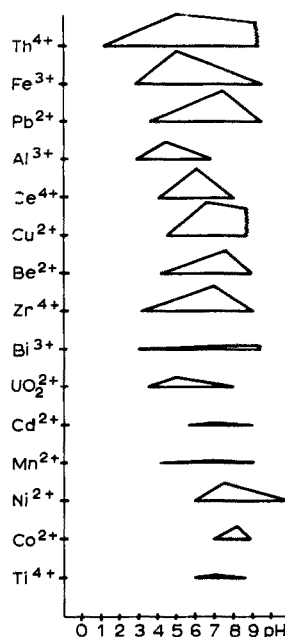


Abb. 4. Extraktion mit Caprylsäure.

### Pelargonsäure

Die Abbildung 5 gibt eine Übersicht über die Extraktionsverhältnisse. Die beste Extraktion ergab Kupfer mit 95%. Auch Aluminium zeigte mit 80%, Uranylion mit 66% und Beryllium mit 80% eine angestiegene Extrahierbarkeit. Auch eine Reihe weiterer Metallionen zeigten eine hohe Extraktion. Die Cerextraktion blieb mit rund 80% gegenüber Caprylsäure unverändert. Eisen mit 75%, Thorium mit 70% und Blei mit 55% zeigten demgegenüber eine Abnahme der Extrahierbarkeit. Nur fünf der untersuchten Metallionen, nämlich jene von Calcium, Barium, Magnesium, Chrom und Zink, zeigten überhaupt keine Extraktion.

### Caprinsäure

Eine Gegenüberstellung der Ergebnisse zeigt Abbildung 6. Auch hier zeigte Kupfer mit 97% die beste Extrahierbarkeit. Die Extraktion von Aluminium mit 80%, Thorium mit 70%, Eisen mit 73% und Uran als Uranylion mit 68%, blieb gleich wie bei dem vorgehenden homologen Glied der Säurereihe. Einen Abfall der Extrahierbarkeit zeigte Cer auf 50%, Beryllium auf 60% und Blei auf 6%. Die Extraktion von

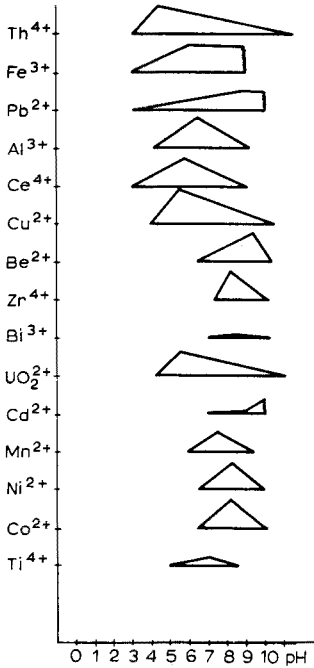


Abb. 5. Extraktion mit Pelargonsäure.

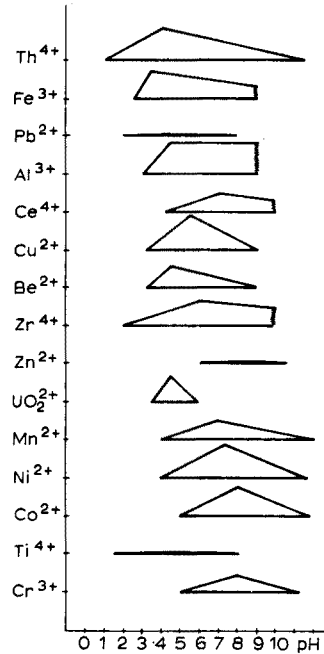


Abb. 6. Extraktion mit Caprinsäure.

Wismut und Cadmium war überhaupt nicht durchführbar, ebenso nicht jene von Calcium, Barium und Magnesium.

#### AUSWERTUNG DER ERGEBNISSE

Mit den niedrigen Homologen der Carbonsäuren war die Anzahl der extrahierbaren Metallionen gering, stieg aber mit wachsender Kohlenstoffkette an. Der Anstieg der Extraktion verlief allerdings nicht immer linear mit dem zunehmenden Molekulargewicht der Säuren, sondern fiel oftmals nach Erreichen eines höchsten Wertes wieder ab, einige Male sogar auf Null. So wurde bei Blei mit Önanthsäure das Maximum von 91% Extraktion erreicht, mit Caprinsäure jedoch betrug die Extraktion nur mehr 6%. Ähnlich verhielten sich auch Thorium, Beryllium, Uran als Uranylion, Eisen, Cer, Cadmium, Wismut und Zink. Es gab jedoch auch Metallionen, die mit dem höchsten untersuchten Homologen der Reihe, mit Caprinsäure, die besten Extraktionsergebnisse lieferten, wie Kupfer, Nickel und Kobalt. Lediglich die Erdalkalien, mit Ausnahme von Beryllium, waren mit keiner der untersuchten Säuren extrahierbar.

Der Grossteil der Extraktionen erfolgte im schwach sauren oder neutralen Bereich. Die beste Extrahierbarkeit verschob sich aber mit zunehmender Kohlenstoffanzahl der Carbonsäuren ins alkalische Gebiet. Mit Caprinsäure war beispielsweise nur Blei und Wismut im alkalischen Gebiet extrahierbar, während mit Pelargonsäure an die sieben Metalle im alkalischen Bereich eine Extraktion zeigten.

Der Vergleich der Extraktionsergebnisse der einzelnen Metallionen bei den

verschiedenen Carbonsäuren lässt auch die Möglichkeit von Trennungen derselben erkennen. So ist Thorium mit Buttersäure bereits nach zweimaliger Extraktion vollständig auszuschütteln, wodurch eine quantitative Abtrennung des Thoriums von einer ganzen Reihe von begleitenden Metallionen möglich war<sup>11</sup>.

#### ZUSAMMENFASSUNG

Es wurde die Extrahierbarkeit von Metallionen mit aliphatischen *n*-Carbonsäuren untersucht. Mit den niedrigen Homologen war die Anzahl der extrahierbaren Metallionen gering, stieg aber mit grösserer Kohlenstoffanzahl der Säuren an. Die im einzelnen sich ergebende Maximalextraktion stieg nicht bei allen untersuchten Metallionen linear, sondern fiel in einigen Fällen nach Erreichung eines Höchstwertes wieder ab. Auf Grund der unterschiedlichen Extrahierbarkeit der Metallionen sind verschiedene Trennungen möglich.

#### SUMMARY

The extractability of 20 metal cations with a series of aliphatic carboxylic acids (C<sub>3</sub>-C<sub>10</sub>) in chloroform was examined over the pH range 2-10. With the lower members of the series, few metals were extracted, but the number of metals extracted increased with increase in the number of carbon atoms in the chain. For a particular metal, percentage extraction did not always increase linearly with chain length; in some cases, it decreased after reaching a maximum with an intermediate member of the series. On the basis of different extractabilities, various separations are possible.

#### RÉSUMÉ

On examine les possibilités d'extraction de 20 cations métalliques avec une série d'acides aliphatiques carboxyliques (C<sub>3</sub>-C<sub>10</sub>) dans le chloroforme, entre les pH 2 et 10. Le nombre de métaux extraits augmente avec le nombre d'atomes de carbone dans la chaîne. Pour un métal particulier, le pourcentage d'extraction n'augmente pas toujours linéairement avec la longueur de la chaîne. Dans certains cas, il diminue après avoir atteint un maximum, avec un acide intermédiaire de la série. En se basant sur les différentes extractibilités, il est possible d'effectuer diverses séparations.

#### LITERATUR

- 1 S. E. JOHNSON, in E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 2nd Edn., Interscience, New York, 1950, p. 537.
- 2 P. W. WEST, F. C. LYONS UND J. K. CARLTON, *Anal. Chim. Acta*, 6 (1952) 400.
- 3 M. TANAKA UND T. NINOMI, *J. Inorg. & Nucl. Chem.*, 27 (1965) 431.
- 4 M. TANAKA, N. NAKASUKA UND S. GOTO, in D. DYRSSEN, J. O. LILJENZIN UND R. RYDBERG, *Solvent Extraction Chemistry*, North Holland, Amsterdam, 1967, p. 154.
- 5 A. K. SUNDARAM UND S. BANARJEE, *Anal. Chim. Acta*, 8 (1953) 526.
- 6 S. BANARJEE, A. K. SUNDARAM UND D. SHARMA HARI, *Anal. Chim. Acta*, 10 (1954) 256.
- 7 L. MEITES, *Handbook of Analytical Chemistry*, McGraw-Hill, New York, 1965, 1st Edn., 10. Abschnitt, S. 10.
- 8 L. L. GALKINA UND L. A. GLAZUNOVA, *Z. Anal. Chem.*, 234 (1968) 281.
- 9 G. F. MILLS UND H. B. WHETSEL, *J. Am. Chem. Soc.*, 77 (1955) 4690.
- 10 F. M. BIFFIN, *Ind. Eng. Chem., Anal. Ed.*, 6 (1934) 169.
- 11 R. PIETSCH UND H. SINIC, *Mikrochim. Acta*, (1968) 1287.

## EXTRACTION OF TRACES OF CERIUM, EUROPIUM, TERBIUM AND LUTETIUM FROM URANIUM(VI) SOLUTIONS WITH DI-2-ETHYLHEXYL PHOSPHORIC ACID

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Di-2-ethylhexyl phosphoric acid (HDEHP) has been widely used for extraction separation of rare earths. Recently this extractant has been used as a stationary phase in extraction chromatography procedures for separation of rare earths. This method allowed successful chromatographic separation of rare earths in trace concentrations, and all the reported results perfectly reflect the extraction behaviour of these elements. However, very few attempts have been made to use extraction chromatography in order to separate mixtures with one element in macro amounts and the other in trace quantity. Such separations are important for possible application in isotope production from an irradiated target, or for studying nuclear reactions. A successful separation of micro amounts of terbium from macro amounts of erbium, with an HDEHP-treated column has been described by SOCHACKA AND SIEKIERSKI<sup>1</sup>, who found that "when the separation factor between two rare earths is  $\geq 17$  (the value of  $\beta$  for Tb-Er pair), practically the whole exchange capacity of column can be made available without affecting separation of the micro amount of the lighter element from the macro amount of the heavier".

In a previous paper<sup>2</sup> the group separation of some fission products in trace quantities from macro amounts of uranium(VI) by means of an HDEHP-treated column has been reported. The presence of uranium in a synthetic mixture of fission products makes impossible the gradual separation of rare earths which was reported before<sup>1</sup>. A suitable temperature and flow rate were applied in order to perform complete elution of radiotracers, as the elution was seriously affected by the presence of uranium on the column.

In this paper an attempt is made to explain the incomplete separation of radiotracers from uranium(VI) under the usual column conditions, and a modified procedure is suggested.

### EXPERIMENTAL

#### *Reagents and radiotracers*

The solution of reagent-grade uranyl nitrate was standardized gravimetrically<sup>3</sup> as  $U_3O_8$ . Di-2-ethylhexyl phosphoric acid (HDEHP; Light and Co.) was purified as described by BLAKE AND SMITH<sup>4</sup>. Radioisotope  $^{144}Ce$  was obtained from the Radiochemical Centre, Amersham;  $^{152,154}Eu$ ,  $^{160}Tb$  and  $^{177}Lu$  were obtained by irradiation

of the corresponding oxides in the nuclear reactor in "Jožef Stefan" Institute, Ljubljana, Yugoslavia. Reagent-grade toluene (Carlo Erba) was used as the diluent.

#### *Column material and measurements*

The fractionated kieselguhr "Hyflo Super Cell" served as a solid support for HDEHP, which was adsorbed by evaporation technique. The ratio of HDEHP to kieselguhr was 1:10 (by weight). The column preparation and characterization were the same as described elsewhere<sup>1</sup>. The same column material was employed in some batch experiments which were performed in the following way: the samples (0.5 g) of column material were brought in contact with aqueous solutions of terbium trace and uranium(VI). The terbium trace was applied first, and adsorbed on the column material. Afterwards, the HDEHP was saturated by addition of uranyl nitrate solution in excess. Finally, the aqueous suspensions were acidified with nitric acid, previously saturated with HDEHP, and shaken for a given period of time. Aqueous phases were centrifuged and analysed radiometrically. In this way, the column conditions were simulated, and the effect of time and temperature on the separation of radiotracer from uranium(VI) could be studied more easily than in the column technique.

#### *Extraction measurements*

The distributions of rare-earth tracers in the presence of uranium(VI), between the organic phase (HDEHP in toluene), and the aqueous phase (HDEHP-saturated column eluent) were studied. The extraction systems were prepared in glass flasks with plastic stopcocks and shaken for a given period of time with a rotating mechanical shaker at 120 shakes per min. The liquid phases were then separated by centrifugation and analysed radiometrically with an Ecko scintillation counter (thallium-activated NaI crystal). "Distribution ratios" were calculated after subtracting U(VI) + UX<sub>1</sub> activity, from the expression:

$$E^0_{\text{a.R.E.}} = \frac{A_{\text{o.R.E.}} - A(\text{U(VI)} + \text{UX}_1)_o}{A_{\text{a.R.E.}} - A(\text{U(VI)} + \text{UX}_1)_a} \quad (1)$$

"Distribution ratio" is given in inverted commas, since the distribution of a rare-earth trace in the presence of uranium(VI) is a time-dependent process and does not reflect the true thermodynamic equilibrium state. The distribution of U(VI) + UX<sub>1</sub> was determined independently by counting techniques.

## RESULTS AND DISCUSSION

#### *Behaviour of rare earths on the column*

The behaviour of rare earths on the HDEHP-treated column has already been described<sup>1</sup>. The retention of rare earths on the column may be explained by a simple ion-exchange mechanism:



as was shown by extraction measurements<sup>5</sup>. This means that the peak position of the eluted rare-earth trace is dependent only on the acidity of the eluent. For example, europium traces are eluted with 0.5 M nitric acid as a symmetrical curve without tailing, with the peak maximum at 3.2 V<sub>0</sub>. However, the elution of europium is seriously

affected by the presence of uranium(VI) in the column (Fig. 1, curve a). The europium trace was first adsorbed on the column, which was then saturated with uranium(VI). The slight elution of europium with 0.2 *M* uranyl nitrate started at the first free volume. Improved, but incomplete, elution was achieved with 0.2 and 0.5 *M* nitric acid. The elution curves have the pronounced tailing reported previously<sup>2</sup>. Complete stripping was achieved with 5 *M* nitric acid, which is in agreement with the reported data<sup>2</sup>.

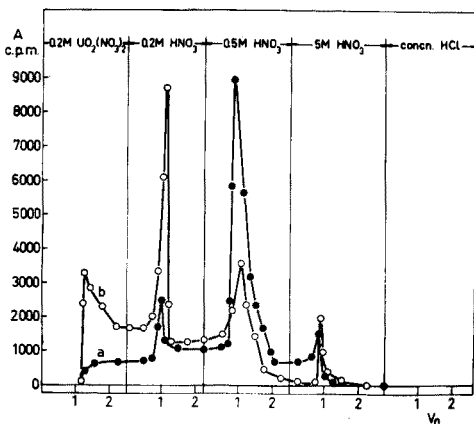
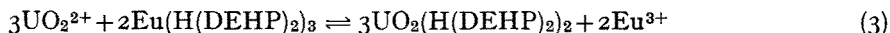


Fig. 1. Elution of europium (a: Eu trace, b: 1 mg of labelled Eu) from the column, saturated afterwards with uranium(VI). Flow rate, 1.1 ml cm<sup>-2</sup> min<sup>-1</sup>. Room temperature.

Curve b in Fig. 1 shows the elution of a macroquantity (1 mg) of labelled europium from the same column, which was saturated with uranium(VI) after introduction of europium. The elution of europium with 0.2 *M* uranyl nitrate could be attributed to the displacement mechanism:



since the ratio of the distribution ratios,  $E^0_{\text{aU(VI)}}/E^0_{\text{aEu}}$ , is  $\gg 1$ . Obviously, the displacement is faster as the quantity of europium bound on the column is increased, indicating that elution of europium is a slow kinetic process. At the high uranium(VI): HDEHP ratios which were obtained on the column, saturation conditions are fulfilled, resulting in the formation of chain polymers with the general formula<sup>6</sup>  $\text{UO}_2(\text{DEHP})_{2n+2}\text{H}_2$ . The three-dimensional polymer of empirical composition  $\text{UO}_2(\text{DEHP})_2$  is formed as a gel-like phase<sup>7</sup> as a limiting case. Since all the available hydrogen functions are exhausted, the traces of rare earths which are afterwards introduced cannot be retained on the column. This was experimentally shown by the complete elution of europium by 0.1 *M* nitric acid in the first free volume without pronounced tailing from a column which had been previously saturated with uranium(VI). This indicates that the tailing effects of radiotracers in mixtures with uranium(VI)<sup>2</sup>, are not caused by physical adsorption, but by chemical interaction of the radiotracer with HDEHP, which was affected by the presence of uranium(VI).

The rate of elution of trace terbium in the presence of uranium(VI) was studied in batch experiments. The results of these measurements are presented in Fig. 2 where the fraction of total terbium activity, stripped from the column material is plotted as

a function of the acidity of the aqueous phase. The fraction of stripped terbium is increased by prolonged shaking, but is independent of the concentration of nitric acid below 2 *M*. Further increase of nitric acid concentration increases the amount of stripped terbium, so that 5 *M* nitric acid strips all the terbium after 5 min of shaking.

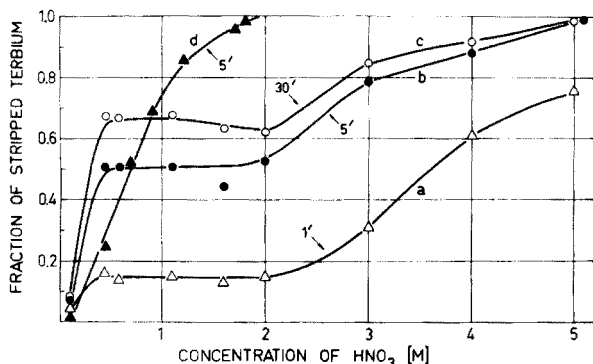


Fig. 2. Stripping of trace terbium from the column material, saturated with uranium(VI), in dependence of the nitric acid concentration. Time of shaking: 1 min (curve a), 5 min (curve b) and 30 min (curve c). Curve d presents the distribution of the Tb in the absence of uranium(VI), after shaking for 5 min. Room temperature.

For these conditions, the distribution ratio of uranium(VI) in HDEHP–nitric acid systems is fairly low, which results in simultaneous stripping of uranium(VI) from the column material. Since such distribution measurements are not convenient for obtaining quantitative and reproducible data, supplementary liquid–liquid extraction studies were carried out.

#### Extraction studies

The distribution of Ce(III), Eu, Tb, and Lu traces between 0.1 *M* HDEHP in toluene and 0.2 *M* nitric acid, was studied in the presence of various concentrations of uranium(VI). Initial volumes of both liquid phases were the same, and when contacted, the formation of a third, gelatinous phase was noticed in each case. This corresponds to the polymer  $\text{UO}_2(\text{DEHP})_2$  complex<sup>6</sup>. On prolonged shaking, the quantity of gelatinous phase decreased, which indicates that the polymer complex  $\text{UO}_2(\text{DEHP})_2$  breaks into smaller fragments through interaction with protons present in the acidic aqueous solution. The trends of “distribution ratios” for Ce(III), Eu, Tb and Lu traces in the presence of uranium(VI) are presented in Figs. 3 and 4. General remarks on the behaviour of rare earths in the investigated extraction systems (the HDEHP-to-uranium(VI) ratio being lower than 5) are as follows: 1. the separation of rare earths from each other is not possible at an early stage of the extraction process; 2. after prolonged shaking the values of the “distribution ratios” decrease; 3. the relative rates of change of the “distribution ratios” ( $\Delta E_a^0/\Delta t$ ) increase in order  $\text{Lu} < \text{Tb} < \text{Eu} < \text{Ce}$ .

This indicates a possibility of separation of rare-earth traces from each other by HDEHP, but only after prolonged shaking. The order of the “distribution ratios” is the same as that of the equilibrium values for pure systems<sup>5</sup>. The only exception is the behaviour of cerium; after an initial decrease,  $E_a^0$  for cerium(III) tends to increase

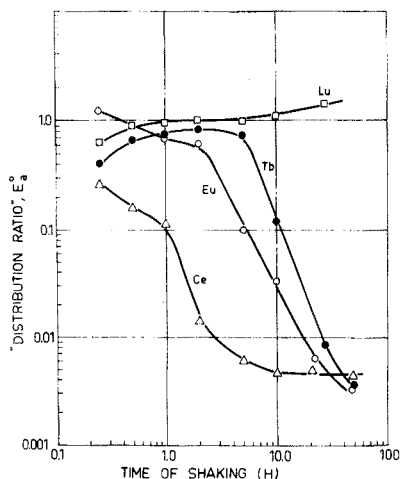


Fig. 3. Distribution of the rare-earth traces between organic and aqueous phase (0.02 *M* in  $\text{UO}_2(\text{NO}_3)_2$ ), as a function of time of shaking. Room temperature; 0.1 *M* HDEHP in toluene as organic phase; 0.2 *M* nitric acid- $\text{UO}_2(\text{NO}_3)_2$ -R.E. trace as aqueous phase; phase ratio, 1:1.

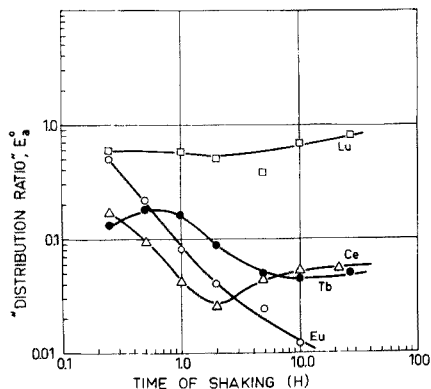
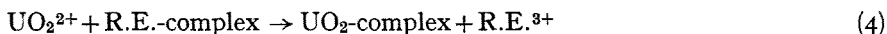


Fig. 4. Distribution of the rare-earth traces between organic and aqueous phase (0.08 *M* in  $\text{UO}_2(\text{NO}_3)_2$ ), as a function of time of shaking. Conditions as in Fig. 3.

with prolonged shaking, possibly because of oxidation of cerium(III) in the presence of nitric acid and uranyl nitrate, cerium(IV) having a higher distribution ratio.

Since the values of the "distribution ratios" did not attain a constant value after 10–50 h of shaking, it could be concluded that the redistribution of rare earth is controlled by some fairly slow process. Possibly the rare-earth trace enters, in a statistical way, into the composition of uranium(VI) polymer complex. The formation of the mixed complex results in virtually enhanced extraction of rare earths into the organic phase. The transition of rare-earth traces into the aqueous phase could be a consequence of two slow processes generally presented as:



where "R.E.-complex" represents a R.E.-U(VI)-HEDHP mixed polymer complex. The first reaction corresponds to the displacement exchange between uranium and the rare-earth trace, while the second reaction shows the dependence of the stability of the mixed complex on the acidity of the extraction system. After prolonged shaking the gel-like phase vanishes, but even when it has completely dissolved, the "distribution ratios" for the rare earths still decrease. This indicates that the rare earth is not adsorbed or coprecipitated on the surface of the gel-like phase, but actually participates in the complex. The change of the "distribution ratio" for europium in the presence of uranium(VI) in dependence on temperature, is presented in Fig. 5. The rate of degradation of the polymer complex is increased with temperature, hence reactions (4) and (5) proceed to the right. This explains why the group separation of some fission products from uranium(VI) by the column method<sup>2</sup> was successful.

From the trends of "distribution ratio" values presented in Figs. 3 and 4, one would expect an equilibrium state to be reached within a reasonable time period if the



ratio of HDEHP to uranium(VI) were increased. The distribution of Ce, Eu, Tb and Lu traces was studied in extraction systems in which the aqueous phase was 0.2 M nitric acid–0.06 M  $\text{UO}_2(\text{NO}_3)_2$ –R.E. trace, and the concentration of HDEHP in toluene was systematically increased in the organic phase. "Distribution ratios" were determined

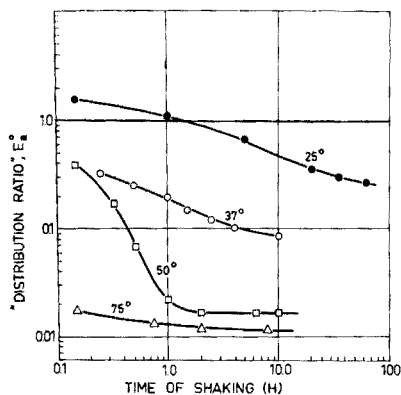


Fig. 5. Distribution of trace europium between organic and aqueous phase (0.04 M in  $\text{UO}_2(\text{NO}_3)_2$ ) as a function of time of shaking at given temperature conditions. Conditions as in Fig. 3, except for temperature.

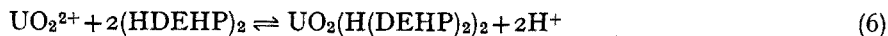
after equilibration for 24 h, with the results shown in Figs. 6 and 7. The trend of distribution ratios for pure rare earths in the same system, is given for comparison. The extraction behaviours of rare-earth traces in the presence of uranium(VI) have certain common properties as outlined below.

1. At low ratios of HDEHP to uranium(VI), the "distribution ratio" is markedly increased in comparison with the distribution ratio of pure rare earths, except for lutetium. The slow redistribution of rare-earth trace is time-dependent (*cf.* Figs. 3 and 4) and can be described by general expressions (4) and (5).

2. At a certain ratio of HDEHP to uranium(VI), which is different for each particular rare earth studied, the "distribution ratio" dropped sharply with increase of HDEHP concentration, the drop being greatest for cerium and lowest for lutetium.

3. At another ratio of HDEHP to uranium(VI), a linear increase of the rare-earth "distribution ratio" was obtained with increase of HDEHP concentration (log scale).

The right linear parts of the distribution curves on Figs. 6 and 7 do not change with prolonged shaking, which means that the rare-earth "distribution ratios" at higher HDEHP:uranium(VI) ratios correspond to real equilibrium values. It is suggested that for these experimental conditions two parallel independent extraction processes take place, one corresponding to eqn. (2) and the other to eqn. (6):



This assumption is consistent with the experimental proof that the linear increase of the "distribution ratio" starts at an HDEHP:uranium(VI) ratio of 6. An exception is lutetium, for which the rise in the "distribution ratio" starts at an HDEHP:uranium(VI) ratio of 2. This indicates that lutetium extraction is least affected by the presence of uranium(VI) in solution.

The slopes of the log  $E_a^0$  (rare earth) *vs.* log HDEHP plots are considerably higher than the theoretical value 3.0, probably because less HDEHP is available as it is consumed for preferential complexation of uranium(VI). This is followed by a slight increase in the acidity of the aqueous phase as shown by eqn. (6), from which the extent of HDEHP bound to uranium can be calculated on the assumption that 4:1 complex is formed. When corrected for this consumption of HDEHP, the slopes tend towards the theoretical value for rare-earth extraction in pure systems.

The most important consequence of these results is that HDEHP acts as a selective extracting agent for separation of rare-earth traces one from another in uranium(VI) solutions when sufficient is present to convert all uranium(VI) to the  $UO_2(H(DEHP)_2)_2$  complex. For these experimental conditions, high separation factors for pairs of investigated rare earths were obtained. For example, at an HDEHP concentration of 0.5 *M* (HDEHP:uranium(VI) = 8.3), the separation factors calculated from the experimental data are as follows:

$$\beta_{Eu-Ce} = 22.1, \beta_{Tb-Eu} = 6.1 \text{ and } \beta_{Lu-Tb} = 320.$$

The separation factors recalculated from extraction chromatography data on separation of rare-earth traces<sup>1</sup> are as follows:

$$\beta_{Eu-Ce} = 16, \beta_{Tb-Eu} = 9.3 \text{ and } \beta_{Lu-Tb} = 370.$$

These data show a reasonable agreement, although they are obtained by different methods and in different systems.

Terbium and lutetium traces, however, were extracted into the organic phase together with uranium(VI) under such experimental conditions. Organic phases were therefore scrubbed with equal volumes of 1 *M* or 2 *M* nitric acid for 10 min, in order to separate the rare-earth traces from uranium(VI), which remained in the organic phase. The extraction slopes remained parallel with the previous slopes, thus confirming the statement that the extraction of rare-earth traces is parallel to, and independent of, the extraction of uranium(VI), when HDEHP is present in excess.

#### CONCLUSION

The separation of rare-earth traces from one another in the presence of milligram quantities of uranium(VI) by means of an HDEHP-treated column is not possible, owing to the formation of an insoluble polymeric uranium(VI)-HDEHP complex, incorporating rare-earth traces. The "distribution ratio" of any rare earth is virtually enhanced. Extraction measurements have shown, that at low HDEHP-uranium(VI) ratios, the extractant cannot separate the rare earths.

When sufficient HDEHP is present to convert uranium(VI) completely to the  $UO_2(H(DEHP)_2)_2$  complex, the extraction of a rare-earth trace was shown to be an independent parallel process. The established separation factors for investigated pairs of rare earths in the presence of uranium(VI) indicate that, under these experimental conditions, HDEHP can be used for separations of rare-earth traces, offering the possibility of a discontinuous type of countercurrent separation.

#### SUMMARY

Extraction measurements have been performed in order to explain the behaviour

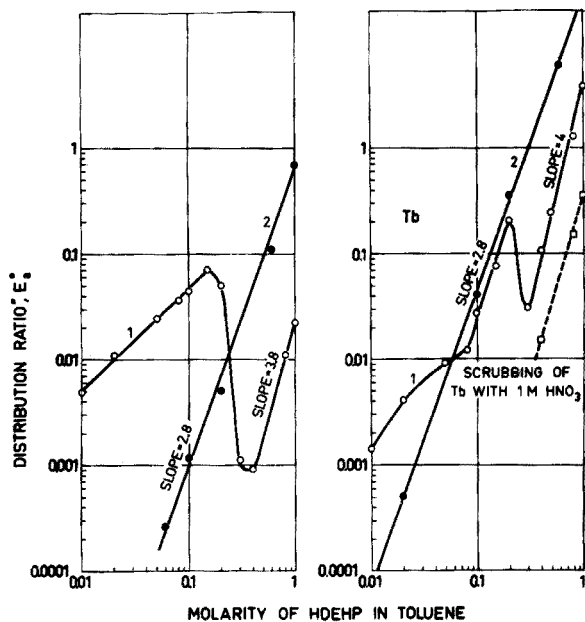


Fig. 6. Dependence of extraction of the Ce and Tb traces from  $0.06\text{ M UO}_2(\text{NO}_3)_2$  solution upon the concentration of HDEHP in toluene. Room temperature; aqueous phase,  $0.2\text{ M}$  nitric acid– $0.06\text{ M UO}_2(\text{NO}_3)_2$ –R.E. trace for curve 1, and  $0.2\text{ M}$  nitric acid–R.E. trace for curve 2; phase ratio, 1:1.

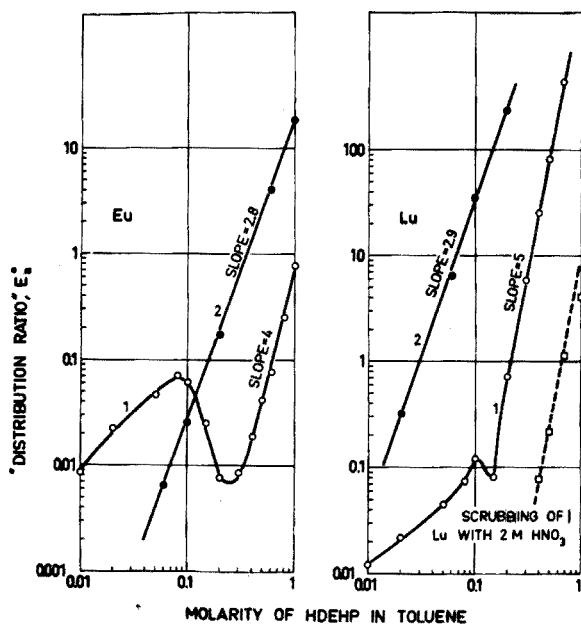


Fig. 7. Dependence of extraction of the Eu and Lu traces from  $0.06\text{ M UO}_2(\text{NO}_3)_2$  solution upon the concentration of HDEHP in toluene. Conditions as for Fig. 6.

of rare-earth traces on an HDEHP-treated chromatographic column in the presence of milligram quantities of uranium(VI). Under column conditions the rare-earth separation factors are lowered, and this impairs the separation. A combined mechanism involving displacement reactions between  $\text{UO}_2^{2+}$  and R.E.<sup>3+</sup>, and degradation of the uranium(VI) polymeric complex, is suggested to explain the retarded transfer of a rare-earth trace into the aqueous phase. It is shown that at HDEHP:uranium(VI) ratios above 6, the extraction of rare earths is not affected by the presence of uranium(VI), which makes possible the gradual separation of rare-earth traces from uranium(VI) solutions.

#### RÉSUMÉ

On a examiné l'extraction de traces de terres rares pour expliquer leur comportement lors de la chromatographie sur colonne traitée avec HDEHP, en présence d'uranium, en quantité de l'ordre du milligramme. Dans les conditions expérimentales de la chromatographie sur colonne, les coefficients de séparation des terres rares diminuent, ce qui empêche leur séparation. On propose un mécanisme combiné de réaction de déplacement entre  $\text{UO}_2^{2+}$ -R.E.<sup>3+</sup> et de dégradation du complexe polymère d'uranium pour expliquer le transfert retardé des traces de terre rare en phase aqueuse. On a constaté que l'extraction des terres rares ne dépend pas de la présence d'uranium(VI), si le rapport HDEHP-uranium(VI) est supérieur à 6. Ceci permet une séparation graduelle des traces de terres rares dans des solutions d'uranium(VI).

#### ZUSAMMENFASSUNG

Zur Klärung des Verhaltens von Spuren Seltener Erden in Gegenwart von Uran(VI) mengen in der Grössenordnung von einigen Milligramm an einer mit HDEHP behandelten Chromatographiersäule wurden Extraktionsversuche durchgeführt. Unter den bei der Säulenchromatographie angewandten Versuchsbedingungen sind die Trennungsfaktoren für die Seltenen Erden so niedrig, dass eine Trennung unmöglich wird. Zur Erklärung der Verzögerung beim Übergang der Spuren der seltenen Erden in die wässrige Phase wird eine gleichzeitige Verdrängung  $\text{UO}_2^{2+}$  und S.E.<sup>3+</sup> und Degradation des polymeren Urankomplexes vorgeschlagen. Wenn das Verhältnis HDEHP zu Uran(VI) grösser als 6 wird, ist die Extraktion der Seltenen Erden nach unseren Ergebnissen von der anwesenden Uranmenge unabhängig, so dass sich unter dieser Bedingung Spuren von Seltenen Erden aus Uran(VI)-salzlösungen abtrennen lassen.

#### REFERENCES

- 1 R. SOCHACKA AND S. SIEKIERSKI, *J. Chromatog.*, 16 (1964) 377.
- 2 B. TOMAŽIČ AND S. SIEKIERSKI, *J. Chromatog.*, 21 (1966) 98.
- 3 C. J. RODDEN, *Analytical Chemistry of the Manhattan Project*, Mc Graw-Hill, New York, 1950.
- 4 J. M. BLAKE AND C. A. SMITH, JR., *ORNL Report nr.* 3548.
- 5 D. F. PEPPARD, G. W. MASSON AND W. J. DRISCOLL, *J. Inorg. & Nucl. Chem.*, 7 (1958) 276.
- 6 C. F. BAES, JR., R. A. ZINGARO AND C. F. COLEMAN, *J. Phys. Chem.*, 62 (1958) 129.
- 7 D. F. PEPPARD AND G. W. MASON, *Nucl. Sci. Eng.*, 16 (1963) 382.

## SOLVENT EXTRACTION OF METALS BY ALKYL-SUBSTITUTED $\beta$ -DIKETONES

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$\beta$ -Diketones are commonly used as a solvent for the extraction of many metals<sup>1</sup>. KRISHEN AND FREISER<sup>2</sup> reviewed studies on solvent extraction with acetylacetone. SHIGEMATSU AND TABUCHI<sup>3</sup> extracted some metal ions with acetylacetone for analytical purposes. Later, STARY AND HLADKY<sup>4</sup> made a systematic investigation of solvent extraction with acetylacetone, benzoylacetone and dibenzoylmethane and calculated the extraction constants. Thenoyltrifluoroacetone can be used for the separation of the lanthanides<sup>5</sup>, and many other applications have been discussed<sup>1,6</sup>.

In the present work, some alkyl-substituted  $\beta$ -diketones were synthesized and their extraction properties were examined. Extractions of various metal ions with dipropionylmethane, diisobutyrylmethane, pivaloylacetylmethane and dipivaloylmethane in benzene were investigated in order to establish the extraction constants. These constants could be used for the prediction of the optimum conditions for the separation of metals. Dipivaloylmethane, one of the  $\beta$ -diketones studied here, has already been used for separation and determination of lithium in an alkaline earth solution<sup>7</sup> and for determination of rare earths by gas chromatography<sup>8</sup>.

### EXPERIMENTAL

#### *Reagents*

The structural formulae, and common and systematic names of each of the  $\beta$ -diketones are given in Table I with the abbreviations used in this paper. Dipropionylmethane, diisobutyrylmethane, pivaloylacetylmethane and dipivaloylmethane were synthesized by the method of HAUSER AND ADAMS<sup>9</sup>. The composition was confirmed by correct elemental analyses.

The stock solutions of metals were prepared as follows: the nitrate or chloride salt was dissolved in distilled water and 5 ml of 60% perchloric acid was added to the solution, which was evaporated to dryness twice, and then the residue was dissolved in water. These stock solutions were standardized by conventional titrimetric or gravimetric methods.

All the other reagents were reagent-grade and were used without further purification.

The buffer solutions used were acetate buffers for pH 2-7 and borate buffers for

TABLE I  
 $\beta$ -DIKETONES USED IN THIS STUDY

| Common name and structural formula   | Systematic name                      | Abbreviation |
|--|--------------------------------------|--------------|
| Dipropionylmethane<br>$\text{C}_2\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$          | Heptan-3,5-dione                     | DPrM         |
| Diisobutyrylmethane<br>$(\text{CH}_3)_2\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}(\text{CH}_3)_2$ | 2,6-Dimethyl-heptan-3,5-dione        | DIBM         |
| Pivaloylacetyl methane<br>$(\text{CH}_3)_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$            | 2,2-Dimethyl-heptan-3,5-dione        | PAM          |
| Dipivaloylmethane<br>$(\text{CH}_3)_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}(\text{CH}_3)_3$     | 2,2,6,6-Tetramethyl-heptan-3,5-dione | DPM          |

pH 7–10. Perchloric acid was used for pH adjustment in the range 1–2 and sodium hydroxide for pH 10–13. The ionic strengths were adjusted to 0.1 with sodium perchlorate.

#### Apparatus

Absorbances were measured with a Hitachi-Perkin Elmer 139 spectrophotometer. A Toadempa HM 8 pH meter was used for the measurement of pH.

#### Procedure

An aqueous sample solution (20 ml), which contained metal ion (in the concentration of  $10^{-3}$ – $10^{-4}$  M), buffer and sodium perchlorate (0.1 M) was shaken with 20

TABLE II

THE ANALYTICAL METHODS USED FOR DETERMINATION OF DISTRIBUTION RATIO OR PERCENTAGE EXTRACTION

| Metal            | Method   |
|------------------|--|
| Fe <sup>3+</sup> | Spectrophotometric with 1,10-phenanthroline (500 nm)<br>Spectrophotometric as $\beta$ -diketonate (435 nm) |
| Al <sup>3+</sup> | Spectrophotometric as oxinate (390 nm)   |
| Cu <sup>2+</sup> | Spectrophotometric with diethyldithiocarbamate (440 nm)  |
| Ni <sup>2+</sup> | Spectrophotometric with dimethylglyoxime (450 nm)  |
| Zn <sup>2+</sup> | Spectrophotometric with zincon (620 nm)  |
| Cd <sup>2+</sup> | Spectrophotometric with dithizone (518 nm)   |
| Mn <sup>2+</sup> | Spectrophotometric with ammonium persulfate (530 nm)<br>Spectrophotometric as $\beta$ -diketone (550 nm)   |
| Co <sup>2+</sup> | Spectrophotometric with nitroso-R salt (570 nm)  |
| Pd <sup>2+</sup> | Spectrophotometric as oxinate (425 nm)   |

ml of 0.10 *M*  $\beta$ -diketone in benzene for about two or three days. After the organic and aqueous phases had been separated by centrifugation, the concentration of the metal in the organic phase and/or in the aqueous phase was determined spectrophotometrically. The pH value of the aqueous phase was measured with a pH meter. During the extraction, the temperature was held at  $20 \pm 2^\circ$ . The analytical methods used are listed in Table II. The acid dissociation constant and distribution coefficient of the  $\beta$ -diketones were determined spectrophotometrically at  $20^\circ$ .

## RESULTS AND DISCUSSION

### Determination of acid dissociation constants of the $\beta$ -diketones

The  $\beta$ -diketones were slightly soluble in water, but considerably soluble in a variety of organic solvents and in an alkaline aqueous solution. A sample (0.1 g) of the  $\beta$ -diketone was dissolved in 500 ml of 0.05 *N* sodium hydroxide solution. Aliquots of the alkaline solution were transferred to 50-ml volumetric flasks, and the solutions were diluted to the mark with solutions of various pH values. The pH values and the absorbances at 294–295 nm were measured.

Let the acid dissociation constant, neutral species, and anionic species of  $\beta$ -diketone be  $K_a$ , [HA] and  $[A^-]$  respectively.

$$K_a = [H^+] [A^-]/[HA] \quad (1)$$

Equation (1) leads to

$$pK_a = pH - \log([A^-]/[HA]) \quad (2)$$

$$= pH - \log(\epsilon - \epsilon_{A^-})/(\epsilon_{HA} - \epsilon) \quad (3)$$

where ( $\epsilon_{HA}$ ) and ( $\epsilon_{A^-}$ ) are the molar absorptivities of [HA] and  $[A^-]$  at 295 nm, and ( $\epsilon$ ) is the total molar absorptivity of [HA] and  $[A^-]$  at any given pH and at the same wavelength.

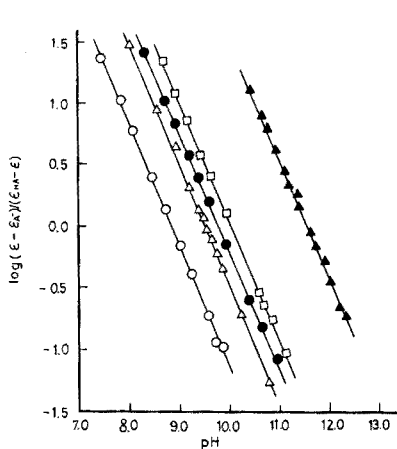


Fig. 1. Dissociation constants of AA, DPrM, DIBM, PAM and DPM. Ionic strength, 0.1 *M*  $\text{NaClO}_4$ ; temperature  $20^\circ$ ; concentration of  $\beta$ -diketone  $2 \cdot 10^{-5}$  *M*. ( $\circ$ ) AA, ( $\Delta$ ) DPrM, ( $\bullet$ ) DIBM, ( $\square$ ) PAM, ( $\blacktriangle$ ) DPM.

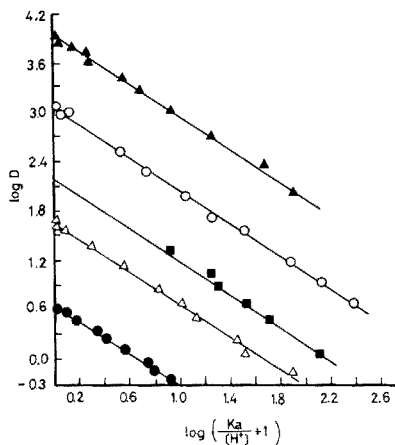


Fig. 2. Distribution ratios of AA, DPrM, DIBM, PAM and DPM between benzene and aqueous solution. Organic phase, 0.05–0.10 *M*  $\beta$ -diketone; aqueous phase, 0.10 *M*  $\text{NaClO}_4$ . ( $\bullet$ ) AA, ( $\Delta$ ) DPrM, ( $\blacksquare$ ) PAM, ( $\circ$ ) DIBM, ( $\blacktriangle$ ) DPM.

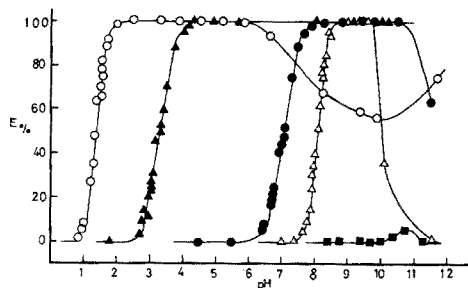


Fig. 3. Extraction of Fe(III), Cu(II), Zn(II), Mn(II) and Cd(II) by 0.10 M dipropionylmethane vs. the pH of the aqueous phase. (○) Fe, (▲) Cu, (●) Zn, (△) Mn, (■) Cd.

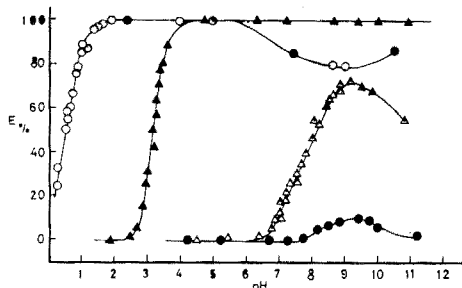


Fig. 4. Extraction of Pd(II), Al(III), Co(II) and Ni(II) by 0.10 M dipropionylmethane vs. the pH of the aqueous phase. (○) Pd, (▲) Al, (△) Co, (●) Ni.

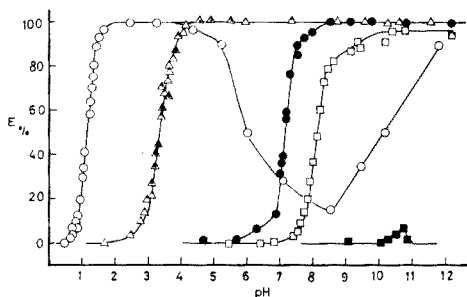


Fig. 5. Extraction of Fe(III), Cu(II), Zn(II), Ni(II) and Cd(II) by 0.10 M diisobutyrylmethane vs. the pH of the aqueous phase. (○) Fe, (△) Cu, (●) Zn, (□) Ni, (■) Cd.

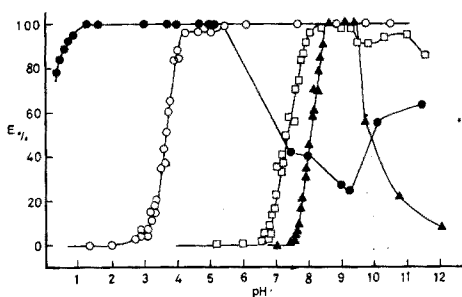


Fig. 6. Extraction of Pd(II), Al(III), Co(II) and Mn(II) by 0.10 M diisobutyrylmethane vs. the pH of the aqueous phase. (●) Pd, (○) Al, (□) Co, (▲) Mn.

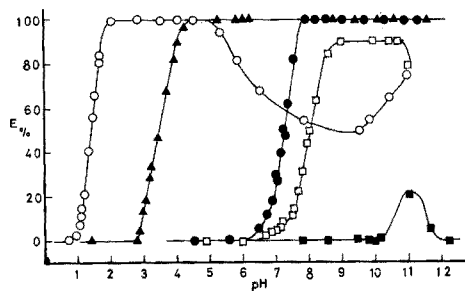


Fig. 7. Extraction of Fe(III), Cu(II), Zn(II), Co(II) and Cd(II) by 0.10 M pivaloylacetyl methane vs. the pH of the aqueous phase. (○) Fe, (▲) Cu, (●) Zn, (□) Co, (■) Cd.

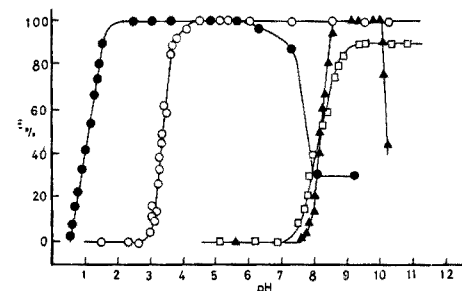


Fig. 8. Extraction of Pd(II), Al(III), Mn(II) and Ni(II) by 0.10 M pivaloylacetyl methane vs. the pH of the aqueous phase. (●) Pd, (○) Al, (▲) Mn, (□) Ni.



Figure 1 shows the linear plots of  $\log (\epsilon - \epsilon_{A^-})/(\epsilon_{HA} - \epsilon)$  vs. pH, when the  $\beta$ -diketones were AA (acetylacetone), DPrM, DIBM, PAM and DPM.

#### Determination of distribution coefficients of the $\beta$ -diketones

To establish the distribution ratios, 20 ml of 0.01 *M* sodium borate buffer solution (ionic strength, 0.1 *M* NaClO<sub>4</sub>) was shaken with 20 ml of 0.10–0.05 *M*  $\beta$ -diketone in benzene solution for 24 h. After the pH value had been measured, the concentration of  $\beta$ -diketone in the aqueous phase was obtained from the absorbance at 295 nm.

The distribution ratio, *D*, and the distribution coefficient, *P*, of the  $\beta$ -diketones were obtained from the following equations:

$$P = [\text{HA}]_{\text{org}}/[\text{HA}] \quad (4)$$

$$D = [\text{HA}]_{\text{org}}/[\text{HA}] + [\text{A}^-] = P/(K_a/[\text{H}^+] + 1) \quad (5)$$

From eqn. (5), one can calculate the value of *P* because *D*, pH and  $pK_a$  are known.

Figure 2 shows the linear plots of  $\log D$  vs.  $\log (K_a/[\text{H}^+] + 1)$  for AA, DPrM, DIBM, PAM and DPM; the slopes are ca. 1. The distribution coefficients of the  $\beta$ -diketones were calculated from the data in Fig. 2, and are summarized in Table III. The mean values of the acid dissociation constants and of the distribution coefficients for AA and DPM are in agreement with previous values<sup>7,10–12</sup>.

TABLE III

ACID DISSOCIATION CONSTANTS AND DISTRIBUTION COEFFICIENTS OF THE  $\beta$ -DIKETONES

|      | $pK_a$           |                    | $\log P$        |   |
|------|------------------|--------------------|-----------------|---|
|      | Found            | Lit. value         | Found           | Lit. value                              |
| AA   | 8.84 $\pm$ 0.04  | 8.82 <sup>10</sup> | 0.65 $\pm$ 0.04 | 0.77 <sup>12</sup> , 0.54 <sup>11</sup> |
| DPrM | 9.55 $\pm$ 0.03  | —                  | 1.61 $\pm$ 0.04 | —                                       |
| DIBM | 9.82 $\pm$ 0.03  | —                  | 3.04 $\pm$ 0.04 | —                                       |
| PAM  | 10.00 $\pm$ 0.04 | —                  | 2.18 $\pm$ 0.04 | —                                       |
| DPM  | 11.57 $\pm$ 0.03 | 11.77 <sup>7</sup> | 3.98 $\pm$ 0.05 | —                                       |

#### Metal extraction with DPrM, DIBM, PAM and DPM

The percentage extraction for palladium, iron, aluminum, copper, nickel, cobalt, zinc, cadmium and manganese by 0.10 *M*  $\beta$ -diketones in benzene under various conditions of pH are shown in Figs. 3–10.

*Palladium(II)*. The extraction of the DPM chelate was incomplete, while the DPrM, DIBM and PAM chelates of palladium were extracted almost quantitatively at pH 2–5. The chelate of DPM was extracted into benzene and was yellow. The plots of distribution ratio,  $\log D_M$  vs. pH for DPrM, DIBM, and PAM had slopes of 2.01, 1.98 and 2.01, respectively, but the plot for DPM deviated from the straight line with slope 2, *i.e.* the theoretical value.

*Iron(III)*. Iron chelates were completely extracted in the pH ranges 2.5–5, 2–3.5, 1.5–4, and 2.5–3.5, for DPrM, DIBM, PAM and DPM, respectively. These chelates were yellow in the organic phases and the solutions exhibited a maximum absorbance at 437–432 nm. The plots of  $\log D_M$  vs. pH were on a straight line with a slope equal to approximately 3 for the  $\beta$ -diketonates.

TABLE IV  
EXTRACTION DATA FOR METAL  $\beta$ -DIKETONE COMPLEXES

|                  | $-\log K_{ex}$   |                  |                  | $\log K_{nQ_n}$ |         |         | $(pH_{1/2})_{0.1}$ |      |      |      |
|------------------|------------------|------------------|------------------|-----------------|---------|---------|--------------------|------|------|------|
|                  | DPM              | DIBM             | PAM              | DPM             | DIBM    | PAM     | DPM                | DIBM | PAM  |      |
| Pd <sup>2+</sup> | $-1.22 \pm 0.09$ | $-2.05 \pm 0.06$ | $-0.18 \pm 0.07$ | 23.54           | 27.77   | 24.54   | —                  | 0.44 | 0.98 | 1.10 |
| Fe <sup>3+</sup> | $0.82 \pm 0.07$  | $0.17 \pm 0.05$  | $0.87 \pm 0.07$  | $32.66$         | $38.41$ | $35.67$ | $45.47$            | 1.28 | 1.28 | 1.39 |
| Al <sup>3+</sup> | $6.12 \pm 0.08$  | —                | $6.77 \pm 0.06$  | 27.36           | —       | 29.77   | —                  | 3.04 | 3.58 | 4.65 |
| Cu <sup>2+</sup> | $4.34 \pm 0.04$  | $4.42 \pm 0.05$  | $4.63 \pm 0.08$  | 17.98           | 21.30   | 19.73   | 25.91              | 3.17 | 3.22 | 3.67 |
| Zn <sup>2+</sup> | $11.76 \pm 0.03$ | $11.74 \pm 0.04$ | $12.08 \pm 0.05$ | 10.56           | 13.98   | 12.28   | —                  | 6.88 | 6.88 | 7.55 |
| Ni <sup>2+</sup> | —                | $13.92 \pm 0.03$ | $13.80 \pm 0.03$ | —               | 11.80   | 10.56   | —                  | —    | 7.96 | 8.45 |
| Co <sup>2+</sup> | —                | —                | —                | —               | —       | —       | —                  | 7.64 | 7.04 | 8.27 |
| Mn <sup>2+</sup> | $20.92 \pm 0.09$ | $20.83 \pm 0.05$ | $20.94 \pm 0.03$ | 12.56           | 17.75   | 15.60   | —                  | 7.97 | 7.94 | 8.59 |

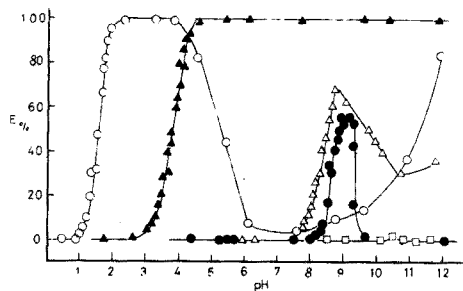


Fig. 9. Extraction of Fe(III), Cu(II), Co(II), Mn(II), Cd(II) by 0.10 *M* dipivaloylmethane vs. the pH of the aqueous phase. (○) Fe, (▲) Cu, (●) Mn, (△) Co, (□) Cd.

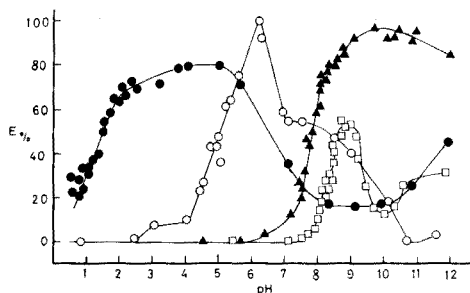


Fig. 10. Extraction of Pd(II), Al(III), Zn(II), Ni(II) by 0.10 *M* dipivaloylmethane vs. the pH of the aqueous phase. (●) Pd, (○) Al, (▲) Zn, (□) Ni.

*Copper(II)*. Copper was completely extracted above pH 4.5 by all the  $\beta$ -diketones and the plots of  $\log D_M$  vs. pH were straight lines with slopes of ca. 2.

*Aluminum(III)*. The extraction of aluminum with DPrM, DIBM, PAM and DPM was quantitative for pH values of 4.5–11, 5.5–11, 4–11, and around 6.2, respectively. The plots of  $\log D_M$  vs. pH were straight lines with slopes of 2.96, 2.00, 2.97, and 1.01 for DPrM, DIBM, PAM and DPM, respectively. These chelates have been reported as 1:3 complexes<sup>13</sup>. The variation in the extraction is probably associated either with the extent of hydrolysis or with the solubility of the chelate.

*Zinc(II)*. Zinc was quantitatively extracted in the pH ranges of 8–10.5, 8.5–12 and 7.5–11 for DPrM, DIBM, and PAM, respectively. The plots of  $\log D_M$  vs. pH for these chelates had slopes of about 2. Approximately 85% of zinc was extracted with DPM at pH 10 and the plot deviated from the straight line with a theoretical slope of 2.

*Cobalt(II)*. Cobalt was extracted incompletely with all the  $\beta$ -diketones studied in the present paper. The maximum percentage extraction was about 72% at pH 8.8, 97% at pH 8.7, 90% at pH 9–10.5 and 67% at pH 8.7 for DPrM, DIBM, PAM and DPM, respectively. During the extraction, the cobalt chelate in the benzene phase was pink at an early stage of extraction, and later changed from pink to green in all cases. Accordingly, it was concluded that cobalt was initially extracted as  $\text{CoA}_2$  (A = anionic species of the  $\beta$ -diketone), and was then transformed slowly into the much more stable  $\text{CoA}_3$  complex.

*Nickel(II)*. Nickel, like cobalt, was extracted incompletely with the  $\beta$ -diketones tested. The maximum percentage extraction was about 10% at pH 9.4, 97% at pH 10.5–11, 90% at pH 9–10.5 and 53% at pH 8.9 for DPrM, DIBM, PAM and DPM, respectively. The complexes extracted with DIBM and DPM were pink in the benzene phase and gave an absorbance maximum at 525 nm. FACKLER AND COTTON have reported<sup>14</sup> that the red hydrocarbon solution of the anhydrous bis(DPM)–nickel chelate exhibits a single absorbance peak at 535 nm in the visible range. Accordingly, it seems that nickel was extracted in an anhydrous form as a 1:2 complex with DIBM or DPM. The plots of  $\log D_M$  vs. pH for DIBM and PAM showed slopes of 1.92 at low pH and 0.96 at high pH. This may be caused by the formation of small amounts of water-soluble complexes such as intermediate complexes or hydroxocomplexes.

*Manganese(II)*. Manganese was completely extracted at pH 8.5–9.5 by DPrM,

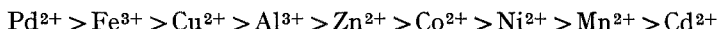
DIBM and PAM. These chelates gave a greenish brown color in the organic phase. The plots of  $\log D_M$  vs. pH were straight lines with slopes of 2.98, 3.00 and 2.98 for DPrM, DIBM and PAM, respectively. With DPM, however, the extraction ratio of manganese reached a maximum of 60% at about pH 9 and a large amount of brown precipitate insoluble in benzene appeared.

*Cadmium(II)*. Cadmium was extracted only to the extent of 2–10% at pH 10.5 with the  $\beta$ -diketones used. A large amount of white precipitate formed between the organic and aqueous phases.

#### CONCLUSIONS

From the distribution data of the metals investigated, the compositions of the extractable complex and the extraction constants,  $K_{ex}$ , were obtained. In addition, the two-phase stability constants,  $K_n Q_n$ , were calculated according to STARÝ's procedure<sup>4,6</sup> from the values of the acid dissociation constant and distribution coefficient of the  $\beta$ -diketones used. The values of the extraction constants, the two-phase stability constants and the  $(pH_{\frac{1}{2}})_{0.1}$  are summarized in Table IV.

As can be seen in Table IV, the extractabilities of the metals with DPrM, DIBM, PAM and DPM in benzene decrease in the following order:



The increase in  $K_n Q_n$  in the order DPrM < DIBM < PAM < DPM, is caused by the increase in the distribution coefficient of the metal complex.

As was mentioned above, nickel was extracted in the form of anhydrous chelate with DIBM and DPM. It is known that the cobalt and nickel acetylacetonates are hydrated easily and the hydrated chelates are usually less soluble than the anhydrous form. Probably, the variation in the maximum percentage extraction of cobalt and nickel is caused by the difference in solubility, or more precisely, by the difference in the distribution coefficient of the chelates of the  $\beta$ -diketones used. The fact that the maximum percentage extraction of the cobalt, aluminum, manganese and nickel chelates with DPM is lower than those of the chelates formed with other  $\beta$ -diketones, is due to steric hindrance effects.

The authors wish to thank Dr. TOTARO GOTO for his helpful advice.

#### SUMMARY

The extractions of  $Pd^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$  and  $Cd^{2+}$  by solutions of dipropionylmethane, diisobutyrylmethane, pivaloylacetylmethane and dipivaloylmethane in benzene, have been studied in relation to the pH values for extraction. The extraction constants and two-phase stability constants of the  $\beta$ -diketonates were calculated. These can be used to establish the optimum conditions for the separation of the metals.

#### RÉSUMÉ

Une étude est effectuée sur l'influence du pH d'extraction de  $Pd^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ ,

$\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$  et  $\text{Cd}^{2+}$  par des solutions de dipropionylméthane, de diisobutyrylméthane, de pivaloylacétylméthane et de dipivaloylméthane dans le benzène. On a calculé les constantes d'extraction et les constantes de stabilité des  $\beta$ -dicétonates. Ceci permet d'établir les conditions optima pour la séparation de ces métaux.

## ZUSAMMENFASSUNG

Es wurde die Extraktion von  $\text{Pd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$  und  $\text{Cd}^{2+}$  mit Lösungen von Dipropionylmethan, Diisobutyrylmethan, Pivaloylacetylmethan und Dipivaloylmethan in Benzol untersucht und zwar in Abhängigkeit vom pH-Wert. Die Extraktionskonstanten und die Zweiphasen Stabilitätskonstanten der  $\beta$ -Diketonate wurden berechnet. Diese können zur Festlegung der optimalen Extraktionsbedingungen verwendet werden.

## REFERENCES

- 1 G. H. MORRISON AND H. FREISER, *Solvent Extraction in Analytical Chemistry*, John Wiley, New York, N.Y., 1957.
- 2 A. KRISHEN AND H. FREISER, *Anal. Chem.*, 31 (1959) 923.
- 3 T. SHIGEMATSU AND M. TABUCHI, *Bull. Inst. Chem. Res. Kyoto Univ.*, 69 (1961) 35.
- 4 J. STARÝ AND E. HLADKY, *Anal. Chim. Acta*, 28 (1963) 227.
- 5 L. GENOW AND G. KASSABOW, *Monatsh. Chem.*, 98 (1967) 364.
- 6 J. STARÝ, *The Solvent Extraction of Metal Chelates*, Pergamon Press, Oxford, 1964.
- 7 G. A. GUTER AND G. S. HAMMOND, *J. Am. Chem. Soc.*, 78 (1956) 5166.
- 8 K. G. EISENTRANT AND R. E. SIEVERS, *J. Am. Chem. Soc.*, 87 (1965) 5254.
- 9 C. R. HAUSER AND J. T. ADAMS, *J. Am. Chem. Soc.*, 66 (1944) 1220.
- 10 J. RYDBERG, *Svensk Kem. Tidsskr.*, 65 (1953) 37.
- 11 V. M. PESHKOVA AND PEN-AN, *Zh. Neorgan. Khim.*, 6 (1961) 2083.
- 12 N. P. RUDENKO AND J. STARÝ, *Tr. Komissii. po Anal. Khim.*, IX (XII) 28 AN USSR, Moscow, 1958.
- 13 G. S. HAMMOND AND D. C. NONHEBEL, *Inorg. Chem.*, 2 (1963) 73.
- 14 J. P. FACKLER AND F. A. COTTON, *J. Am. Chem. Soc.*, 83 (1961) 2818.

## A STUDY OF EQUILIBRIUM ISOTOPE EFFECTS OF TERTIARY AMINES BY NMR AND POTENTIOMETRY

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Although a fairly large number of papers concerning hydrogen-deuterium isotope effects have been published, many of these consider the kinetic effects of deuterium oxide rather than effects on solution equilibria. LI *et al.*<sup>1</sup> studied equilibrium isotope effects on a number of amino acids by means of the glass electrode. They noted that the isotope effect on the acid dissociation constant depended to a large extent on the specific bond affected<sup>1</sup>. SALOMAA *et al.* also used the glass electrode to study phosphoric and arsenic acids<sup>2</sup>, and several other weak acid systems in H<sub>2</sub>O-D<sub>2</sub>O mixtures<sup>3</sup>. These authors developed an empirical equation to give  $pD_n$ , the generalized equivalent of pH, in solutions containing  $n$  mole fraction of deuterium. In the case of a strong acid dissolved in pure D<sub>2</sub>O,  $pD$  is equal to the pH meter reading plus 0.41. This result was confirmed more recently by BATES and co-workers, who conducted a detailed study of the feasibility using the glass electrode in heavy water solutions<sup>4</sup>. Thus potentiometry has been found to be very useful in determining the effects of D<sub>2</sub>O on acid-base equilibria.

An entirely different approach to the determination of isotope effects was proposed by LEYDEN AND REILLEY<sup>5</sup>, who showed that NMR could be used effectively to determine isotope effects of tertiary amines. This method utilizes direct measurement of the relative concentrations of the protonated species H<sup>+</sup>NR<sub>3</sub> and D<sup>+</sup>NR<sub>3</sub> in solutions of high acidity. Equilibrium isotope effects determined under these conditions have an important use in studies of protolysis reactions of nitrogen-containing compounds in H<sub>2</sub>O-D<sub>2</sub>O solvents. This method of studying solution equilibria is of interest as a supplement to potentiometric techniques; the usefulness of the two methods in determining equilibrium isotope effects of a series of tertiary amines is compared in the present paper.

### EXPERIMENTAL

The NMR spectra were recorded with a Varian HA-100 high resolution spectrometer. Potentiometric measurements were made with a Corning Model 12 pH meter and a Corning triple-purpose glass electrode. All pH measurements were taken at  $25.0 \pm 0.05^\circ$ , NBS-approved buffer solutions were used for standardization of the pH meter.

Most compounds used were commercially available and were vacuum-distilled before use. Benzylmethyl-2-chloroethylamine was prepared from benzylmethylethanolamine (Aldrich Chemical Company). Deuterium oxide (Columbia Organic Chemicals) was found to be 99.7% pure. Deuterium chloride was prepared from deuterium

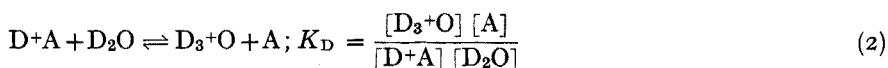
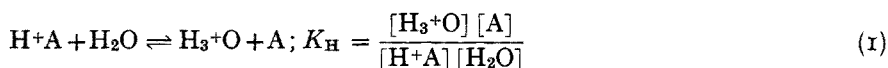
oxide and benzoyl chloride under nitrogen, and the potassium deuterio-oxide prepared from potassium metal and deuterium oxide, also under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Potentiometric studies

Potentiometric determination of the  $pK_a$  in water-heavy water solutions was accomplished by the differential potentiometric technique of BACARELLA *et al.*<sup>6</sup>. This method was found to be most useful and accurate when the amines were at least partially soluble in their basic form. Two pH measurements were taken, one in a solution containing an excess of acid, and the other in a solution obtained by neutralization of the acid form of the amine. The  $pK_H$  was then calculated by a computer program based upon previously derived equations<sup>6</sup>. Similarly, the  $pK_D$  value in  $D_2O$  was determined for each amine, from the observed pH, corrected for the mole fraction  $D_2O$  by the empirical relationship found by LONG *et al.*<sup>2</sup>. The isotope effect is reported as the ratio of  $K_H$ , the dissociation constant in water, to  $K_D$ , the dissociation constant in pure  $D_2O$ .

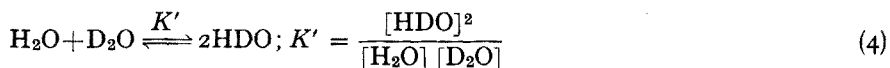
Isotope effects under different conditions, *i.e.* in solutions of fairly high concentration and sufficiently high acidity to stop rapid exchange of the hydrogen or deuterium, may be determined by NMR techniques. For an amine in a solution of mixed  $H_2O$ - $D_2O$  composition, two possible equilibria are shown in eqns. (1) and (2).



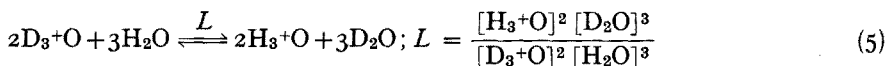
Another possible relationship is the following:



The equilibrium between  $H_2O$  and  $D_2O$



has been considered previously, and  $K'$  has been assigned a value of 3.96 by UREY<sup>7</sup>, which is very nearly the expected statistical value<sup>8</sup> of 4.0. The isotope effect for converting hydrogen ion in the proton aggregate to solvent can be represented by the expression



The value of  $L$  has been determined by combining free energy changes of electrolytic cells, and exchange constants of reactions between hydrogen isotopes and isotopic water mixtures<sup>8</sup>. Its value has most recently been determined<sup>8</sup> to be 11.0. This was also confirmed by NMR methods<sup>9</sup>.

### NMR studies

When the methyl resonance portion of the spectrum of each tertiary amine in a

highly acidic H<sub>2</sub>O–D<sub>2</sub>O solution is examined, an overlapping doublet and singlet is observed. The doublet arises from the coupling of the methyl protons with the N–H proton in the case of tertiary amine molecules protonated by hydrogen ions. In the case of amine molecules protonated by a deuterium ion, a singlet rather than a triplet is observed, owing to the interaction of the deuterium quadrupole with the asymmetric electrical field gradients about the deuterium nucleus<sup>5</sup>. Thus by measuring the relative areas of the NMR resonance peaks resulting from the two types of molecules, the ratio [D<sup>+</sup>A]/[H<sup>+</sup>A] can be evaluated. From eqn. (4), one can determine the ratio [H<sub>2</sub>O]/[D<sub>2</sub>O]. Knowledge of these two ratios permits the calculation of the value of *K* for each compound. When eqns. (3) and (5) are combined, eqn. (6) is obtained:

$$\sqrt{K \cdot L} = \sqrt{\frac{[D^+A]^2 [H_3^+O]^2 [D_2O]^2}{[H^+A]^2 [D_3^+O]^2 [H_2O]^2}} = \frac{[D^+A]}{[H^+A]} \cdot \frac{[D_2O]}{[H_2O]} \cdot \frac{[H_3^+O]}{[D_3^+O]} = \frac{K_H}{K_D} \quad (6)$$

which is a relationship between the isotope effect and the dissociation constant of the amine.

Results are shown in Table I. Except for two compounds, dimethyl-*t*-butylamine and benzylmethyl-2-chloroethylamine, the results of the potentiometric and NMR techniques agree within estimated experimental error. In view of the large differences in ionic strength between the two techniques, the general agreement is surprisingly good.

TABLE I  
COMPARISON OF ISOTOPE EFFECTS OBTAINED BY POTENTIOMETRY AND NMR TECHNIQUES

| Amine                      | <i>pK<sub>A</sub></i> | <i>log K<sub>H</sub>/K<sub>D</sub></i> |             |
|----------------------------|-----------------------|--|-------------|
|                            |                       | Potentiometry                          | NMR         |
| Dimethyl- <i>t</i> -butyl  | 10.52                 | 0.69 ± 0.01                            | 0.57 ± 0.02 |
| Dimethylethanol            | 9.31                  | 0.66                                   | 0.63        |
| Dimethylbenzyl             | 8.95                  | 0.73                                   | 0.72        |
| Diethanolmethyl            | 8.52                  | 0.61                                   | 0.62        |
| Benzylmethylethanol        | 8.41                  | 0.72                                   | 0.69        |
| Dibenzylmethyl             | 8.0                   | — <sup>a</sup>                         | 0.66        |
| Benzylmethyl-2-chloroethyl | 7.30                  | 0.76                                   | 0.66        |

<sup>a</sup> The *pK<sub>A</sub>* of this compound was estimated from potentiometric titration. However, low solubility of the neutral amine prevented an accurate determination of the isotope effect by potentiometry.

This indicates that at least in the NMR technique, medium effects tend to cancel in the determination of the isotope effect ratio. The NMR technique also offers a definite advantage in that determination of isotope effects can be accomplished in a single experiment.

Several papers have shown that the isotope effect for a given functional group can be expected to follow a linear equation of the form shown by eqn. (7):

$$\Delta pK = pK_D - pK_H = a + b pK_H \quad (7)$$

where *a* and *b* are empirical constants<sup>1,10</sup>. This tendency was noted in the compounds studied in the present work, although a plot of *pK* vs. *log K<sub>H</sub>/K<sub>D</sub>* shows a different slope and intercept for the alkylamines and the amines containing a benzyl group.

A difference in chemical shift between methyl protons on amine molecules protonated by hydrogen, and those protonated by deuterium was very noticeable. The



magnitude of this isotopic chemical shift difference ranged from 0.18 to 0.32 cycles/sec at 100 MHz. It has been noted previously that the shielding constant of a nucleus is increased when a neighboring nucleus is replaced by a heavier isotope, and this is attributable to differences in ground state vibrational amplitudes of the two isotopes<sup>11</sup>. In the case of the tertiary amines in the present study, a down-field shift of the methyl resonance is observed when the deuterium ion protonates the amine, compared with hydrogen protonation. In the previously reported cases, the isotopic substitution was performed on a central atom bonded to the nucleus under observation. In the present cases, the isotopic substitutions are three bonds removed from the observed nuclei. The former examples result in an increased shielding of the observed nuclei whereas in the present case there is a deshielding.

A definite relationship was also noticed between the isotopic effect on chemical shift and the coupling constant of the methyl protons. The coupling constant decreases with increasing chemical shift difference over the range of compounds studied. This observation is comparable to an empirical relationship found by FRANKISS<sup>12</sup> for  $^{19}\text{F}(\text{C}^{13}\text{-C}^{12})$  isotope chemical shifts and  $J_{\text{CF}}$  coupling constants for several saturated compounds containing fluorine.

This investigation was supported in part by Public Health Service Grant GM-13935 from the National Institute of Health.

#### SUMMARY

A comparative study of solvent isotope effects on the dissociation constant of amine salts, by means of potentiometric and nuclear magnetic resonance techniques has been performed. Agreement of the results of the two techniques was generally good. The magnetic resonance technique offers an advantage in cases in which the amine is insoluble in neutral or basic solutions. An observed correlation between the isotopic shift of N-methyl proton chemical shift and the spin coupling between the methyl protons and the N-H proton is mentioned.

#### RÉSUMÉ

On a effectué une étude comparative de l'influence d'isotopes sur la constante de dissociation de sels d'amines par potentiométrie et résonance magnétique nucléaire. La concordance des résultats obtenus avec ces deux techniques est généralement bonne. La résonance magnétique présente l'avantage d'être applicable à des amines insolubles dans des solutions neutres ou basiques. On mentionne également la relation du transfert isotopique du proton N-méthyle et du spin entre les protons méthyle et le proton N-H.

#### ZUSAMMENFASSUNG

Eine vergleichende Untersuchung der Isotopieeffekte auf die Dissoziationskonstante von Aminalszen wurde mittels potentiometrischer und KMR-Methoden durchgeführt. Im allgemeinen ist die Übereinstimmung der Ergebnisse beider Methoden gut. Die KMR bietet bei den Fällen Vorteile, bei denen das Amin in neutralen

oder basischen Lösungen unlöslich ist. Es wurde eine Beziehung zwischen der isotopischen Verschiebung des N-Methyl-Protons und der Spinkopplung zwischen den Methylprotonen und den N-H-Protonen beobachtet.

## REFERENCES

- 1 N. C. LI, P. TANG AND R. MATHUR, *J. Phys. Chem.*, 65 (1961) 1074.
- 2 P. SALOMAA, L. L. SCHALEGER AND F. A. LONG, *J. Am. Chem. Soc.*, 86 (1964) 1
- 3 P. SALOMAA, L. L. SCHALEGER AND F. A. LONG, *J. Phys. Chem.*, 68 (1964) 410.
- 4 A. K. COVINGTON, M. PAABO, R. A. ROBINSON AND R. G. BATES, *Anal. Chem.*, 40 (1968) 700.
- 5 D. E. LEYDEN AND C. N. REILLEY, *Anal. Chem.*, 37 (1965) 1333.
- 6 A. L. BACARELLA, E. GRUNWALD, H. P. MARSHALL AND E. L. PURLEE, *J. Org. Chem.*, 20 (1955) 747.
- 7 H. C. UREY, *J. Chem. Soc.*, (1947) 562.
- 8 E. L. PURLEE, *J. Am. Chem. Soc.*, 81 (1959) 263.
- 9 A. J. KRESGE AND A. L. ALLRED, *J. Am. Chem. Soc.*, 85 (1963) 1541.
- 10 R. B. MARTIN, *Science*, 139 (1963) 1198.
- 11 J. W. EMSLEY, J. FEENY AND L. H. SUTCLIFFE, *High Resolution Nuclear Magnetic Resonance*, Vol. 1, Pergamon Press, New York, 1965, p. 99.
- 12 S. G. FRANKISS, *J. Phys. Chem.*, 67 (1963) 752.

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## ANODIC VOLTAMMETRIC DETERMINATION OF PLUTONIUM DIFFUSION COEFFICIENTS OF PLUTONIUM(III) IN MINERAL ACIDS\*

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The analytical chemistry of plutonium has been well documented by METZ AND WATERBURY<sup>1</sup>. The electropositive potentials of plutonium (both the plutonium(III)–plutonium(IV) and the plutonium(V)–plutonium(VI) couple) prevent the investigation of these couples at the dropping mercury electrode unless the plutonium is complexed. When complexed, the plutonium potentials become more negative, and the dropping mercury electrode may then be used.

COOK *et al.*<sup>2</sup> investigated the reduction of the plutonyl ion in several complexing media, and their best results were obtained in an oxalate medium. MILNER AND WOOD<sup>3</sup> developed a method for the determination of plutonium in a citrate medium by reducing plutonium(IV). A preliminary report by JEFTIĆ *et al.*<sup>4</sup> describes the behavior of plutonium carbonate complex at a hanging mercury drop electrode. KOYAMA<sup>5</sup> studied the reduction of plutonium(IV) at a stationary platinum electrode in hydrochloric acid and nitric acid using square-wave polarography.

ZITTEL AND MILLER<sup>6</sup> were the first to suggest the use of glassy carbon as an electrode, and they used it as a counter electrode in studies of the iodine system<sup>7,8</sup>. YOSHIMORI *et al.*<sup>9</sup> used this electrode to determine gold by anodic stripping; and the electrode was applied by DOLEZAL AND STULÍK for acid–base titrations in aqueous media<sup>10</sup>. The glassy carbon electrode was also used as the indicating electrode in the determination of neptunium at a stationary electrode<sup>11</sup>, and for the investigation of several neptunyl complexes<sup>12,13</sup>. The effect of several organic materials on the glassy carbon electrode has also been reported<sup>14</sup>.

This paper describes the determination of plutonium by the oxidation of plutonium(III) to plutonium(IV) at the glassy carbon electrode, and the determination of plutonium(III) diffusion coefficients in four mineral acids.

### EXPERIMENTAL

#### *Apparatus*

All voltammograms were obtained with a calibrated Sargent Model XV recording polarograph. None of the measurements were damped. The electrolysis cell was an H-form cell which contained a saturated calomel electrode. The sample compartment was connected to the saturated calomel electrode by means of an agar satu-

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

rated potassium chloride bridge. The glassy carbon electrode (G.C.E.) and the electrode mounting have been described<sup>11,12</sup>.

Extreme care must be exercised in the handling of plutonium because of its toxicity. All work with plutonium was performed in a glove box.

### Reagents

A stock solution of plutonium(III) perchlorate was prepared from plutonium metal standard 949a (U.S. National Bureau of Standards) by dissolving the metal in 6 M perchloric acid and diluting to 100 ml with water. The standardization of the stock solution was checked daily by a controlled potential coulometric titration<sup>15</sup>. The rate of air oxidization of the plutonium(III) to plutonium(IV) was negligible.

All other chemicals were reagent grade and prepared in the usual manner.

### Calibration procedure

A calibration curve for plutonium was prepared by pipetting aliquots of the standard stock solution into 25-ml volumetric flasks. The solutions were diluted to volume with 0.5 M perchloric acid, and a portion was transferred to the electrolysis cell.

Plutonium solutions of eight different concentrations (three solutions each) were prepared and electrolyzed. The data are shown in Table I. A plot of the plutonium concentration ( $C$ ) vs. the limiting current ( $i_l$ ) was linear over the range  $2.24 \cdot 10^{-4}$ – $4.48 \cdot 10^{-3}$  M, and the mean limiting current quotient ( $i_l/C$ ) was  $36.5 \mu\text{A}/\text{mmol/l}$  with a relative standard deviation of 3.84%.

TABLE I

LIMITING CURRENT AS A FUNCTION OF THE PLUTONIUM CONCENTRATION

(Electrolyte: 0.5 M HClO<sub>4</sub>)

| $\text{Pu}^{3+}$ concn.<br>(mol/l) | $i_l$<br>( $\mu\text{A}$ ) | $i_l/C$<br>( $\mu\text{A}/\text{mmol/l}$ ) |
|------------------------------------|----------------------------|--|
| $2.24 \cdot 10^{-4}$               | 8.4                        | 37.5                                       |
| $4.48 \cdot 10^{-4}$               | 16.4                       | 36.6                                       |
| $6.73 \cdot 10^{-4}$               | 23.2                       | 34.5                                       |
| $8.97 \cdot 10^{-4}$               | 33.8                       | 37.4                                       |
| $1.34 \cdot 10^{-3}$               | 51.0                       | 38.1                                       |
| $1.79 \cdot 10^{-3}$               | 65.3                       | 36.5                                       |
| $2.24 \cdot 10^{-3}$               | 80.0                       | 35.7                                       |
| $4.48 \cdot 10^{-3}$               | 161.0                      | 35.9                                       |

## RESULTS AND DISCUSSIONS

### Effect of different acids

The effects of various acids and acid concentrations on the plutonium(III) wave were investigated at the glassy carbon electrode. The plutonium(III) concentration was maintained constant at  $8.97 \cdot 10^{-4}$  M, while the concentrations of the acid were varied. In the range 0.02–4.0 M perchloric acid, the half-wave potential of plutonium(III) was 0.726 V vs. S.C.E., which is in good agreement with reported values<sup>16,17</sup>. The limiting current for plutonium(III) was constant in the acid concentration range

0.10–4.0 *M* with an average value of  $34.1 \pm 0.8 \mu\text{A}$ . The limiting current quotient was  $38.0 \mu\text{A}/\text{mmol/l}$  which is in fair agreement with the values obtained when the calibration curve was prepared (Table I). Below a concentration of 0.10 *M* perchloric acid, the limiting current decreased, which would indicate the possible formation of plutonium hydroxide.

In 0.02–1.5 *M* hydrochloric acid, the half-wave potential of plutonium(III) was constant at 0.717 V vs. S.C.E., which is in fair agreement with previously reported values<sup>16,17</sup>. Above an acid concentration of 1.5 *M*, this potential became more negative, and above 3.5 *M* acid, the plutonium(III) waves became ill defined. The limiting current in 0.02–1.5 *M* hydrochloric acid was constant with an average value of  $32.3 \pm 0.8 \mu\text{A}$  and a limiting current quotient of  $36.0 \mu\text{A}/\text{mmol/l}$ , which is in good agreement with the values in Table I for  $i_l/C$ . Above an acid concentration of 1.5 *M*, the limiting current decreased, which would indicate a changing composition of the plutonium(III) species.

In 0.02–3.5 *M* nitric acid the half-wave potential of plutonium(III) became more negative as the acid concentration was increased. Above 3.5 *M* acid, the plutonium(III) waves became ill-defined. The limiting current was constant in the acid concentration range 0.02–3.0 *M* with an average value of  $31.6 \pm 0.9 \mu\text{A}$  and a limiting current quotient of  $35.2 \mu\text{A}/\text{mmol/l}$  which are again in good agreement with Table I. Above 3.0 *M* in nitric acid, the limiting current decreased as the acid concentration increased, indicating, in this case, the oxidation of plutonium(III) by the nitric acid. When the nitric acid concentration exceeded 3.5 *M*, the plutonium(III) waves became ill-defined.

Sulfuric acid has more effect on the half-wave potential and the limiting current of plutonium(III) than any of the other three acids. In the range 0.02–0.30 *M* sulfuric acid, the half-wave potential became more negative quite rapidly, changing 250 mV/mol/l over this acid range. In the 0.30–1.0 *M* acid range, the plutonium(III) half-wave potential continued to become more negative, but at a much slower rate of 10 mV/mol/l of acid. When the sulfuric acid concentration exceeded 1.0 *M*, the change in the half-wave potential was 5 mV/mol/l of acid. The limiting current was constant in the acid concentration range 0.02–0.50 *M* with an average value of  $33.4 \pm 0.8 \mu\text{A}$  and a limiting current quotient of  $37.2 \mu\text{A}/\text{mmol/l}$ , which is in good agreement with the values in Table I. Above an acid concentration of 0.5 *M*, the limiting current decreased as the acid concentration increased, indicating a change of the plutonium(III) species.

Attempts were made to use phosphoric acid, but even with low concentrations of phosphoric acid (0.02 *M*), a precipitate was formed.

The best shaped plutonium(III) waves were those obtained in sulfuric acid medium. However, the calibration was not performed in this medium because of the narrow range (0.02–0.50 *M*) in which the limiting current was constant in comparison with the perchloric acid concentration range (0.10–4.0 *M*). If one could be certain that the sulfuric acid concentration was less than 0.50 *M*, it would be preferable to use this medium for analysis.

#### *Investigation of interferences*

The effect of various foreign ions on the determination of plutonium was investigated. The test solutions were 0.5 *M* in perchloric acid, and contained 214  $\mu\text{g}/\text{ml}$  of plutonium and 600  $\mu\text{g}/\text{ml}$  of the foreign ion. It was found that Ag(II), Br(V), Ce(IV), Cr(VI), Fe(II), Mn(VII), V(V), and Xe(VIII) seriously interfere. All of these ions ex-

cept iron(II) oxidize the plutonium(III) to plutonium(IV) and cause low results. Iron(II) is oxidized along with the plutonium(III) and causes high results. The ions which did not interfere are Ag(I), Cd(II), Ce(III), Co(II), Cr(III), Ga(III), Ni(II), U(VI), and Zn(II).

#### *Analysis of standard plutonium solutions*

Six standard plutonium(III) solutions in the range 50.0–600  $\mu\text{g/ml}$  were prepared from a plutonium stock solution and analyzed by controlled potential coulometry<sup>13</sup>. The average percent recovery for these six solutions, by the above method, was 101% with a standard deviation of 0.04%.

#### *Plutonium(III) diffusion coefficients*

The diffusion coefficients of plutonium(III) were determined at a stationary glassy carbon electrode from the following equation<sup>18</sup>:

$$D^{\ddagger} = \frac{i_p}{2.72 \cdot 10^5 n^{\ddagger} AC V^{\ddagger}}$$

where  $i_p$  = peak current (A);  $A$  = electrode area ( $\text{cm}^2$ );  $C$  = concentration (mol/l);  $V$  = voltage scan rate (V/sec); and  $n$  = number of Faradays.

The solutions were  $8.97 \cdot 10^{-4} M$  in plutonium(III) and were 0.50  $M$  in the respective acids. The electrode surface area was  $0.12 \text{ cm}^2$  and the voltage scan rate was  $5.0 \cdot 10^{-3} \text{ V/sec}$ . At  $25^\circ$  the diffusion coefficients were  $0.32 \cdot 10^{-5} \text{ cm}^2/\text{sec}$  in perchloric acid and hydrochloric acid,  $0.30 \cdot 10^{-5} \text{ cm}^2/\text{sec}$  in sulfuric acid, and  $0.33 \cdot 10^{-5} \text{ cm}^2/\text{sec}$  in nitric acid. As expected, the diffusion coefficients were essentially the same.

Since sulfuric acid had the greatest effect on both the half-wave potential and the limiting current of the plutonium(III), the diffusion coefficients were determined in 1.0, 2.0, and 3.0  $M$  sulfuric acid, and found to be  $0.25 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ ,  $0.18 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ , and  $0.16 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ , respectively.

#### SUMMARY

Plutonium(III) can be determined at the glassy carbon electrode by anodic voltammetry in the concentration range  $2.24 \cdot 10^{-4}$ – $4.48 \cdot 10^{-3} M$  in 0.5  $M$  perchloric acid. Any oxidizing substance and iron(II) interfere. Hydrochloric, nitric and sulfuric acids also interfere at various concentrations. Diffusion coefficients were determined in 0.5  $M$  perchloric, hydrochloric, nitric and sulfuric acids.

#### RÉSUMÉ

On décrit une méthode pour le dosage du plutonium(III) par voltammétrie anodique. Les concentrations vont de  $2.24 \cdot 10^{-4}$  à  $4.48 \cdot 10^{-3} M$  dans l'acide perchlorique 0.5  $M$ . Les oxydants et le fer(II) gênent, de même que les acides chlorhydrique, nitrique et sulfurique. Les coefficients de diffusion ont été déterminés dans ces acides 0.5  $M$ .

#### ZUSAMMENFASSUNG

Plutonium(III) kann durch anodische Voltammetrie mit glasiger Kohlenstoff-

elektrode und in 0,5 M Perchlorsäure im Konzentrationsbereich von  $2.24 \cdot 10^{-4}$ – $4.48 \cdot 10^{-3}$  M bestimmt werden. Oxydierende Substanzen und Eisen(II) stören, ebenso Salz-, Salpeter- und Schwefelsäure. Die Diffusionskoeffizienten des Plutoniums wurden in 0,5 M Perchlor-, Salz-, Salpeter- und Schwefelsäure bestimmt.

## REFERENCES

- 1 C. F. METZ AND G. R. WATERBURY, in I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Vol. 9, Part II, Interscience, New York, 1962, p. 189.
- 2 G. P. COOK, J. K. FOREMAN AND E. F. KEMP, *Anal. Chim. Acta*, 19(1958) 174.
- 3 G. W. C. MILNER AND A. J. WOOD, *J. Electroanal. Chem.*, 7 (1964) 190.
- 4 LJ. JEFTIĆ, J. CAJA AND M. BRANICA, *Croat. Chem. Acta*, 39 (1967) 225.
- 5 K. KOYAMA, *Anal. Chem.*, 32 (1960) 523.
- 6 H. E. ZITTEL AND F. J. MILLER, *Anal. Chem.*, 37 (1965) 200.
- 7 F. J. MILLER AND H. E. ZITTEL, *J. Electroanal. Chem.*, 11 (1966) 85.
- 8 H. E. ZITTEL AND F. J. MILLER, *J. Electroanal. Chem.*, 13 (1967) 193.
- 9 T. YOSHIMORI, M. ARAKAWA AND T. TAKEUCHI, *Talanta*, 12 (1965) 147.
- 10 J. DOLEZAL AND K. STULÍK, *J. Electroanal. Chem.*, 17 (1968) 87.
- 11 C. E. PLOCK, *J. Electroanal. Chem.*, 18 (1968) 289.
- 12 C. E. PLOCK, *J. Inorg. & Nucl. Chem.*, 30 (1968) 3023; *Anal. Chim. Acta*, 43 (1968) 281; *J. Electroanal. Chem.*, in press.
- 13 C. E. PLOCK, *Anal. Chim. Acta*, 47 (1969) 27.
- 14 C. E. PLOCK, *U.S. At. Energy Comm. Rept. RFP-1221*, 1968.
- 15 W. D. SHULTS, *Talanta*, 10 (1963) 833.
- 16 L. MEITES, in L. MEITES, *Handbook of Analytical Chemistry*, McGraw-Hill, New York, 1963, p. 5-10.
- 17 T. W. STROMATT, R. M. PEEKEMA AND F. A. SCOTT, *U.S. At. Energy Comm. Rept. HW-58212*, 1958.
- 18 P. DELAHAY, *New Instrumental Methods in Electrochemistry*, Interscience, New York, 1954, p. 119.

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## THE SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM WITH ERIOCHROME BRILLIANT VIOLET B

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In spectrophotometric studies of various triphenylmethane dyes as reagents, it has been found that eriochrome brilliant violet R (4''-diethylamino-4'-hydroxy-3,3'-dimethylfuchstone-5,5'-dicarboxylic acid; C.I. 43565) and eriochrome brilliant violet B (2''-chloro-4''-diethylamino-4'-hydroxy-3,3'-dimethylfuchstone-5,5'-dicarboxylic acid; C.I. 43570) react very sensitively toward beryllium. The two dyes show a similar sensitivity to beryllium, but the color system with the former dye is less stable, and the reagent blank value is high, hence the precision is poor and the determination range narrow (see Table III). Consequently, only the spectrophotometric determination of beryllium with eriochrome brilliant violet B is discussed in this paper.

The method is based on the highly sensitive color reaction of eriochrome brilliant violet B with beryllium in an acetate buffer solution. Under the optimal conditions described below, eriochrome brilliant violet B is a more sensitive reagent for beryllium than chromazurol S<sup>1</sup>, eriochrome cyanine R<sup>2</sup>, pontachrome azure blue B<sup>3</sup>, or chromal blue G<sup>4</sup>, which are similar in structure to the proposed reagent, which has also recently been used for spectrophotometric determination of scandium<sup>5</sup>.

### EXPERIMENTAL

#### *Apparatus*

Spectrophotometric measurements were made with a Hitachi Model 139 spectrophotometer in matched 1-cm silica cells, and pH was measured with a Hitachi-Horiba pH meter, Model M-4.

#### *Reagents*

*Standard beryllium solution.* Prepare a stock solution (100  $\mu\text{g}$  Be/ml) by dissolving 196.4 mg of beryllium sulfate tetrahydrate (Mitsuwa Chemicals) in distilled water, adding small amounts of hydrochloric acid to prevent possible hydrolysis and diluting the solution to 100 ml. Prepare working solutions by suitable dilution.

*Eriochrome brilliant violet B solution.* Purify eriochrome brilliant violet B (Geigy Company Inc., New York) by recrystallization from methanol. Prepare a 0.1% (w/v) solution in 95% ethanol. The solution is stable for at least a month.

*Buffer solution (pH 6.2).* Mix suitable amounts of 0.2 M acetic acid and 0.2 M sodium acetate solution.

All other reagents were of analytical grade.



### Standard procedure

Transfer an aliquot of the sample containing 0.5–4  $\mu\text{g}$  of beryllium to a 25-ml volumetric flask, and add 2.0 ml of the 0.1% reagent solution, and then about 10 ml of an acetate–acetic acid buffer solution (pH 6.2). After diluting to the mark with water, mix, leave the color to develop for 20 min, and measure the absorbance of the solution at 560 nm against a reference solution containing the same amount of eriochrome brilliant violet B and buffer.

## RESULTS AND DISCUSSION

### Absorbance spectra

The absorbance curves of eriochrome brilliant violet B have been presented previously<sup>5</sup>; the two absorbance maxima occur at 465 nm and 570 nm below pH 6.5, and the color intensities decrease above pH 6. The spectra of the beryllium–eriochrome brilliant violet B complex at various pH values are shown in Fig. 1. Between pH 5.5 and 9.5, the curves are of identical shape, with one absorption maximum at 560 nm. Above pH 10 and below pH 5, the absorbance maximum shows a bathochromic shift; below pH 5.0, the maximum absorbance is found at about 500 nm.

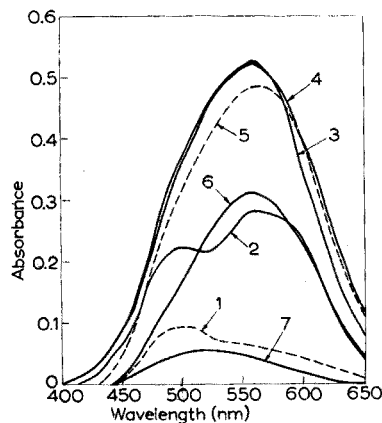


Fig. 1. Absorbance spectra of beryllium complex at various pH values measured against reagent blanks. Be, 0.08 p.p.m.; reagent 80 p.p.m.; pH: (1) 4.0, (2) 5.0, (3) 6.0, (4) 7.0, (5) 8.0, (6) 9.0, (7) 10.0.

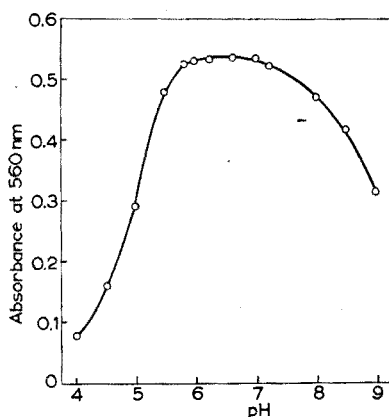


Fig. 2. Effect of pH. Reagent 80 p.p.m., Be 0.08 p.p.m. measured at 560 nm against a reagent blank.

### Effect of pH

The effect of pH on the absorbance of the beryllium–eriochrome brilliant violet B complex was examined as shown in Fig. 2. It can be seen that maximum intensity was obtained in the pH range 5.8–7.0 at 560 nm. An acetate–acetic acid or a borate–boric acid buffer solution, pH 6.2, was found satisfactory in this pH region. The amount of the buffer solution (pH 6.2 and 0.2 *M* in acetate) added had no effect on the absorbance measured by the standard procedure over the range 5–10 ml of the solution.

*Effect of time and temperature*

The color of the beryllium complex developed gradually at room temperature; maximum color development was attained in 20 min after preparation. The absorbance then remained almost constant for at least 2 h. The absorbance for a given amount of beryllium was independent of temperature in the range 10–30°.

*Effect of reagent concentration*

The effect of changes in the concentration of eriochrome brilliant violet B on the absorbance of the complex at pH 6.2 was determined at 560 nm. Figure 3 shows that the absorbance is increased by an increase in the reagent concentration, hence it is necessary to keep the reagent concentration constant. Addition of 2 ml of a 0.1% reagent solution sufficed for less than 0.15 p.p.m. of beryllium. This concentration represents a 10-fold molar excess of reagent over the maximum concentration of beryllium determined under the given conditions.

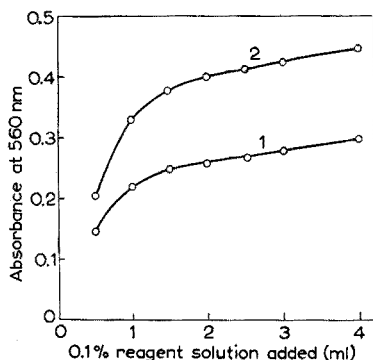


Fig. 3. Effect of reagent concentration. pH 6.2. Reference: reagent blank. Be: (1) 0.04 p.p.m., (2) 0.06 p.p.m.

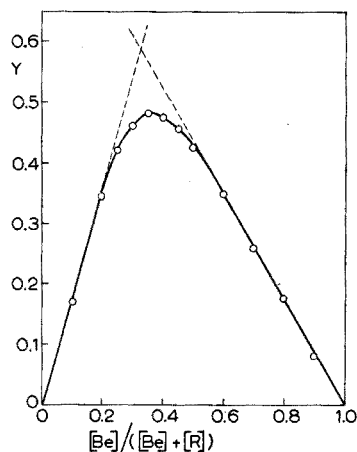


Fig. 4. Continuous variation method.  $[Be] + [R] = 4.44 \cdot 10^{-5} M$ ; pH 6.2.

*Calibration curve, sensitivity and precision*

Calibration curves for the beryllium determination were prepared by the standard procedure. Beer's law was obeyed over the range 0.02–0.15 p.p.m. of beryllium. The molar absorptivity was 59500 at 560 nm, and the sensitivity of the reaction as expressed by Sandell's notation was 0.0002  $\mu\text{g}$  of beryllium per  $\text{cm}^2$ .

A standard solution containing 0.1 p.p.m. of beryllium was analyzed 10 times by the standard procedure. The standard deviation was 0.0015 p.p.m. (relative standard deviation 1.5%), with a relative error of  $\pm 3.0\%$ .

*Effect of diverse ions*

In order to examine the effect of 26 cations and some anions on the beryllium determination, absorbance measurements were made for solutions containing 2.0  $\mu\text{g}$  of beryllium and diverse ions. The results are summarised in Table I, from which it

TABLE I

EFFECT OF DIVERSE IONS ON THE DETERMINATION OF BERYLLIUM

(2.00  $\mu\text{g}$  of beryllium taken)

| <i>Ion</i> | <i>Added</i>      | <i>as</i>                         | <i>Be found</i><br>( $\mu\text{g}$ ) | <i>Ion</i> | <i>Added</i>      | <i>as</i>                                       | <i>Be found</i><br>( $\mu\text{g}$ ) |
|------------|-------------------|-----------------------------------|--------------------------------------|------------|-------------------|---|--------------------------------------|
| Ba(II)     | 100 $\mu\text{g}$ | BaCl <sub>2</sub>                 | 2.0                                  | Y(III)     | 30 $\mu\text{g}$  | YCl <sub>3</sub>                                | 3.1                                  |
| Sr(II)     | 100 $\mu\text{g}$ | SrCl <sub>2</sub>                 | 2.0                                  | Sc(III)    | 2 $\mu\text{g}$   | ScCl <sub>3</sub>                               | 2.9                                  |
| Mg(II)     | 100 $\mu\text{g}$ | MgCl <sub>2</sub>                 | 2.1                                  | La(III)    | 30 $\mu\text{g}$  | LaCl <sub>3</sub>                               | 2.8                                  |
| Ca(II)     | 100 $\mu\text{g}$ | CaCl <sub>2</sub>                 | 2.2                                  | Ce(III)    | 30 $\mu\text{g}$  | CeCl <sub>3</sub>                               | 2.9                                  |
| Mn(II)     | 100 $\mu\text{g}$ | MnSO <sub>4</sub>                 | 2.1                                  | Nd(III)    | 30 $\mu\text{g}$  | NdCl <sub>3</sub>                               | 2.9                                  |
| Cu(II)     | 30 $\mu\text{g}$  | CuSO <sub>4</sub>                 | 4.7                                  | Gd(III)    | 30 $\mu\text{g}$  | GdCl <sub>3</sub>                               | 2.9                                  |
| Zn(II)     | 100 $\mu\text{g}$ | ZnCl <sub>2</sub>                 | 2.0                                  | Dy(III)    | 30 $\mu\text{g}$  | DyCl <sub>3</sub>                               | 2.9                                  |
| Cd(II)     | 100 $\mu\text{g}$ | CdCl <sub>2</sub>                 | 2.4                                  | Er(III)    | 30 $\mu\text{g}$  | ErCl <sub>3</sub>                               | 2.9                                  |
| Ni(II)     | 100 $\mu\text{g}$ | NiSO <sub>4</sub>                 | 2.3                                  | Th(IV)     | 30 $\mu\text{g}$  | Th(NO <sub>3</sub> ) <sub>4</sub>               | 2.8                                  |
| Co(II)     | 100 $\mu\text{g}$ | CoSO <sub>4</sub>                 | 2.2                                  | Mo(VI)     | 100 $\mu\text{g}$ | Na <sub>2</sub> MoO <sub>4</sub>                | 2.1                                  |
| Pb(II)     | 100 $\mu\text{g}$ | Pb(NO <sub>3</sub> ) <sub>2</sub> | 2.2                                  | U(VI)      | 30 $\mu\text{g}$  | UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> | 3.4                                  |
| Hg(II)     | 100 $\mu\text{g}$ | HgCl <sub>2</sub>                 | 2.0                                  | Chloride   | 50 mg             | NaCl  | 2.0                                  |
| Al(III)    | 5 $\mu\text{g}$   | Al(NO <sub>3</sub> ) <sub>3</sub> | 4.4                                  | Acetate    | 50 mg             | CH <sub>3</sub> COONa                           | 1.95                                 |
| Fe(III)    | 5 $\mu\text{g}$   | FeCl <sub>3</sub>                 | 3.0                                  | Nitrate    | 50 mg             | NaNO <sub>3</sub>                               | 2.1                                  |
| Cr(III)    | 100 $\mu\text{g}$ | Cr-alum                           | 3.7                                  | Sulfate    | 50 mg             | Na <sub>2</sub> SO <sub>4</sub>                 | 2.2                                  |

can be concluded that many ions, especially copper(II), aluminum, iron(III), chromium(III), thorium(IV), uranium(VI), yttrium, scandium, and the rare earth elements interfere seriously. These cations also form colored complexes with eriochrome brilliant violet B under the present experimental conditions<sup>5</sup>. Chloride, nitrate, sulfate, and acetate do not interfere even when the concentration is as high as 2000 p.p.m. Fluoride, citrate, and oxalate bleach the color of the complex, even when only a small amount is present. These interfering ions must be eliminated or masked before the determination of beryllium.

#### *Separation of beryllium from interfering ions*

Several methods were tried for elimination of the interfering cations. The acetylacetone-chloroform extraction method<sup>6,7</sup> effected a good separation of beryllium.

*Procedure.* Add 2 ml of 10% EDTA solution and 2.5 g of sodium chloride to the sample solution containing 0.5–4  $\mu\text{g}$  of beryllium, and dilute to about 30 ml with distilled water. Adjust the pH to 7–8 by the addition of diluted sodium hydroxide solution and diluted hydrochloric acid, add 1 ml of aqueous 5% acetylacetone, and readjust the pH to 7–8. Transfer the solution to a separatory funnel, and then extract it for 1 min with a 20-ml portion of chloroform. Withdraw the organic phase into another separatory funnel, and wash it with two 50-ml portions of 0.1 *N* sodium hydroxide solution. Evaporate this organic phase to dryness, and destroy acetylacetonate by adding 2 ml of 60% perchloric acid and heating to dryness. Dissolve the residue in 10 ml of distilled water, and determine beryllium in this solution.

Beryllium was determined in the presence of certain other ions by the method described above. The results are shown in Table II.

#### *Comparison with other methods*

Many organic reagents which are very sensitive to beryllium have been used for the spectrophotometric determination: chromazurol S<sup>1</sup>, eriochrome cyanine R<sup>2</sup>,

aluminon<sup>8</sup>, neothorin<sup>9</sup>, acetylacetone<sup>6</sup>, beryllon-II<sup>10</sup>, beryllon-III<sup>11</sup>, xylenol orange<sup>12</sup>, 8-hydroxyquinoline<sup>13</sup>, pontachrome azure blue B<sup>3</sup>, pontacyl violet 4BSN<sup>14</sup>, sodium *p*-chlorophenolazo-1,8-dihydroxynaphthalene-3,6-disulfonate<sup>15</sup>, naphthochrome green G<sup>16</sup>, and chromal blue G<sup>4</sup>. The new reagent is compared with some other reagents of similar structure in Table III. It can be seen that the proposed method is

TABLE II  
DETERMINATION OF BERYLLIUM

| Solutions analyzed |                         | Found Be <sup>a</sup> | Error |
|--------------------|-------------------------|-----------------------|-------|
| Ion                | Added ( <i>p.p.m.</i> ) | ( <i>p.p.m.</i> )     | (%)   |
| (1) Al(III)        | 3.00                    |                       |       |
| Fe(III)            | 3.00                    |                       |       |
| Sc(III)            | 3.00                    |                       |       |
| Cu(II)             | 3.00                    |                       |       |
| Be(II)             | 0.32                    | 0.32                  | ± 0   |
| (2) Al(III)        | 10.0                    |                       |       |
| Fe(III)            | 10.0                    |                       |       |
| Cr(III)            | 10.0                    |                       |       |
| Sc(III)            | 10.0                    |                       |       |
| Cu(II)             | 10.0                    |                       |       |
| Be(II)             | 0.48                    | 0.52                  | + 8.3 |
| (3) Y(III)         | 2.00                    |                       |       |
| Sc(III)            | 2.00                    |                       |       |
| La(III)            | 2.00                    |                       |       |
| Nd(III)            | 2.00                    |                       |       |
| Dy(III)            | 2.00                    |                       |       |
| Er(III)            | 2.00                    |                       |       |
| Th(IV)             | 2.00                    |                       |       |
| Be(II)             | 0.32                    | 0.33                  | + 3.1 |

<sup>a</sup> These values are the averages of three repeated determinations.

TABLE III  
COMPARISON WITH OTHER SPECTROPHOTOMETRIC METHODS FOR BERYLLIUM

| Method                                | Molar absorptivity<br>( $\cdot 10^4$ ) | Precision <sup>b</sup><br>(%) | Be range<br>( <i>p.p.m.</i> ) |
|---------------------------------------|--|-------------------------------|-------------------------------|
| Aluminon <sup>8</sup>                 | 0.26 <sup>a</sup> (535 nm)             | 12                            | 0.1 -1.0                      |
| Eriochrome cyanine R <sup>2</sup>     | 2 <sup>a</sup> (512 nm)                |                               | 0 -0.2                        |
| Chromazurol S <sup>1</sup>            | 1.55 <sup>a</sup> (575 nm)             | 1.15 <sup>a</sup>             | 0.004-0.2                     |
| Naphthochrome green G <sup>16</sup>   | 3.88 (652 nm)                          | Error $\leq 3$                | 0.01 -0.16                    |
| Xylenol orange <sup>12</sup>          | 1.5 <sup>a</sup> (495 nm)              |                               | 0 -0.24                       |
| Pontachrome azure blue B <sup>3</sup> | 4.5 (570 nm)                           | 1.8                           | 0.05 -0.3                     |
| Chromal blue G <sup>4</sup>           | 3.1 (610 nm)                           | 0.65                          | 0.04 -0.32                    |
| Eriochrome brilliant<br>violet R      | 5.4 (580 nm)                           | 8.9                           | 0.04 -0.08                    |
| Eriochrome brilliant<br>violet B      | 5.95 (560 nm)                          | 1.8                           | 0.02 -0.16                    |

<sup>a</sup> The value calculated from the reference.

<sup>b</sup> Relative standard deviation.

the most sensitive for beryllium. The best reproducibilities are obtained by the chromal blue G method<sup>4</sup> and the worst with the eriochrome brilliant violet R method. However, the reproducibility is adequate for most purposes for all except the eriochrome brilliant violet R method.

#### *Composition of complex*

The method of the continuous variation was employed to establish the beryllium-reagent ratio. Measurements were made at pH 6.2 and 560 nm. The constant overall concentration of beryllium and the reagent was  $4.44 \cdot 10^{-5}M$ . Figure 4 shows that a 1:2 complex is formed between beryllium and the reagent. These results were confirmed by the mole ratio method.

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#### SUMMARY

Beryllium can be determined spectrophotometrically with eriochrome brilliant violet B (C.I. 43570). The complex shows maximum absorbance at pH 5.8–7.0; Beer's law is obeyed over the range 0.02–0.15 p.p.m. of beryllium at 560 nm. The molar absorptivity is 59500 and the sensitivity is 0.0002  $\mu g$  of beryllium per  $cm^2$ , corresponding  $\log I_0/I = 0.001$ . The mole ratio of beryllium and eriochrome brilliant violet B in the complex is estimated to be 1:2. Copper(II), cadmium, nickel, aluminum, iron(III), chromium(III), yttrium, and the rare earth elements interfere seriously; a method of separation is described.

#### RÉSUMÉ

Le béryllium est dosé spectrophotométriquement avec le violet B ériochrome brillant (C.I.43570). Ce complexe présente une absorption maximum entre les pH 5.8 et 7.0. La loi de Beer s'applique de 0.02 à 0.15 p.p.m. de béryllium, à 460 nm. Le coefficient d'extinction molaire est de 59500. Cuivre(II), cadmium, nickel, aluminium, fer(III), chrome(III), yttrium, scandium et terres rares gênent considérablement: une méthode de séparation est proposée.

#### ZUSAMMENFASSUNG

Beryllium kann spektralphotometrisch mit Eriochrombrilliantviolett B bestimmt werden. Der Komplex zeigt eine maximale Absorption beim pH 5.8–7.0. Das Beersche Gesetz wird bei 560 nm im Bereich von 0.02–0.15 p.p.m. Beryllium befolgt. Die molare Extinktion beträgt 59500, die Empfindlichkeit 0.0002  $\mu g$  Be/ $cm^2$ . Das Molverhältnis des Berylliums zum Komplexbildner im Komplex wird mit 1:2 geschätzt. Kupfer(II), Cadmium, Nickel, Aluminium, Eisen(III), Chrom(III), Yttrium, Scandium und die seltenen Erden stören stark. Eine Methode zu ihrer Abtrennung wird beschrieben.

## REFERENCES

- 1 L. SILVERMAN AND M. E. SHIDELER, *Anal. Chem.*, 31 (1959) 152.
- 2 U. T. HILL, *Anal. Chem.*, 30 (1958) 521.
- 3 Y. KATSUBE, K. UESUGI AND J. H. YOE, *Bull. Chem. Soc. Japan*, 34 (1961) 72.
- 4 K. UESUGI, *Bull. Chem. Soc. Japan*, 42 (1969) 2998.
- 5 K. UESUGI, in press.
- 6 T. SHIGEMATSU AND M. TABUSHI, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 80 (1959) 159, 162.
- 7 T. SHIGEMATSU, M. TABUSHI, M. MATSUI, Y. NISHIKAWA AND S. GODA, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 84 (1963) 263.
- 8 G. E. KOSEL AND W. F. NEUMAN, *Anal. Chem.*, 22 (1950) 936.
- 9 S. SHIBATA, F. TAKEUCHI AND T. MATSUMAE, *Bull. Chem. Soc. Japan*, 31 (1958) 888.
- 10 A. M. LUKIN AND G. B. ZAVRIKHINA, *Zh. Analit. Khim.*, 11 (1956) 393.
- 11 P. PAKALNS AND W. W. FLYNN, *Analyst*, 90 (1965) 300.
- 12 M. OTOMO, *Bull. Chem. Soc. Japan*, 38 (1965) 780.
- 13 K. MOTOJIMA, *Bull. Chem. Soc. Japan*, 29 (1956) 75.
- 14 T. SHIGEMATSU, M. TABUSHI AND K. UESUGI, *Japan Analyst*, 12 (1966) 1369.
- 15 K. UESUGI AND Y. KATSUBE, *Bull. Chem. Soc. Japan*, 39 (1966) 194.
- 16 T. FUJINAGA, T. KUWAMOTO, K. KUWABARA AND S. IKEZAWA, *Japan Analyst*, 13 (1964) 1213.

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## ÜBER DIE VERWENDUNG VON OXAZINEN IN DER ANALYTIK

### II. MITTEILUNG. SPEKTRALPHOTOMETRISCHE BESTIMMUNG VON JODID UND BROMID MIT NILBLAU\*

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Die analytische Bestimmung von Jodid bereitet keine Schwierigkeiten, solange die zu erfassenden Mengen nicht zu klein und die verlangte Genauigkeit der Analyse nicht zu hoch sind. Die meist mit Extraktionsverfahren kombinierten photometrischen Methoden beruhen auf der Oxydation von Jodid zu Jod oder Jodat. Die äquivalente Menge Jod kann mit Hilfe von Stärke<sup>1</sup>, und Jodat mittels *p*-Aminophenol<sup>2</sup> als Reagens kolorimetriert werden. Eine Reihe von indirekten Bestimmungsverfahren nützen die katalytische Wirkung der Jodidionen aus. BALLCZO<sup>3</sup> beschreibt eine sehr empfindliche Methode, die auf einer durch Jodid katalysierten Tetrabasenoxydation beruht.

Photometrische Verfahren zur Bestimmung von Bromid basieren auf der Oxydation zu Brom mittels Chloramin T, Kaliumbromat, Kaliumpermanganat oder Chlorwasser. Das freigesetzte Brom reagiert mit Fluorescein<sup>4</sup>, Phenolrot<sup>5,6</sup> oder fuchsinchwefeliger Säure<sup>7</sup> zu Färbungen, die kolorimetriert werden können.

Direkte spektralphotometrische Bestimmungsmethoden für Jodid und Bromid mit ausreichender Empfindlichkeit und Genauigkeit sind bislang nicht bekannt. Die grosse praktische Bedeutung, die die Lösungsmittelextraktion heute in der analytischen Chemie hat, legt die Anwendung des raschen Flüssig-Flüssig-Extraktionsverfahrens für die Abtrennung und anschliessende kolorimetrische Bestimmung des Jodids bzw. Bromids nahe.

In einer früheren Mitteilung<sup>8</sup> berichteten wir darüber, dass verschiedene Anionen im wässrigen Medium mit Nilblau Farbkomplexe bilden, die mit organischen Lösungsmitteln extrahiert werden können. Farbgebende Komponente ist immer der protonisierte Farbstoff, sodass die Absorptionsspektren der einzelnen Farbkomplexe nur unbedeutende Verschiebungen aufweisen. Die Extrahierbarkeit eines Nilblau-X-Komplexes (und somit die Empfindlichkeit der Bestimmung von X) wird von seiner Bildungskonstante abhängen, da nur der Bruchteil des undissoziiert gelösten Farbkomplexes in das organische Lösungsmittel extrahiert werden kann. Die umgekehrten Überlegungen gelten für das anzuwendende Reagens. Da die freie Base des Nilblaus nur wenig wasserlöslich ist, verwendet man als Reagens ein Nilblausalz, das möglichst wenig extrahiert wird. Der Blindwert kann so in vernünftigen Grenzen gehalten werden. Dafür geeignet sind Nilblausulfat (Nilblau A) und Nilblauschlorid. Diese Annahmen wurden durch quantitative Messungen bestätigt, die die Ausarbeitung einer Jodid- und Bromidbestimmung ermöglichten. Um die optimalen Reaktionsbedingungen

\* I. Mitteilung: *Anal. Chim. Acta*, 42 (1968) 253.

TABELLE I

BROMID- UND JODIDBESTIMMUNG MIT NILBLAU IN ABHÄNGIGKEIT VOM VERWENDETEN EXTRAKTIONS-MITTEL

| Extraktionsmittel       | Absorptions-<br>maximum<br>(nm) | Extinktion*    |                   |                  |
|-------------------------|---------------------------------|----------------|-------------------|------------------|
|                         |                                 | Blind-<br>wert | Bromid<br>(50 µg) | Jodid<br>(50 µg) |
| Chloroform              | 626                             | 0.385          | 0.305             | 0.553            |
| Trichloräthylen         | 650                             | 0.105          | 0.156             | 0.241            |
| Tetrachlorkohlenstoff   | 640                             | 0.030          | 0.104             | 0.163            |
| Benzol                  | 615                             | 0.140          | 0.267             | 0.490            |
| Chlorbenzol             | 642                             | 0.180          | 0.298             | 0.536            |
| <i>o</i> -Dichlorbenzol | 650                             | 0.235          | 0.337             | 0.580            |
| <i>n</i> -Butylacetat   | 632                             | 0.430          | 0.148             | 0.230            |

\* Blindwert gemessen gegen Extraktionsmittel; Bromid und Jodid gemessen gegen den jeweiligen Blindwert.

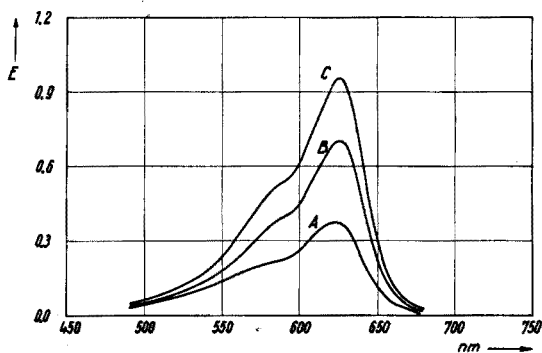


Fig. 1. Absorptionsspektren von Nilblauchlorid (A), Nilblaubromid (B) und Nilblaujodid (C) in Chloroform (gemessen in 1-cm Küvetten gegen Chloroform).

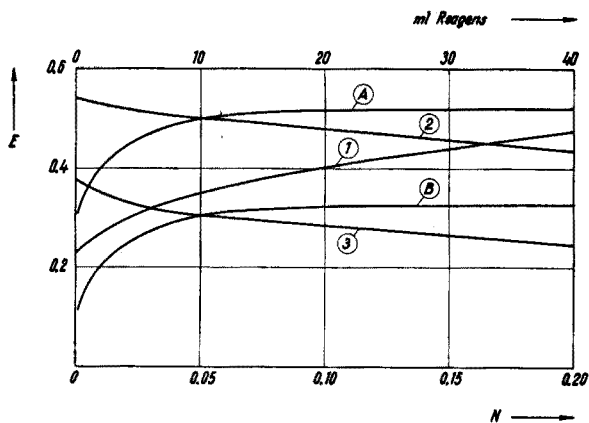


Fig. 2. Abhängigkeit der Bestimmung von der Säurenormalität (1: Blindwert, 2: Jodid, 3: Bromid) und der Reagensmenge (A: Jodid, B: Bromid). Blindwert gemessen gegen Chloroform; Jodid und Bromid gemessen gegen den jeweiligen Blindwert in 1-cm Küvetten bei 626 nm.



festzulegen, wurde der Einfluss des Extraktionsmittels, der Säurenormalität und der Reagenzmenge studiert.

#### EXPERIMENTELLES

##### *Apparate*

Die Absorptionskurven wurden mit einem Perkin-Elmer Spektralphotometer 137 UV aufgenommen. Die Einzelmessungen erfolgten mit einem Zeiss Spektralphotometer PMQ II in 1-cm Glasküvetten.

##### *Reagenzien*

Nilblausulfat (Nile blue A: G. F. Smith Chemical Co., Columbus, Ohio) oder Nilblausulfat (Merck Nr. 1291). Kaliumjodid, Kaliumbromid, Schwefelsäure, diverse organische Lösungsmittel, diverse Salze zur Ermittlung des Fremdioneneinflusses, zur Analyse Merck.

##### *Standardlösungen*

*Reagenslösung.* 0.005%-ig in 0.25 N Schwefelsäure. 50 mg Nilblausulfat oder Nilblausulfat werden in 250 ml 1 N Schwefelsäure gelöst und mit Wasser auf 1 l aufgefüllt.

*Jodidstandardlösung.* 130.8 mg Kaliumjodid werden mit Wasser zu 1 l gelöst. Diese Lösung wird mit Wasser 1:10 verdünnt; sie enthält  $10 \mu\text{g } J^-/\text{ml}$ .

*Bromidstandardlösung.* 148.9 mg Kaliumbromid werden mit Wasser zu 1 l gelöst. Diese Lösung wird mit Wasser 1:10 verdünnt; sie enthält  $10 \mu\text{g } Br^-/\text{ml}$ .

##### *Einfluss der Reaktionsbedingungen*

Die eingangs erwähnten Reaktionsparameter beeinflussen die Bestimmung gegenseitig. Die endgültige Arbeitsvorschrift wurde so erstellt, dass bei möglichst kleinem Blindwert eine grosse Empfindlichkeit der Halogenidbestimmung resultiert.

Das Extraktionsmittel übt den grössten Einfluss auf die Höhe des Blindwertes aus. Ausserdem ergeben sich etwas verschiedene Absorptionsmaxima. Für diese Versuche wurden in einem Schütteltrichter 40 ml neutrale Probelösung ( $50 \mu\text{g } J^-$  oder  $Br^-$  enthaltend) vorgelegt, mit 10.0 ml Reagenslösung versetzt und dann dreimal mit je 5 ml der einzelnen Lösungsmittel extrahiert. Die Extrakte wurden in einem 25-ml Messkolben gesammelt, mit dem Lösungsmittel bis zur Marke aufgefüllt und gegen einen ohne Halogenid hergestellten Blindwert gemessen. Im Vergleich zum reinen Extraktionsmittel ergab sich die Extinktion des Blindwertes. Wie aus Tabelle I hervorgeht, sind *o*-Dichlorbenzol und Chloroform am besten geeignet. Wir entschieden uns für Chloroform, da bei diesem Lösungsmittel die Reproduzierbarkeit der erhaltenen Messwerte am besten und die Phasentrennungsgeschwindigkeit am grössten sind. Figur 1 zeigt die Absorptionsspektren von Nilblausulfat (Blindwert), Nilblaubromid und Nilblaujodid mit Chloroform als Extraktionsmittel.

Da Nilblau als acidobasischer Indikator bekannt ist, konnte ein Einfluss der Säurenormalität auf die Bestimmung angenommen werden. In einem Schütteltrichter wurden 20 ml neutrale Probelösung ( $50 \mu\text{g } J^-$  oder  $Br^-$  enthaltend) vorgelegt, mit 10.0 ml wässriger Reagenslösung ( $50 \text{ mg/l}$ ) versetzt und das Volumen mit verschieden normaler Schwefelsäure auf 50 ml gebracht. Dann wurde dreimal mit je 5 ml Chloro-

form extrahiert, die Extrakte in einem 25-ml Messkolben gesammelt und mit Chloroform bis zur Marke aufgefüllt. Die Extinktion bei 626 nm ergab sich durch Vergleichen mit einem analog hergestellten Blindwert.

Der Einfluss der Reagensmenge auf die Extinktionswerte wurde unter den gleichen Arbeitsbedingungen wie zuvor ermittelt, jedoch wurde die Normalität der wässrigen Phase mit 0.05 eingehalten und nunmehr die zugesetzte Farbstoffmenge variiert. Aus Figur 2 ist ersichtlich, dass mit steigender Acidität die Empfindlichkeit der Jodid- bzw. Bromidbestimmung abnimmt, die Extinktion des Blindwertes jedoch zunimmt. Dies würde ein Arbeiten im neutralen Gebiet für angebracht erscheinen lassen. 0.05 N an Schwefelsäure erwies sich dennoch als am günstigsten, da kleine Aciditätsschwankungen erst bei dieser Normalität nicht stören. Ausserdem geht aus Figur 2 hervor, dass erst bei Anwendung von mehr als 10 ml Reagenslösung optimale Extinktionswerte erhalten werden.

#### Arbeitsvorschrift

In einem 100-ml Schütteltrichter werden 40 ml Probelösung, die zuvor mit Schwefelsäure bzw. Natronlauge auf pH 2–3 gebracht worden ist, mit 10.0 ml Reagenslösung versetzt und dreimal mit je 5 ml Chloroform extrahiert. Die organischen Extrakte sammelt man in einem 25-ml Messkolben und füllt mit Chloroform bis zur Marke auf. Die Extinktion wird in 1-cm Glasküvetten bei 626 nm gegen einen analog hergestellten Blindwert gemessen. Die Bestimmung ist für Gehalte von 10–70  $\mu\text{g}$  Jodid oder 20–150  $\mu\text{g}$  Bromid geeignet. Zur Aufstellung der Eichkurve wird anstelle der Probelösung die entsprechende Standardlösung eingesetzt, wobei man das Volumen vor der Reagenszugabe mit Wasser auf 40 ml ergänzt.

#### Statistische Prüfung der Verfahren

Die Analysenverfahren wurden nach den Vorschlägen von GOTTSCHALK<sup>9</sup> statistisch getestet. Zur Prüfung wurden aus Kaliumjodid und Kaliumbromid hergestellte Standardlösungen benützt. Nach der Arbeitsvorschrift gelangten je 24 Proben fünf verschiedener Konzentrationen (0.5–3.0  $\mu\text{g}$  J<sup>-</sup>/ml; 1–6  $\mu\text{g}$  Br<sup>-</sup>/ml) zur Messung. Die

TABELLE II

STATISTISCHE PRÜFUNG DER BESTIMMUNG VON JODID UND BROMID MIT NILBLAU

| Bezeichnung  | Methode zur Bestimmung von |                   |
|--|----------------------------|-------------------|
|  | Jodid                      | Bromid            |
| Prüfgrösse: $\tau_r$ [ $< t$ (95) = 2.074]   | 0.526                      | 0.476             |
| Verfahrenskonstante: $\omega$ (nmol ml <sup>-1</sup> )                                   | 28.07                      | 81.80             |
| Molarer Extinktionskoeffizient: $\epsilon_{626}$ (l mol <sup>-1</sup> cm <sup>-1</sup> ) | 35630                      | 12220             |
| Standardabweichung: $s_x$ (nmol ml <sup>-1</sup> )                                       | $\pm 0.265$                | $\pm 1.021$       |
| Grenzwerte der Varianzen: $V_o$ (Rel.-%)   | $\pm 1.40$                 | $\pm 1.36$        |
| $V_u$ (Rel.-%)   | $\pm 8.40$                 | $\pm 8.15$        |
| Fehlerbereiche: $T(99)$ (nmol ml <sup>-1</sup> )   | $\pm 0.75$                 | $\pm 2.88$        |
| $T(99.9)$ ( $\mu\text{g}$ ml <sup>-1</sup> )   | $\equiv \pm 0.10$          | $\equiv \pm 0.23$ |
| $T(99.9)$ (nmol ml <sup>-1</sup> )   | $\pm 1.01$                 | $\pm 3.87$        |
| $T(99.9)$ ( $\mu\text{g}$ ml <sup>-1</sup> )   | $\equiv \pm 0.13$          | $\equiv \pm 0.31$ |
| Bestimmungsgrenze: $b_N$ (nmol ml <sup>-1</sup> )  | 1.43                       | 5.48              |
| $b_N$ ( $\mu\text{g}$ ml <sup>-1</sup> )   | $\equiv 0.18$              | $\equiv 0.44$     |
| Empfindlichkeit ( $E = 0.001$ ) ( $\mu\text{g}$ cm ml <sup>-1</sup> )                    | 0.0036                     | 0.0065            |

Korrelationsrechnung ergab, dass das Lambert-Beersche Gesetz in den untersuchten Konzentrationsbereichen streng erfüllt wird. Durch Ausgleichsrechnung ergaben sich weiters die in Tabelle II angeführten Werte. Die Angaben des molaren Extinktionskoeffizienten und der Empfindlichkeit wurden nach SANDELL<sup>10</sup> ermittelt.

### Beeinflussung durch Fremdionen

Jodid und Bromid stören gegenseitig die jeweilige Bestimmung sehr stark. Nun wurde der Einfluss anderer Ionen studiert. Lösungen verschiedener Konzentrationen der einzelnen Ionen wurden sowohl mit als auch ohne Jodid bzw. Bromid (50 µg) nach der angegebenen Arbeitsvorschrift behandelt und gemessen. Dabei wurde ein Fehler bis zur doppelten relativen Standardabweichung toleriert. Der Störeinfluss von Ionenkonzentrationen grösser als 1000 µg wurde nicht untersucht. Die erhaltenen Ergebnisse werden in Tabelle III aufgezeigt. Bei der Bestimmung von Bromid ist die doppelte Menge an Fremdionen erlaubt.

TABELLE III

EINFLUSS VERSCHIEDENER IONEN AUF DIE BESTIMMUNG VON JODID MIT NILBLAU

| Ion  | Zugegeben als  | µg erlaubt | Ion                            | Zugegeben als                                   | µg erlaubt |
|--|--|------------|--------------------------------|---|------------|
| Ag <sup>+</sup>  | Ag <sub>2</sub> SO <sub>4</sub>                              | 0          | Fe <sup>3+</sup>               | Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 1000       |
| Al <sup>3+</sup>   | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>              | 800        | Hg <sup>+</sup>                | Hg <sub>2</sub> SO <sub>4</sub>                 | 0          |
| AsO <sub>4</sub> <sup>3-</sup>                             | Na <sub>3</sub> AsO <sub>4</sub>                             | 1000       | K <sup>+</sup>                 | K <sub>2</sub> SO <sub>4</sub>                  | 1000       |
| Bi <sup>3+</sup>   | (BiO) <sub>2</sub> SO <sub>4</sub>                           | 1000       | Mg <sup>2+</sup>               | MgSO <sub>4</sub>                               | 1000       |
| BO <sub>3</sub> <sup>3-</sup>                              | Na <sub>3</sub> BO <sub>3</sub>                              | 1000       | Mn <sup>2+</sup>               | MnSO <sub>4</sub>                               | 500        |
| Ca <sup>2+</sup>   | Ca(CH <sub>3</sub> COO) <sub>2</sub>                         | 1000       | Na <sup>+</sup>                | Na <sub>2</sub> SO <sub>4</sub>                 | 1000       |
| Cd <sup>2+</sup>   | CdSO <sub>4</sub>  | 1000       | NH <sub>4</sub> <sup>+</sup>   | (NH <sub>4</sub> ) <sub>4</sub> SO <sub>4</sub> | 1000       |
| CH <sub>3</sub> COO <sup>-</sup>                           | NaCH <sub>3</sub> COO  | 1000       | Ni <sup>2+</sup>               | NiSO <sub>4</sub>                               | 500        |
| C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> <sup>2-</sup> | Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> | 150        | NO <sub>3</sub> <sup>-</sup>   | KNO <sub>3</sub>                                | 10         |
| C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>                | K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>                 | 1000       | Pb <sup>2+</sup>               | Pb(CH <sub>3</sub> COO) <sub>2</sub>            | 1000       |
| Cl <sup>-</sup>  | KCl  | 5          | PO <sub>4</sub> <sup>3-</sup>  | Na <sub>2</sub> HPO <sub>4</sub>                | 1000       |
| ClO <sub>4</sub> <sup>-</sup>                              | KClO <sub>4</sub>  | 100        | SiO <sub>3</sub> <sup>2-</sup> | Na <sub>2</sub> SiO <sub>3</sub>                | 1000       |
| CrO <sub>4</sub> <sup>2-</sup>                             | Na <sub>2</sub> CrO <sub>4</sub>                             | 600        | SO <sub>4</sub> <sup>2-</sup>  | K <sub>2</sub> SO <sub>4</sub>                  | 1000       |
| Co <sup>2+</sup>   | CoSO <sub>4</sub>  | 1000       | Tl <sup>+</sup>                | Tl <sub>2</sub> SO <sub>4</sub>                 | 800        |
| Cu <sup>2+</sup>   | CuSO <sub>4</sub>  | 700        | Zn <sup>2+</sup>               | ZnSO <sub>4</sub>                               | 1000       |

### ZUSAMMENFASSUNG

Der Oxazinfarbstoff Nilblau ist zur Bestimmung von Mikromengen Jodid und Bromid geeignet. Die Farbsalze werden in Chloroform extrahiert und spektralphotometrisch bei 626 nm ausgewertet. Das Lambert-Beersche Gesetz ist im Bereich von 0,5 bis 3 p.p.m. Jodid und 1 bis 6 p.p.m. Bromid erfüllt. Der Einfluss von Fremdionen wurde untersucht und die Verfahren statistisch geprüft.

### SUMMARY

The determination of micro amounts of iodide or bromide with the oxazine dye-stuff Nile Blue is described. The salt of the dye is extracted into chloroform and measured spectrophotometrically at 626 nm. Beer's law is obeyed over the range 0.5-3 p.p.m. for iodide and 1-6 p.p.m. for bromide. The methods are evaluated statistically and the effects of diverse ions are described.

## RÉSUMÉ

On décrit une méthode de microdosage des iodures et des bromures à l'aide d'un colorant oxazine Bleu Nil. Le sel du colorant est extrait dans le chloroforme et mesuré spectrophotométriquement à 626 nm. La loi de Beer s'applique de 0.5 à 3 p.p.m. d'iodure et de 1 à 6 p.p.m. de bromure. L'influence de divers ions est examinée.

## LITERATUR

- 1 W. G. GROSS, L. K. WOOD UND J. S. MCHARGUE, *Anal. Chem.*, 20 (1948) 900.
- 2 J. FUCHS, E. JUNGREIS UND L. BEN-DOR, *Anal. Chim. Acta*, 31 (1964) 187.
- 3 H. BALLCZO, *Z. Anal. Chem.*, 245 (1969) 20.
- 4 F. A. POHL, *Z. Anal. Chem.*, 149 (1956) 68.
- 5 V. A. STENGER UND I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 57 (1935) 831.
- 6 M. PERONNET UND S. ROCQUES, *Ann. Fals. Fraudes*, 45 (1952) 347.
- 7 J. FREZOULS, *Ann. Fals. Fraudes*, 27 (1934) 351.
- 8 G. POKORNY UND W. LIKUSSAR, *Anal. Chim. Acta*, 42 (1968) 253.
- 9 G. GOTTSCHALK, *Statistik in der quantitativen chemischen Analyse*, F. Enke Verlag, Stuttgart, 1962.
- 10 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1959.

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## SPECTROPHOTOMETRIC STUDY OF THE REACTION OF NICKEL(II) WITH 4-(2-PYRIDYLAZO)-RESORCINOL IN ALKALINE MEDIA

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At pH 5 nickel(II) forms with 4-(2-pyridylazo)-resorcinol (PAR) a red complex with a metal: ligand molar ratio of 1:2<sup>1-3</sup>. In order to increase the limited solubility of the complex, the reaction must be carried out in presence of an organic solvent.

GEARY *et al.*<sup>4</sup> reported that at pH 8.0 the absorbance spectrum of the nickel(II)-PAR complex shows a peak at 490 nm. This complex was found, by Job's method, to have a metal/ligand ratio of 1:3. The same authors showed that nickel(II) behaves anomalously when the formation curve of the complex with PAR was obtained by potentiometric titration<sup>5</sup>.

SHIJO AND TAKEUCHI<sup>6</sup> have determined nickel(II) spectrophotometrically with PAR at pH 9.3 and 494 nm.

The variation in the absorbance of the nickel(II)-PAR complex with pH has been studied with different buffered solutions<sup>3</sup>, and the extremely high absorbance at pH 8 and 490-495 nm, has been confirmed. The complex formed is soluble in aqueous solutions at pH 6-10 even in presence of excess of PAR; it is orange in colour and so is the deprotonated form of the reagent ( $\lambda_{max}$  485 nm)<sup>4</sup>. It would be expected that the stoichiometry of the complex would be different from that of the complex formed at pH 5; obviously, a very sensitive reaction for nickel(II) should be possible. The description of the properties and the stability of this complex given in the present paper should extend the analytical application of the reaction.

### EXPERIMENTAL

#### *Reagents*

*4-(2-Pyridylazo) resorcinol (Koch-Light)*. A 10<sup>-3</sup> M solution was prepared from the monosodium salt of the reagent. A 10<sup>-4</sup> M solution was obtained and standardized by spectrophotometric titration with 1.011 · 10<sup>-4</sup> M nickel(II) solution at pH 8.0. The PAR concentration found was 1.05 · 10<sup>-4</sup> M. The same results were obtained by titration with cobalt(II), also at pH 8.0.

*Nickel(II) nitrate (Schering-Kahlbaum, p.a.)*. A 10<sup>-2</sup> M solution was standardized by titration with 1.017 · 10<sup>-2</sup> M EDTA, murexide serving as indicator. The working solution prepared by volumetric dilution was 1.011 · 10<sup>-4</sup> M.

*Buffer pH 8*. This was prepared from 0.1 M dipotassium hydrogen phosphate (A.R. Riedel-de Haën) and 0.1 M sodium hydroxide (Schering, p.a.) solutions by mixing and pH meter control. A borate buffer was not used, to avoid complexation with nickel(II)<sup>7</sup>.

A 1 M solution of sodium nitrate was used to maintain the ionic strength constant at 0.1.

### Apparatus

The absorbance curves were recorded on a SF-10 spectrophotometer (USSR). Spectrophotometric titration was carried out in the cell of a SPEKOL spectrocolorimeter (Zeiss). All quantitative measurements were performed on a VSU-1 universal spectrophotometer (Zeiss).

A pH meter (L. Seibold, type GNE) was used with a glass electrode.

### Composition and properties of the complex

The metal/ligand molar ratio<sup>4</sup> of 1 : 3 at pH 8 was confirmed by Job's method of continuous variations, by the molar ratio method, and by the isosbestic point method<sup>8</sup>. Among the absorbance curves of the isomolar series, the curve corresponding to the 1 : 3 composition of the complex passed through the isosbestic point and had the highest absorbance. When the ratio of PAR to nickel(II) exceeded 3, an appreciable absorbance was produced at 420 nm by the free ligand, which at pH 8 is in the form of the mono-ionic species  $HR^-$  ( $H_2R = PAR$ )<sup>4</sup>.

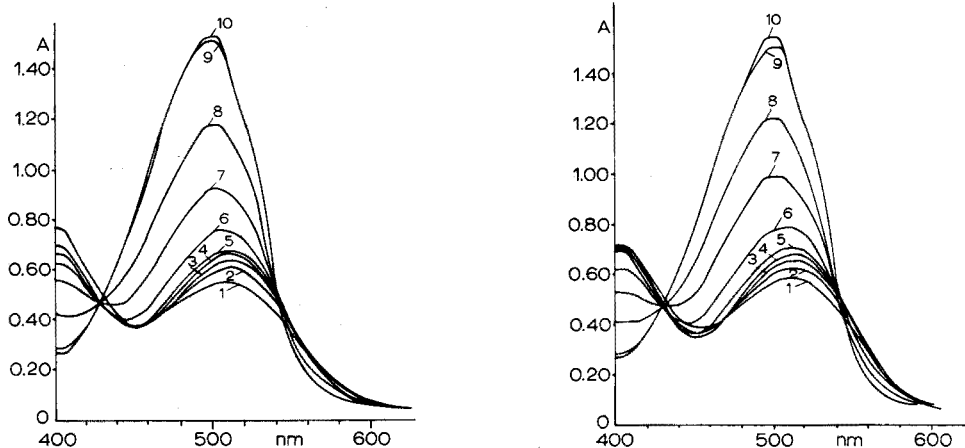


Fig. 1. Dependence of absorbance spectra on pH in water.  $C_{Ni} = 4.04 \cdot 10^{-4} M$ ,  $C_{PAR} = 1.05 \cdot 10^{-5} M$ ; pH: (1) 2.95, (2) 3.35, (3) 3.85, (4) 4.35, (5) 4.80, (6) 5.40, (7) 5.90, (8) 6.40, (9) 7.60, (10) 7.90.

Fig. 2. Dependence of absorbance spectra on pH in 10% ethanol.  $C_{Ni} = 4.04 \cdot 10^{-4} M$ ,  $C_{PAR} = 1.05 \cdot 10^{-5} M$ ; pH: (1) 2.85, (2) 3.25, (3) 3.75, (4) 4.40, (5) 4.80, (6) 5.30, (7) 5.90, (8) 6.30, (9) 7.45, (10) 7.90.

The high absorbance of the complex at pH 8 in the presence of an excess of PAR was first observed in 40% ethanolic solution, to prevent precipitation of the complex<sup>8</sup>. However, the 1 : 3 complex should be water-soluble owing to its negative charge, hence absorbance spectra in aqueous solution at pH 8 were recorded. To establish the influence of the solvent, the same spectral measurements were also made in 10% dioxane solution. The effect of these three solvents on the absorbance is illustrated in Figs. 1-3; the spectra show that in alkaline medium, in presence of dioxane, the absorbance decreases to a large extent whereas the presence of 10% ethanol enhances the absorbance

slightly. The spectra also show a shoulder at 530 nm, probably caused by a 1:2 complex.

The molar absorptivity of the reaction was determined in presence of an approximately 10-fold excess of PAR. The least squares procedure was applied to the straight line  $\Delta A = \epsilon c l$ ,  $\Delta A$  being the absorbance of the complex. Thirteen points were used and a value of  $\epsilon = 76,400 \pm 300$  was found. The sensitivity was calculated to be  $0.00077 \mu\text{g Ni cm}^{-2}$ . A comparison of sensitivities of various methods<sup>9,10</sup> is given in Table I.

Beer's law was found to be followed in the range  $0.024\text{--}0.82 \mu\text{g Ni ml}^{-1}$ .

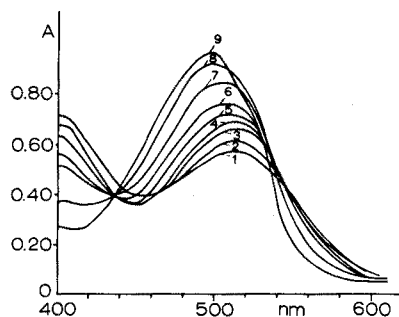


Fig. 3. Dependence of absorbance spectra on pH in 10% dioxane.  $C_{\text{Ni}} = 4.04 \cdot 10^{-4} M$ ,  $C_{\text{PAR}} = 1.05 \cdot 10^{-5} M$ ; pH: (1) 2.90, (2) 3.35, (3) 3.90, (4) 4.65, (5) 5.25, (6) 5.65, (7) 5.85, (8) 6.35, (9) 7.45.

TABLE I

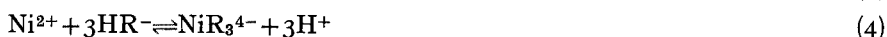
SENSITIVITIES OF SOME METHODS FOR COLORIMETRIC DETERMINATION OF NICKEL(II)

| Method                  | $\mu\text{g Ni cm}^{-2}$<br>( $\log I_0/I = 0.001$ ) | Molar<br>absorptivity |
|-------------------------|--|-----------------------|
| PAN                     | 0.0011   | 61,000                |
| Diethyldithiocarbamate  | 0.0018   | —                     |
| Ni(IV)-dimethylglyoxime | 0.0042   | —                     |
| Ni(II)-dimethylglyoxime | 0.017  | —                     |
| PAR (pH 6)              | —  | 38,700                |
| PAR (pH 8)              | 0.00077  | 76,400                |

#### Establishment of the stability constants

To explain the chelation at pH 8, the number of protons released during complexation was examined for solutions containing excess of nickel(II) as well as solutions with excess of PAR.

Solutions containing excess of nickel ion,  $C_M/C_R = 40$ . At pH 8 a 1:3 complex is evidently formed, hence one of the following equilibria must be valid:



HR<sup>-</sup> is the ligand present in the solution within the pH range studied. To establish which of the above reactions is valid, the dependence  $\log [\text{Ni}(\text{HR})_3]/[\text{HR}] = f(\text{pH})$  was plotted, where  $\text{Ni}(\text{HR})_3$  is the general formula of the complex. The concentration of  $\text{Ni}(\text{HR})_3$  was determined by calculating the ratio  $A/\epsilon c l$  (where  $\epsilon c$  denotes the molar absorptivity of the complex). The concentration of the ligand was calculated from the equation  $[\text{HR}] = C_R - 3(A/\epsilon c l)$ . The plot was a straight line with a slope about 2, *i.e.* reaction (3) is valid. Accordingly the equation:

$$\log \frac{[\text{Ni}(\text{HR})_3]}{[\text{HR}]^3} = \log K_{\text{eq}} + \log [\text{Ni}^{2+}] + 2\text{pH} \quad (5)$$

can be evaluated. When regression analysis was applied to the straight line shown in Fig. 4 (eight points), the intercept  $\log K_{\text{eq}} + \log [\text{Ni}^{2+}]$  was calculated to be  $-2.90$  and the slope 2.30. From the intercept, the equilibrium constant  $K_{\text{eq}}$  was found as 0.49. The stability constant  $\beta_3 = [\text{Ni}(\text{HR})_3]/[\text{Ni}] [\text{HR}]^3$  may be obtained by dividing  $K_{\text{eq}}$  by  $K_3^2$ , the latter being the dissociation constant of the *o*-hydroxy group of PAR. The value  $\text{p}K_3 = 12.31$  was used and a  $\log \beta_3$  value of 25.1 was obtained.

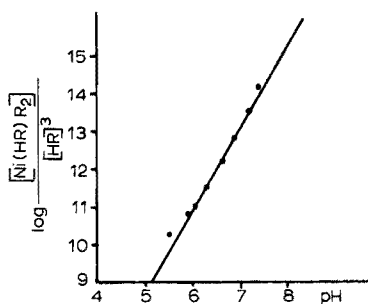


Fig. 4. Logarithmic plot according to eqn. (5).  $C_{\text{Ni}}/C_{\text{PAR}} = 40$ .

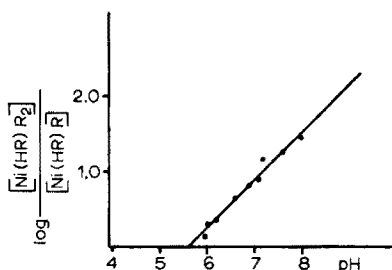


Fig. 5. Logarithmic plot according to eqn. (7).  $C_{\text{PAR}}/C_{\text{Ni}} = 25$ .

The assumption that reaction (3) is valid, is in good agreement with the supposition of GEARY *et al.*<sup>4</sup> that the high mole ratio determined spectrophotometrically originates from coordination through the nitrogen of the heterocyclic ring, without the corresponding release of hydrogen ions, *i.e.* the two protons would be expected to split off by coordination through the hydroxyl groups (each to one molecule of the monodissociated reagent).

*Solutions containing excess of PAR,  $C_R/C_M = 25$ .* When an excess of ligand is present at pH 5, the 1:2 complex is precipitated. This turbidity disappears (the solubility increases) when the pH of the solution is increased. It can be assumed that the following reaction takes place:

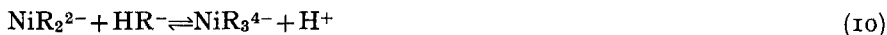
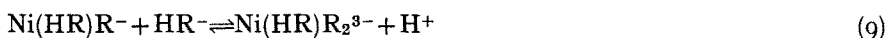


To prove whether or not hydrogen ions are released during complexation the logarithmic dependence was plotted according to the following equation:

$$\log \frac{\Delta A}{\epsilon c C_M - \Delta A} = \log K_{\text{eq}} + \log [\text{HR}^-] + n \text{pH} \quad (7)$$



The concentration of the reagent bound in the complex is negligible, hence  $[\text{HR}^-] \sim C_R$ . Slopes approaching unity ( $n=0.7-1$ ) were always found, therefore the results confirm the release of one proton. Accordingly, one of the following equilibria should be valid:



It is difficult to establish which reaction actually takes place. On the basis of the results for the composition of the complex obtained with excess of metal and the constant values of the molar absorptivities in the two cases, the loss of one proton is presumably due to reaction (9), *i.e.*:

$$\log \frac{\Delta A}{\varepsilon_c C_M - \Delta A} = \log \frac{[\text{Ni}(\text{HR})\text{R}_2]}{[\text{Ni}(\text{HR})\text{R}]}$$

Regression analysis of the straight line in Fig. 5 plotted according to eqn. (7) (nine points) gave the intercept  $-3.94$  and a slope  $0.69$ . The equilibrium constant  $K_{\text{eq}}$  of this reaction was calculated to be  $0.06$ , and the formation constant  $\log k_3 = 12.4^a$ . This value agrees well with the corresponding  $\log k_1 = 13.2$  and  $\log k_2 = 12.8$  given by CORSINI *et al.*<sup>2</sup>.

For the calculation of the stability constants in the present paper, the value  $\text{p}K_2^*$  was taken as equal to  $\text{p}K_3^{2,11,12}$ .

#### SUMMARY

Nickel(II) forms an orange complex with 4-(2-pyridylazo)-resorcinol in aqueous solutions at pH 8. Maximum absorbance is obtained at 495 nm and the metal/ligand ratio is 1:3. The molar absorptivity is  $76,400 \pm 300$  and the spectrophotometric sensitivity is  $0.00077 \mu\text{g Ni cm}^{-2}$  for  $A=0.001$ . Beer's law is followed in the range  $0.024-0.82 \mu\text{g Ni ml}^{-1}$ . Equilibrium constants have been calculated.

#### RÉSUMÉ

Le nickel forme un complexe orange avec le 4-(2-pyridylazo)-résorcinol en solution aqueuse au pH 8, avec absorption maximum à 495 nm. Le rapport métal: ligand est 1:3. Le coefficient d'extinction molaire est de  $76,400 \pm 300$  et la sensibilité spectrophotométrique de  $0.00077 \mu\text{g Ni/cm}^2$  pour  $A=0.001$ . La loi de Beer s'applique de  $0.024$  à  $0.82 \mu\text{g Ni/ml}$ . On a calculé les constantes d'équilibre.

#### ZUSAMMENFASSUNG

Nickel(II) bildet mit 4-(2-Pyridylazo)-resorcinol in wässrigen Lösungen beim pH 8 einen orangenen Komplex. Eine maximale Absorption wurde bei 495 nm erhalten.

$$^a k_3 = \frac{[\text{Ni}(\text{HR})\text{R}_2]}{[\text{Ni}(\text{HR})\text{R}][\text{R}]}$$

Das Metall:Ligand-Verhältnis ist 1:3. Die molare Extinktion beträgt 76,400 und die Empfindlichkeit  $0.00077 \mu\text{g Ni cm}^{-2}$ . Das Beersche Gesetz wird im Bereich von 0.024 bis  $0.82 \mu\text{g Ni ml}^{-1}$  befolgt. Die Gleichgewichtskonstanten wurden berechnet.

## REFERENCES

- 1 T. IWAMOTO, *Bull. Chem. Soc. Japan*, 34 (1961) 605.
- 2 A. CORSINI, I. M. YIH, Q. FERNANDO AND H. FREISER, *Anal. Chem.*, 34 (1962) 1090.
- 3 D. NONOVA AND Z. BOJKOVA, *Annuaire Univ. Sofia "Cl. Ochridski"*, 61 (1966-7) 403.
- 4 W. J. GEARY, G. NICKLESS AND F. H. POLLARD, *Anal. Chim. Acta*, 26 (1962) 575.
- 5 W. J. GEARY, G. NICKLESS AND F. H. POLLARD, *Anal. Chim. Acta*, 27 (1962) 71.
- 6 Y. SHIJO AND T. TAKEUCHI, *Japan Analyst*, 14 (1965) 511; *Anal. Abstr.*, (1967) 1422.
- 7 L. G. SILLÉN AND A. E. MARTELL, *Stability Constants of Metal-ion Complexes*, The Chemical Society, London, 1964.
- 8 E. ASMUS, A. BULL AND F. WALLSDORF, *Z. Anal. Chem.*, 193 (1963) 81.
- 9 R. PÜSCHEL, *Z. Anal. Chem.*, 221 (1966) 132.
- 10 G. H. MORRISON (Editor), *Trace Analysis, Physical Methods*, Interscience, New York-London-Sydney, 1965.
- 11 L. SOMMER AND V. M. IVANOV, *Talanta*, 14 (1967) 171.
- 12 M. HNILIČKOVÁ AND L. SOMMER, *Talanta*, 16 (1969) 83.

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## DETERMINATION OF NIOBIUM IN ROCKS BY AN ISOTOPE DILUTION-SPECTROPHOTOMETRIC METHOD\*

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Most spectrophotometric methods for the determination of niobium are based on the color formed with thiocyanate<sup>1-3</sup> or with various azo-dyes<sup>4-6</sup>. Two of the thiocyanate procedures have been applied to rock analysis<sup>7,8</sup>. GRIMALDI's method<sup>8</sup> has been used for several years with good results. However, GRIMALDI noted interference from zirconium, noble metals, and several other elements. These interferences are unimportant in the analysis of most rocks and minerals, but have hindered determination of niobium in zircons and meteorites, an important aspect of present studies of meteorites and other extra-terrestrial materials. To obviate this problem, a procedure has been devised which separates niobium from all other elements, does not require quantitative recovery of niobium, and allows analyses of eight samples per man-day.

### EXPERIMENTAL

#### *Reagents*

*Buffer solution.* Dissolve 80 g of ammonium acetate and 6.0 ml of glacial acetic acid in water and dilute to 1000 ml. Adjust the pH to 6.0-6.2 with acetic acid or ammonium acetate after dilution.

*Standard niobium solution.* Fuse 0.2 g of niobium pentoxide with 3 g of potassium bisulfate. Dissolve the melt by heating with 30 ml of concentrated sulfuric acid and dilute with water to 200 ml in a volumetric flask. This solution contains 1 mg Nb<sub>2</sub>O<sub>5</sub> per ml. Prepare dilute standards by dilution with 7 M sulfuric acid.

*Tracer solution.* Carrier-free <sup>95</sup>Nb tracer is commercially available, but can be prepared by irradiating 3 g of zirconium dioxide for 14 h in a nuclear reactor with a thermal neutron flux of 5 · 10<sup>12</sup> n cm<sup>-2</sup> sec<sup>-1</sup>. After decay for 2-3 days, the zirconium is fused with sodium peroxide, and niobium impurity is separated as in the procedure described below. The aqueous phase from the MIBK extraction is retained, and the <sup>95</sup>Nb (formed by β-decay of 65-day <sup>95</sup>Zr) is periodically milked by extraction into MIBK. The <sup>95</sup>Nb is back-extracted into 1 M hydrofluoric acid-0.25 M hydrochloric acid and diluted to give a counting rate of 50-100 counts sec<sup>-1</sup> ml<sup>-1</sup>.

#### *Anion-exchange columns*

The Teflon columns used (4 in long, 0.25 in i.d., with a 2 × 1 in reservoir) have been described previously<sup>9</sup>. The tip of the column is plugged with a moistened wad of

\* Publication authorized by the Director, U.S. Geological Survey.

filter paper pulp and the column is loaded with a slurry of Dowex 1-X8 (100–200 mesh) resin in 1 *M* hydrofluoric acid–0.25 *M* hydrochloric acid. The flow rate is about 0.3 ml/min. The resin is discarded after each use.

#### *Counting apparatus*

A 4 × 4 in NaI(Tl) detector coupled to a single-channel analyzer is used for counting <sup>95</sup>Nb. The window of the analyzer is adjusted to encompass only the 776-keV photopeak, thus maximizing the ratio of sample to background counts.

#### *Procedure*

Add about 1 g of sodium hydroxide and 1.0 ml of tracer solution to a zirconium crucible and evaporate to dryness at 120°. Prepare a counting standard at the same time by diluting 1.0 ml of tracer solution to 50 ml in a volumetric flask. Weigh sufficient sample to contain 1–10 μg of niobium (usually 0.5 g) into the crucible, followed by 50 mg of 200-mesh metallic iron, and 5 g of sodium peroxide and fuse to a red heat over a Bunsen burner. A clear melt should be obtained. When the melt has cooled, transfer the crucible to a beaker and decompose the fusion cake by the careful addition of water. Chemical losses from this point on may be ignored. Transfer the crucible contents to the beaker with water, heat for 10–15 min on a hot plate to decompose hydrogen peroxide, and then separate the precipitate by centrifuging and discarding the supernate.

Dissolve the precipitate in 15 ml of 6 *M* sulfuric acid–2 *M* hydrofluoric acid mixture (a clear solution is seldom obtained; ignore the cloudy precipitate containing zirconium and silicon). Extract for 5 min with 15–20 ml of methyl isobutyl ketone (MIBK). Discard the aqueous phase, extract the organic phase with 10 ml of the 6 *M* sulfuric acid–2 *M* hydrofluoric acid solution for 1 min, and again discard the aqueous phase. Extract the organic phase for 5 min with 10 ml of 1 *M* hydrofluoric acid–0.25 *M* hydrochloric acid solution; discard the organic phase.

Transfer this aqueous phase to the top of the ion-exchange column. When this has drained, add 10 ml of 5 *M* hydrofluoric acid–2.5 *M* hydrochloric acid solution to the column. After draining, elute niobium from the column with 10 ml of 2.6 *M* ammonium chloride–1 *M* hydrofluoric acid solution.

Collect this final eluate in a beaker and add 1.0 ml of aqueous 25% (w/v) tartaric acid, 5.0 ml of 0.02 *M* EDTA (disodium salt), and 10 ml of aqueous saturated boric acid solution. Prepare a reference solution by making the same additions to 10 ml of 2.6 *M* ammonium chloride–1 *M* hydrofluoric acid solution. Adjust the pH to 6.0–6.4 (pH meter) by dropwise addition of 6 *M* sodium hydroxide and 6 *M* hydrochloric acid. Add 5.0 ml of buffer solution, and 5.0 ml of an aqueous solution of 4-(2-pyridylazo)-resorcinol (0.295 g of the disodium salt per l), and dilute to volume in a 50-ml volumetric flask.

Let the color develop for 1 h, and then determine the absorbance in 5-cm cells at 550 nm against the reference solution. Determine the niobium content of the solution by comparison with the standard curve.

While the color is developing, count the samples and counting standard with the NaI(Tl) detector, correcting the observed rates for the background. With the tracer solution used here, counting intervals of 100 sec were required to maintain the statistical counting error at < 2%.

*Preparation of standard curve*

Pipette aliquots of the niobium standard solutions into beakers to cover the 1–10  $\mu\text{g}$  range. Add 10 ml of 2.6 *M* ammonium chloride–1 *M* hydrofluoric acid solution, and then follow the same procedure as for the reference solution. The standard curve should be checked when new reagents are made.

*Calculation of results*

The niobium content, in p.p.m., is calculated as follows:

$$X = \frac{mR_s}{MR_x}$$

where *m* is the mass of niobium determined spectrophotometrically ( $\mu\text{g}$ ), *M* is the mass of sample taken for analysis (g), and  $R_s/R_x$  is the ratio of the counting rate of the standard to that of the sample.

## RESULTS AND DISCUSSION

The procedure described above relies on three separations to isolate niobium completely from all other elements. The alkaline leach removes most of the silica and amphoteric elements; the MIBK extraction<sup>10</sup> separates niobium (and tantalum) almost completely from other elements; the ion-exchange separation (based on data of NELSON *et al.*<sup>11</sup>) completes the purification of niobium by separating it from tantalum (retained by the column). The final spectrophotometric determination of niobium with 4-(2-pyridylazo)-resorcinol is essentially that of BELCHER *et al.*<sup>6</sup>, who have shown that the color is unaffected by traces of most elements that might survive the preliminary separations.

The efficacy of this procedure for separating niobium from tantalum was thoroughly tested, because tantalum is the element most likely to interfere with color development<sup>6</sup> and the least completely separated<sup>10</sup>. Table I shows the effect of

TABLE I

MAXIMUM EFFECT OF ADDED TANTALUM ON DETERMINATION OF NIOBIUM IN U.S. GEOLOGICAL SURVEY STANDARD ROCK G-2

| <i>Ta added (mg)</i>                               | <i>p.p.m. Nb</i>  |
|--|-------------------|
| None   | 13.3 <sup>a</sup> |
| 2 (metal foil)                                     | 14.6              |
| 4.7 (Ta <sub>2</sub> O <sub>5</sub> ) <sup>b</sup> | 16.3              |
| 4.9 (Ta <sub>2</sub> O <sub>5</sub> )              | 17.8              |

<sup>a</sup> Average from Table III.

<sup>b</sup> Ta<sub>2</sub>O<sub>5</sub> was obtained from two suppliers. The error corresponds to 200–300 p.p.m. Nb impurity in added material or, if Nb-free, a maximum error of 0.25  $\mu\text{g}$  Nb per mg Ta.

adding milligram amounts of tantalum to a rock before fusion. The difference in the niobium content of the rock before and after additions corresponds either to an impurity of 200–300 p.p.m. niobium in the added tantalum compound or, if this is niobium-free, to a maximum error of 0.25  $\mu\text{g}$  of niobium per mg of tantalum. Even this maximum effect is completely negligible for all geological (and most other)

materials. The effect of tantalum was studied further with radioactive tantalum tracer to determine the fraction of tantalum appearing in the final niobium solution. Before the fusion, 36  $\mu\text{g}$  of tantalum spiked with  $^{182}\text{Ta}$  tracer, was added to 0.5 g of rock (G-2). Niobium was separated as described above, and counting of the final niobium-bearing solution showed less than 0.02% of the original tantalum.

The separations do not yield a quantitative recovery of niobium; a chemical yield of 50–60% from rocks and 80–90% from pure standards is usual. Table II shows the results of monitoring the amount of niobium lost in each separation step

TABLE II

LOSSES IN CHEMICAL SEPARATION OF NIOBIUM FROM ROCK SAMPLES

| Step  | Percentage of original Nb lost* |
|---|---------------------------------|
| NaOH  | 0.50                            |
| MIBK extraction   | 35.5                            |
| MIBK wash   | 0.60                            |
| MIBK back-extraction  | 7.6                             |
| Ion exchange: 1 M HF–0.25 M HCl   | 0.10                            |
| Ion exchange: 5 M HF–2.5 M HCl  | 0.07                            |
| Ion exchange: left on column after 2.6 M $\text{NH}_4\text{Cl}$ –1 M HF | 6.9                             |
| Total lost  | 51.3                            |

\* Average of 8 samples.

when the procedure is used on rocks. The major loss of niobium occurs during the MIBK extraction; this loss must be due to retention of niobium by the cloudy precipitate in the aqueous phase, since only 5–10% of the niobium in pure standards is lost at this point. The loss during back-extraction of niobium from MIBK could be

TABLE III

DETERMINATION OF Nb IN U.S. GEOLOGICAL SURVEY STANDARD ROCKS

| Sample<br>U.S.G.S. std.<br>rock | This work          |         | E. Y. Campbell<br>(mean values) <sup>a</sup> | Other<br>methods <sup>b</sup> |
|---------------------------------|--------------------|---------|--|-------------------------------|
|                                 | Individual         | Average |  |                               |
| G-1                             | 24.3, 22.3<br>24.5 | 23.7    | 23.3   | 20                            |
| W-1                             | 9.3, 10.7<br>8.5   | 9.5     | 9.0  | 10                            |
| G-2                             | 13.7, 13.0<br>13.2 | 13.3    | 12.6   | 8–20                          |
| GSP-1                           | 29.6, 29.3<br>29.2 | 29.4    | 27.5   | 24–36                         |
| AGV-1                           | 15.5, 14.5         | 15.0    | 16.0   | 16–30                         |
| BCR-1                           | 14.4, 13.3<br>12.9 | 13.5    | 23.6   | 10–43                         |
| PCC-1                           | < 2                | < 2     | 1.1  | —                             |
| DTS-1                           | < 3                | < 3     | —  | —                             |

<sup>a</sup> Spectrophotometric results by GRIMALDI's<sup>8</sup> method. G-1 and W-1 values are unpublished data; other values cited by FLANAGAN<sup>12</sup>.

<sup>b</sup> G-1 and W-1 are "recommended" values given by FLEISCHER<sup>13</sup>. Other figures are range of values cited by FLANAGAN<sup>12</sup>.

decreased by substituting water for 1 *M* hydrofluoric acid–0.25 *M* hydrochloric acid solution, but the acids would then have to be added before the ion-exchange separation. The niobium retained by the column after the final elution could be regained by continued elution but has been sacrificed here to ensure a more complete separation from tantalum. Finally, the amount of niobium lost during the sodium peroxide leach is negligible because of the addition of metallic iron to the fusion mixture; without this addition, as much as 50% may be lost during the leach.

The accuracy of this procedure was evaluated by determining niobium in the eight standard rocks prepared by the U. S. Geological Survey<sup>12,13</sup>. As Table III shows, the values obtained agree well with spectrophotometric results obtained by GRIMALDI'S<sup>8</sup> method and with the "recommended" values for G-1 and W-1. This comparison confirms the accuracy of this method; the replicate values in Table III indicate the analytical precision to be expected.

We are grateful to F. S. GRIMALDI and I. MAY for a critical reading of the manuscript and many helpful comments. D. ADER-BARLAS, Israeli Mining Industry, Institute for Research, Israel, very kindly performed the tantalum tracer experiment.

#### SUMMARY

Rocks and minerals are fused with sodium peroxide in the presence of carrier-free <sup>95</sup>Nb. The fusion cake is leached with water and the precipitate dissolved in hydrofluoric–sulfuric acid mixture. Niobium is extracted into methyl isobutyl ketone and further purified by ion exchange. The amount of niobium is determined spectrophotometrically with 4-(2-pyridylazo)-resorcinol, and the chemical yield of the separations determined by counting <sup>95</sup>Nb. This procedure is faster and less sensitive to interferences than previously proposed methods for determining niobium in rocks. The high purity of the separated niobium makes the method applicable to nearly all matrices.

#### RÉSUMÉ

Des roches et des minerais sont fondus avec du peroxyde de sodium, en présence de <sup>95</sup>Nb exempt d'entraîneur. Le résidu de fusion est traité avec de l'eau; le précipité est dissous dans un mélange acide fluorhydrique–acide sulfurique. Le niobium est extrait dans la méthylisobutylcétone et purifié ensuite par échangeur d'ions. Le niobium est alors dosé spectrophotométriquement par le 4-(2-pyridylazo)-résorcinol. Le rendement chimique des séparations est déterminé par comptage de <sup>95</sup>Nb. Ce procédé est plus rapide et moins sensible aux interférences que les méthodes précédemment proposées pour le dosage du niobium dans les roches. La grande pureté du niobium séparé permet d'appliquer cette méthode à presque toutes les matrices.

#### ZUSAMMENFASSUNG

Gesteine und Mineralien werden in Gegenwart von trägerfreiem <sup>95</sup>Nb mit Natriumperoxid geschmolzen. Die Schmelze wird mit Wasser ausgelaugt und der Niederschlag in einer Mischung aus Flusssäure und Schwefelsäure gelöst. Niob wird dann mit

Methylisobutylketon extrahiert und weiter mit einem Ionenaustauscher gereinigt. Der Niobgehalt wird spektralphotometrisch mit 4-(2-Pyridylazo)-resorcinol bestimmt und die chemische Ausbeute durch Zählen des  $^{95}\text{Nb}$  ermittelt. Dieses Verfahren ist schneller und weniger empfindlich gegenüber Störungen als die früher vorgeschlagenen Methoden zur Bestimmung von Niob in Gesteinen. Die hohe Reinheit des abgetrennten Niobs macht diese Methode für nahezu alle Materialien anwendbar.

## REFERENCES

- 1 C. E. CROUTHAMEL, B. E. HJELTE AND C. E. JOHNSON, *Anal. Chem.*, 27 (1955) 507.
- 2 A. B. H. LAUW-ZECHA, S. S. LORD AND D. N. HUME, *Anal. Chem.*, 24 (1952) 1169.
- 3 R. VILLAREAL AND S. A. BARKER, *Anal. Chem.*, 41 (1969) 611.
- 4 I. P. ALIMARIN AND S. B. SAVVIN, *Talanta*, 13 (1966) 689.
- 5 V. PATROVSKY, *Talanta*, 12 (1965) 971.
- 6 R. BELCHER, T. V. RAMAKRISHNA AND T. S. WEST, *Talanta*, 10 (1963) 1013.
- 7 F. N. WARD AND A. P. MARRANZINO, *Anal. Chem.*, 27 (1955) 1325.
- 8 F. S. GRIMALDI, *Anal. Chem.*, 32 (1960) 119.
- 9 L. P. GREENLAND, *Anal. Chim. Acta*, 42 (1969) 365.
- 10 G. W. C. MILNER, G. A. BARNETT AND A. A. SMALES, *Analyst*, 80 (1955) 380.
- 11 F. NELSON, R. M. RUSH AND K. A. KRAUS, *J. Am. Chem. Soc.*, 82 (1960) 339.
- 12 F. J. FLANAGAN, *Geochim. Cosmochim. Acta*, 33 (1969) 81.
- 13 M. FLEISCHER, *Geochim. Cosmochim. Acta*, 33 (1969) 65.

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## ACIDITE DE CATIONS METALLIQUES EN SOLUTION DANS L'ACIDE ACETIQUE ANHYDRE

### VARIATION DU POUVOIR REDUCTEUR DE METAUX ET D'AMALGAMES EN FONCTION DU $pH$

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Il est bien connu que le pouvoir réducteur des métaux—soit purs, soit à l'état d'alliages liquides avec le mercure ("amalgames")—dépend de la forme sous laquelle existent, dans la solution au contact, leurs produits d'oxydation. En solution aqueuse, le  $pH$  est un facteur primordial dont l'élévation entraîne une augmentation du pouvoir réducteur, résultant du caractère "acide" des cations métalliques hydratés. Un comportement semblable a lieu également dans les solvants autres que l'eau, mais avec des propriétés particulières de chaque métal ou amalgame différentes de celles observées en solution aqueuse, en raison de: (a) un état de solvatation différent des cations métalliques; (b) une acidité différente de ces cations solvatés.

L'utilisation d'un solvant comme l'acide acétique apporte ainsi ces deux types de modification. Notamment, l'acidité des cations métalliques solvatés par la molécule d'acide acétique  $AcOH$  correspond ici, non plus à la formation d'espèces hydroxydes (complexes ou insolubles) comme en solution aqueuse, mais à celle des acétates, l'ion acétate  $AcO^-$  étant la base forte de ce solvant. Une modification supplémentaire qui apparaît et qui a été maintes fois soulignée est celle provenant du phénomène de formation d'associations ioniques (paires d'ions) résultant de la faible constante diélectrique du milieu.

De telles modifications du pouvoir réducteur des métaux et des amalgames par suite du changement de solvant sont exploitables pratiquement, notamment pour la réduction quantitative des produits organiques solubles dans l'acide acétique; ces applications peuvent faire l'objet de prévisions systématiques si l'on possède les données nécessaires: valeurs des potentiels d'équilibre des couples métal-cation métallique solvaté et des constantes de formation des complexes acétate de ce dernier (ou des constantes d'acidité, ou des produits de solubilité). Dans le travail que nous présentons ici, nous nous sommes proposé d'effectuer cette détermination pour quelques éléments présentant un intérêt pratique: l'argent, le mercure et ceux dont on réalise fréquemment des amalgames, bismuth, cadmium, cuivre, plomb, étain, thallium, zinc; nous avons aussi cherché à y inclure l'indium. Les amalgames des métaux alcalins et alcalino-terreux, trop réducteurs, réduisent spontanément l'acide acétique.

Un certain nombre de renseignements sur le problème qui nous intéressait

nous ont été fournis par les résultats d'études précédemment publiées. En particulier, des potentiels de demi-vague de réduction polarographique de cations métalliques dissous dans l'acide acétique figurent dans les mémoires de BACHMAN ET ASTLE<sup>1</sup>, de CIHALIK ET SIMEK<sup>2</sup>, de ULERY<sup>3</sup>, de COULTER ET IWAMOTO<sup>4,5</sup>; la dissociation ionique d'acétates métalliques dissous dans l'acide acétique a fait l'objet d'études conductimétriques<sup>6,7</sup>; des équilibres acides-bases avec la participation d'acétates métalliques divers ont été étudiés par titrages potentiométriques<sup>8-12</sup> et par mesures spectrophotométriques<sup>13</sup>. Beaucoup plus exploitables dans le sens que nous voulions prendre étaient les études, effectuées par polarographie cathodique ou anodique en explorant la majeure partie du domaine d'acidité accessible dans l'acide acétique, pour l'acidité de l'ion mercure(I)<sup>14</sup>, pour celle de l'ion cadmium(II)<sup>4,15</sup>, pour l'ion plomb(II)<sup>16</sup> et pour les ions cadmium(II) et plomb(II)<sup>17</sup>. Néanmoins, la confrontation des résultats de ces différents auteurs nous a révélé des divergences et il nous a paru nécessaire de reprendre l'étude pour ces éléments.

Cette étude ne prétend pas être exhaustive, ne serait-ce qu'en raison du choix unique de l'anion perchlorate et du cation lithium comme ions d'association "inertes" pour la formation obligatoire des paires d'ions dans l'acide acétique. Les propriétés d'oxydo-réduction et d'acidité observées sont certainement légèrement tributaires de ce choix.

#### ÉTUDE EXPÉRIMENTALE

Les mesures effectuées sont principalement des mesures du potentiel d'équilibre d'électrodes de métal au contact de solutions de l'ion métallique correspondant, l'acidité étant fixée par de l'acide perchlorique ou de l'acétate de lithium, en présence de perchlorate de lithium 0.5 M. Quelques déterminations supplémentaires ont été effectuées par chronopotentiométrie et par polarographie anodique avec une électrode à gouttes d'amalgames (Bi et Pb), pour confirmer les résultats obtenus potentiométriquement.

#### *Technique expérimentale*

Nous avons utilisé comme solvant de l'acide acétique purifié selon la technique déjà décrite<sup>14</sup> et contenant moins de 9 mg d'eau par litre (dosée selon la méthode de K. FISCHER par titrage coulométrique). Les solutions d'acide perchlorique, de perchlorate de lithium et d'acétate de lithium dans l'acide acétique anhydre ont été préparées également selon le mode opératoire habituel.

Les ions métalliques ont été introduits dans ces solutions par oxydation coulométrique (à intensité constante) d'une électrode du métal correspondant. Par la même occasion, les rapports entre la quantité d'électricité consommée et la perte de masse de l'électrode ont fourni les valeurs du degré d'oxydation de l'ion métallique produit.

Les électrodes métalliques utilisées pour les mesures potentiométriques d'équilibre étaient soigneusement repolies avant d'être plongées dans la solution étudiée; la reproductibilité des résultats s'est ainsi révélée satisfaisante. Pour la polarographie anodique, nous avons réalisé des électrodes à gouttes d'amalgames, en préparant ces derniers par dissolution de métal "ultra-pur" dans du mercure, jusqu'à saturation de la phase liquide. Le titre de l'amalgame a été déterminé par titrage sélectif après redissolution du métal en solution aqueuse par l'acide nitrique. L'amal-

game placé dans le réservoir de l'électrode à gouttes a été protégé de l'oxydation atmosphérique en le recouvrant d'une couche de tétrachlorure de carbone et d'une atmosphère d'azote.

L'électrode de référence utilisée était constituée par le système mercure-acétate de mercure(I) saturé-acétate de lithium saturé dans l'acide acétique + perchlorate de lithium 0.5 *M*. Elle diffère de celle décrite par DURAND ET TRÉMILLON<sup>14</sup> par l'emploi de sels de lithium à la place de sels de sodium. La jonction entre le compartiment de l'électrode de référence et la cellule de mesure se terminait par un capillaire, incliné à 45°, dont l'extrémité était placée très voisine de l'électrode indicatrice.

Les mesures potentiométriques ont été effectuées au moyen d'un millivoltmètre Tacussel S6 ER 2, la détermination chronopotentiométrique au moyen de l'appareil Beckman Electroscan 30 et la polarographie anodique au moyen d'un ensemble Tacussel PRG pour polarographie avec trois électrodes.

Les mesures ont été effectuées à 20°.

### Résultats expérimentaux

Toutes les concentrations sont exprimées en molarité (mole l<sup>-1</sup>).

#### Bismuth

L'oxydation du bismuth conduit au bismuth(III) en solution; c'est le seul degré d'oxydation existant dans l'acide acétique car le bismuth(III) est inoxydable et n'est réductible qu'avec dépôt du métal.

Avec une électrode de bismuth poli, le système Bi/Bi(III) obéit à la loi de Nernst, en milieu acide perchlorique comme en milieu acétate de lithium. Nous l'avons vérifié d'après l'influence sur le potentiel d'équilibre des variations de concentration du bismuth(III) et de celles de la concentration de perchlorate de lithium, prouvant dans ce dernier cas que l'on est en droit d'admettre que le perchlorate de bismuth n'est pratiquement pas dissocié en ions libres en présence de perchlorate de lithium. En effet, dans cette hypothèse et en milieu suffisamment acide pour que

TABLEAU I

COUPLE Bi/Bi(III): VÉRIFICATION DE L'EXPRESSION (2) DU POTENTIEL D'ÉQUILIBRE

| (a) acidité et [ClO <sub>4</sub> <sup>-</sup> ] fixées (HClO <sub>4</sub> 0.138 <i>M</i> et LiClO <sub>4</sub> 0.5 <i>M</i> ), en fonction de la concentration de Bi(III): |                      | (b) acidité et [Bi(III)] fixées (HClO <sub>4</sub> 0.25 <i>M</i> et Bi(III) 0.5 <i>M</i> ) en fonction de la concentration de ClO <sub>4</sub> <sup>-</sup> libre: |                      |
|--|----------------------|--|----------------------|
| $-\log [Bi(III)]$  | $E_{eq}$ mesuré (mV) | $-\log [ClO_4^-]$  | $E_{eq}$ mesuré (mV) |
| 2.30   | - 85.5               | 2.33   | - 127                |
| 2.40   | - 87.5               | 2.36   | - 125                |
| 2.70   | - 94.5               | 2.39   | - 125                |
| 3.00   | - 100.5              | 2.43   | - 122                |
| 3.24   | - 105                | 2.46   | - 119                |
| 3.40   | - 108.5              | 2.49   | - 116                |
| 3.70   | - 114                | 2.51   | - 115                |
| 4.00   | - 119.5              |  |                      |
| 4.30   | - 122                |  |                      |

TABLEAU II

POTENTIELS D'ÉQUILIBRE MESURÉS AVEC UNE ÉLECTRODE DE MÉTAL EN PRÉSENCE D'ION MÉTALLIQUE  $2.5 \cdot 10^{-4} M$ , DE PERCHLORATE DE LITHIUM  $0.5 M$  ET D'ACIDE PERCHLORIQUE À CONCENTRATION VARIABLE

| $10^3[HClO_4]$<br>(mole l <sup>-1</sup> ) | $E_{eq}(mV)$     | $10^3[HClO_4]$<br>(mole l <sup>-1</sup> ) | $E_{eq}(mV)$ |
|---|------------------|---|--------------|
| <i>Couple Bi Bi(III)</i>                  |                  |   |              |
| 0   | -219.5           | 25.1                                      | -115         |
| 0.10                                      | -211             | 34.3                                      | -112         |
| 0.195                                     | -200             | 40.8                                      | -115         |
| 0.31                                      | -189             | 50  | -113         |
| 0.575                                     | -180             | 75  | -112         |
| 0.767                                     | -173             | 100                                       | -114         |
| 1.53                                      | -161             | 150                                       | -114         |
| 1.95                                      | -156             | 200                                       | -113.5       |
| 3.9                                       | -143             | 252                                       | -115; -112   |
| <i>Couple Pb Pb(II)</i>                   |                  |   |              |
| 0   | -674; -674; -673 | 0.468                                     | -674.5       |
| 0.191                                     | -674.5           | 0.915                                     | -672.5       |
| <i>Couple Sn Sn(II)</i>                   |                  |   |              |
| 0   | -635.5           | 200                                       | -564         |
| 0.112                                     | -626             | 251                                       | -564         |
| 0.162                                     | -623.5           | 299                                       | -558; -559   |
| 0.209                                     | -619             | 376                                       | -558; -559   |
| 0.31                                      | -615             | 500                                       | -558; -558   |
| 130                                       | -561.5; -564     | 832                                       | -559         |
| 166                                       | -562; -564       |   |              |
| <i>Couple Cd Cd(II)</i>                   |                  |   |              |
| 0   | -793; -793       | 0.191                                     | -793; -793.5 |
| 0.095                                     | -794; -793       | 0.254                                     | -793.5       |
| 0.126                                     | -794             |   |              |
| <i>Couple Cu Cu(I)</i>                    |                  |   |              |
| 0   | -72              | 3.32                                      | -69          |
| 0.532                                     | -67              | 10  | -70          |
| 0.968                                     | -68; -72         | 83.2                                      | -66          |
| 1.37                                      | -72              | 500                                       | -77          |
| <i>Couple Hg Hg(I)</i>                    |                  |   |              |
| 0   | 215              | 500                                       | 274          |
| 129                                       | 272              | 677                                       | 273          |
| 200                                       | 273              | 912                                       | 273          |
| 324                                       | 273              |   |              |
| <i>Couple Ag Ag(I)</i>                    |                  |   |              |
| 0   | 144.5; 146.5     | 24  | 146          |
| 0.966                                     | 146.5            | 65.3                                      | 144.5        |
| 10  | 146.5            |   |              |
| <i>Couple Tl Tl(I)</i>                    |                  |   |              |
| 0   | -1028            | 10  | -1028        |

le bismuth(III) ne forme aucun complexe acétate, le système oxydo-réducteur est le suivant:



Et le potentiel d'équilibre a pour expression théorique:

$$E_{eq} = E^0_{Bi} + 0.019 \log[Bi(III)] - 0.058 \log[ClO_4^-] \quad (2)$$

Les symboles [ ] représentent les concentrations, peu différentes des activités dans l'acide acétique<sup>18</sup>;  $E^0_{Bi}$  est le potentiel normal apparent du couple Bi/Bi(III). La concentration de l'anion perchlorate libre peut être calculée, connaissant les concentrations totales de  $LiClO_4$  et de  $HClO_4$  et les constantes de dissociation ionique de ces deux paires d'ions (respectivement  $10^{-5.31}$ , d'après réf. 17, et  $10^{-4.87}$ , d'après réf. 8). Les valeurs expérimentales sont reportées dans le Tableau I. La formule (2) se trouve vérifiée de façon satisfaisante; la méthode des moindres carrés donne les pentes respectives  $18.9 \pm 1.5$  mV pour la variation de  $E_{eq}$  en fonction de  $\log[Bi(III)]$  et  $68 \pm 15$  mV pour celle en fonction de  $-\log[ClO_4^-]$ .

A concentration de bismuth(III) fixée ( $2.5 \cdot 10^{-4}$  M), nous avons alors déterminé les variations du potentiel d'équilibre d'une électrode de bismuth en fonction de l'acidité. Les valeurs sont reportées dans les Tableaux II et III.

Nous avons également effectué, en milieu acétate de lithium et dans les mêmes conditions que précédemment, des mesures du potentiel d'équilibre d'une électrode d'amalgame de bismuth saturé. Nous avons trouvé des valeurs en concordance avec celles du Tableau III.

Enfin, la polarographie anodique avec une électrode à gouttes de cet amalgame, en milieu  $LiClO_4$  0.5 M +  $HClO_4$  ou  $LiOAc$  a fourni les courbes voltampérométriques de la Fig. 1.

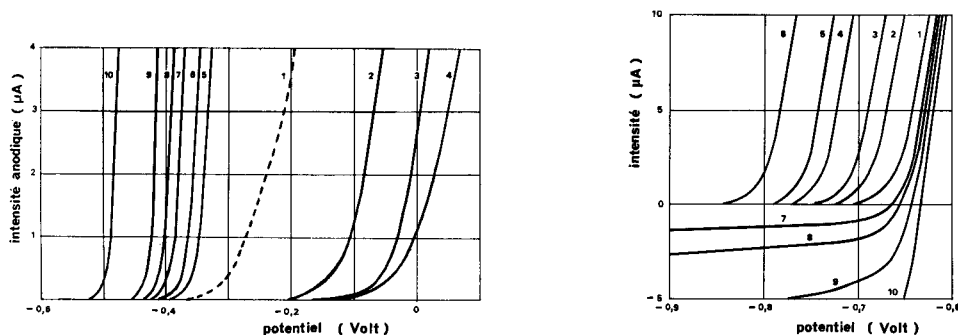


Fig. 1. Courbes polarographiques anodiques à une électrode à gouttes d'amalgame de bismuth saturé, dans l'acide acétique anhydre +  $LiClO_4$  0.5 M (1), +  $HClO_4$   $10^{-3}$  M (2),  $2.8 \cdot 10^{-3}$  M (3),  $\cong 5 \cdot 10^{-3}$  M (4), ou +  $LiOAc$   $5 \cdot 10^{-3}$  M (5),  $10^{-2}$  M (6),  $2 \cdot 10^{-2}$  M (7),  $4 \cdot 10^{-2}$  M (8),  $8 \cdot 10^{-2}$  M (9), 0.5 M (10).

Fig. 2. Courbes polarographiques anodiques à une électrode à gouttes d'amalgame de plomb saturé, dans l'acide acétique anhydre +  $LiClO_4$  0.5 M (1), +  $LiOAc$   $4.75 \cdot 10^{-3}$  M (2),  $9.9 \cdot 10^{-3}$  M (3),  $5.05 \cdot 10^{-2}$  M (4), 0.102 M (5), 0.39 M (6), ou +  $HClO_4$   $4.9 \cdot 10^{-3}$  M (7),  $9.3 \cdot 10^{-3}$  M (8),  $2 \cdot 10^{-2}$  M (9),  $4.4 \cdot 10^{-2}$  M (10).

### Plomb

L'oxydation du plomb conduit au plomb(II). L'existence de plomb(IV) en solution dans l'acide acétique a été reconnue par plusieurs auteurs et une étude électrochimique du système Pb(II)/Pb(IV) a été récemment effectuée<sup>19</sup>. La réversibilité polarographique du couple Pb/Pb(II) a déjà été vérifiée, aussi bien en milieu acide qu'en milieu basique.

Les valeurs de potentiel d'équilibre d'une électrode de plomb poli pour diverses concentrations soit d'acide perchlorique soit d'acétate de lithium sont reportées dans les Tableaux II et III.

TABLEAU III

POTENTIELS D'ÉQUILIBRE MESURÉS AVEC UNE ÉLECTRODE DE MÉTAL EN PRÉSENCE D'ION MÉTALLIQUE  $2.5 \cdot 10^{-4} M$ , DE PERCHLORATE DE LITHIUM  $0.5 M$  ET D'ACÉTATE DE LITHIUM À CONCENTRATION VARIABLE

| $10^3[\text{LiOAc}]$<br>(mole $l^{-1}$ ) | $E_{eq}(mV)$         | $10^3[\text{LiOAc}]$<br>(mole $l^{-1}$ ) | $E_{eq}(mV)$   |
|--|----------------------|--|----------------|
| <i>Couple Bi Bi(III)</i>                 |                      |  |                |
| 0  | -219.5               | 12.5                                     | -339           |
| 0.10                                     | -227                 | 15.1                                     | -344           |
| 0.177                                    | -237.5               | 17.3                                     | -347           |
| 0.38                                     | -251                 | 19.4                                     | -350           |
| 3.63                                     | -308                 | 23.4                                     | -354.5         |
| 4.26                                     | -312.5               | 25.1                                     | -356           |
| 5.01                                     | -316                 | 32.3                                     | -363           |
| 5.62                                     | -319                 | 41.6                                     | -369           |
| 6.16                                     | -322                 | 47.8                                     | -374           |
| 6.91                                     | -324                 | 52.4                                     | -376           |
| 8.51                                     | -328                 | 75.8                                     | -386           |
| 9.77                                     | -332.5               | (100                                     | -450)          |
| 11.2                                     | -336                 |  |                |
| <i>Couple Pb Pb(II)</i>                  |                      |  |                |
| 0  | -673; -674; -674     | 350                                      | -800           |
| 0.158                                    | -674                 | 398                                      | -805.5         |
| 0.501                                    | -675                 | 446                                      | -809           |
| 1.0                                      | -677.5               | 501                                      | -812           |
| 1.99                                     | -682                 | 549                                      | -815           |
| 3.98                                     | -691                 | 602                                      | -818           |
| 7.94                                     | -700                 | 645                                      | -821           |
| 15.8                                     | -709                 | 700                                      | -824           |
| 31.6                                     | -728.5               | 750                                      | -825.5         |
| 50.1                                     | -742                 | 794                                      | -828           |
| 100                                      | -757; -759           | 851                                      | -830.5         |
| 149                                      | -773                 | 901                                      | -833           |
| 199                                      | -782.5               | 955                                      | -835           |
| 251                                      | -789                 | 1000                                     | -836.5         |
| 298                                      | -795                 |  |                |
| <i>Couple Sn Sn(II)</i>                  |                      |  |                |
| 0  | -635.5               | 19.9                                     | -756           |
| 0.12                                     | -644                 | 25.1                                     | -764.5         |
| 0.305                                    | -656                 | 50.1                                     | -786           |
| 0.421                                    | -659.5               | 63.0                                     | -795           |
| 0.668                                    | -661                 | 74.9                                     | -801           |
| 1.27                                     | -680.5               | 100                                      | -812           |
| 1.56                                     | -685.5               | 125                                      | -822           |
| 1.88                                     | -692                 | 151                                      | -827           |
| 2.51                                     | -699.5               | 199                                      | -838.5         |
| 3.80                                     | -711.5               | 251                                      | -846           |
| 5.12                                     | -720                 | 398                                      | -865           |
| 7.49                                     | -728                 | 446                                      | -869           |
| 10.0                                     | -736.5               | 630                                      | -882           |
| 15.1                                     | -750                 | 1000                                     | -900           |
| <i>Couple Cd Cd(II)</i>                  |                      |  |                |
| 0  | -793; -793           | 50.1                                     | -878; -880     |
| 0.075                                    | -794; -794           | 63.1                                     | -885; -885.5   |
| 0.10                                     | -794.5; -795; -795.5 | 100                                      | -902.5; -902.5 |
| 0.148                                    | -794                 | 126                                      | -909; -910     |
| 0.184                                    | -795; -796           | 151                                      | -914; -915.5   |
| 0.305                                    | -796                 | 199                                      | -924; -925     |
| 0.421                                    | -799                 | 251                                      | -933; -934     |

TABLEAU III (suite)

| $10^3[\text{LiOAc}]$<br>(mole l <sup>-1</sup> ) | $E_{eq}(mV)$               | $10^3[\text{LiOAc}]$<br>(mole l <sup>-1</sup> ) | $E_{eq}(mV)$                   |
|---|----------------------------|---|--------------------------------|
| <b>Couple Cd Cd(II)</b>                         |                            |   |                                |
| 0.53  | -800; 801.5                | 301   | -939                           |
| 0.794   | -801; -802                 | 347   | -944.5; -945; -946             |
| 1.27  | -803; -805; 806.5          | 400   | -949; -950                     |
| 1.88  | -809.5; -810.5             | 450   | -954.5                         |
| 2.42  | -813; -813                 | 500   | -958                           |
| 3.8   | -818.5; -819               | 600   | -965.5; -966                   |
| 5.12  | -822; -822.5               | 631   | -966                           |
| 6.23  | -826; -827                 | 800   | -976                           |
| 7.49  | -830; -830                 | 912   | -981.5                         |
| 10.0  | -835.5; -836               | 1060  | -988                           |
| 15.1  | -846; -846.5               | 1230  | -993.5                         |
| 19.9  | -850; -851.5               | 1330  | -996                           |
| 25.1  | -860; -860.5               | 1450  | -998                           |
| 37.1  | -869.5; -870; -871.5       | 1580  | -1005                          |
| <b>Couple Zn Zn(II)</b>                         |                            |   |                                |
| 0   | -1083; -1083.5; -1084      | 5.0   | -1106.5; -1107                 |
| 0.126   | -1084                      | 10  | -1122; -1123                   |
| 0.20  | -1083.5                    | 15  | -1128; -1130                   |
| 0.31  | -1084; -1083.5             | 20  | -1137; -1138                   |
| 0.62  | -1081.5; -1082; -1082.5    | 25  | -1146.5; -1147; -1147.5; -1148 |
| 0.93  | -1084; -1085               | 37.5  | -1155.5                        |
| 1.25  | -1086.5; -1086.5; -1089    | 50  | -1164; -1164; -1164; -1166     |
| 2.5   | -1095; -1095; -1097; -1099 | 62.5  | -1167; -1171.5; -1171.5        |
| 4.0   | -1100; -1102               | 75  | -1174                          |
| <b>Couple Cu Cu(I)</b>                          |                            |   |                                |
| 0   | -72                        | 55.5  | -178.5                         |
| 0.112   | -73                        | 83.1  | -193                           |
| 6.02  | -119                       | 100   | -211                           |
| 7.94  | -124                       | 125   | -238                           |
| 9.77  | -131                       | 166   | -265                           |
| 10.0  | -133                       | 199   | -285                           |
| 12.3  | -136.5                     | 251   | -311                           |
| 16.9  | -145.5                     | 298   | -327                           |
| 19.9  | -150                       | 375   | -350                           |
| 23.9  | -156                       | 412   | -366                           |
| 30.1  | -163                       | 446   | -369                           |
| 38.9  | -168.5                     | 631   | -404                           |
| 45.7  | -175                       | 1000  | -450                           |
| <b>Couple Hg Hg(I)</b>                          |                            |   |                                |
| 0   | 215                        | 28.1  | 101.5                          |
| 0.10  | 206.5                      | 31.6  | 98                             |
| 0.158   | 199.5                      | 47.8  | 87                             |
| 0.223   | 194.5                      | 50.1  | 86                             |
| 0.316   | 188                        | 316   | 32                             |
| 0.501   | 182.5                      | 354   | 28                             |
| 0.794   | 175.5                      | 398   | 22                             |
| 1.25  | 168.5                      | 446   | 19                             |
| 5.01  | 150                        | 501   | 15; 14                         |
| 7.07  | 140                        | 575   | 19                             |
| 8.70  | 134                        | 630   | 6                              |
| 10.0  | 129                        | 691   | 1                              |
| 14.1  | 121                        | 794   | -3                             |
| 16.5  | 116                        | 891   | -7                             |
| 22.3  | 107.5                      | 1000  | -11                            |

TABLEAU III (suite)

| $10^3[\text{LiOAc}]$<br>(mole l <sup>-1</sup> ) | $E_{eq}(mV)$ | $10^3[\text{LiOAc}]$<br>(mole l <sup>-1</sup> ) | $E_{eq}(mV)$ |
|---|--------------|---|--------------|
| <i>Couple Ag Ag(I)</i>                          |              |   |              |
| 0   | 144.5; 146.5 | 30.2  | 136.5        |
| 0.31  | 146.5        | 39  | 134.5        |
| 0.631   | 145.5        | 45.8  | 132          |
| 1.66  | 145          | 55.7  | 129          |
| 2.51  | 142.5        | 65.4  | 126.5        |
| 3.31  | 144.5        | 74.1  | 122.5        |
| 4.95  | 142          | 83.2  | 121          |
| 7.33  | 141.5        | 100   | 116.5        |
| 10.0  | 142.5        | 115   | 111          |
| 12.3  | 140.5        | 130   | 105.5        |
| 17  | 140.5        | 166   | 92.5         |
| 24  | 139.5        |   |              |
| <i>Couple Tl Tl(I)</i>                          |              |   |              |
| 0   | -1028        | 5.0   | -1028.5      |
| 0.31  | -1028        | 10  | -1028.5      |
| 0.616   | -1028        | 20  | -1028.5      |
| 1.26  | -1028        | 500   | -1028.5      |
| 2.52  | -1028.5      | 1000  | -1026        |

La polarographie anodique avec une électrode à gouttes d'amalgame de plomb saturé, en milieu  $\text{LiClO}_4$  0.5 M + LiOAc a fourni les courbes voltampérométriques Fig. 2. En présence d'acide perchlorique, nous avons constaté que l'amalgame est suffisamment réducteur pour réduire  $\text{H}^+$  et l'on obtient des courbes telles que celles représentées sur cette même figure (courbes 7 à 10); le palier de réduction est proportionnel à la concentration de l'acide perchlorique.

#### *Étain, cadmium, zinc*

Pour ces trois éléments, l'oxydation du métal conduit au degré d'oxydation +2 (il existe également étain (IV)). Nous avons vérifié que le potentiel du couple  $\text{Sn}(s)/\text{Sn}(\text{II})$  obéissait à la formule de Nernst. Pour  $\text{Cd}/\text{Cd}(\text{II})$ , cette vérification avait déjà été faite; quant à  $\text{Zn}/\text{Zn}(\text{II})$ , la loi théorique n'est suivie qu'approximativement en milieu basique et elle ne peut être vérifiée en milieu acide car  $\text{H}^+$  oxyde le métal.

Les valeurs de potentiel d'équilibre des électrodes de ces trois métaux pour diverses concentrations d'acétate de lithium ou d'acide perchlorique (sauf pour le zinc) sont reportées dans les Tableaux II et III.

#### *Cuivre*

Pour cet élément, il a déjà été signalé l'existence des degrés d'oxydation +1 et +2 en solution dans l'acide acétique<sup>4,5</sup>. Lors d'expériences répétées, l'oxydation du métal nous a conduit à un mélange de cuivre(I) et de cuivre(II)—où le cuivre(I) est prédominant—, ce qui s'explique par la proximité des valeurs des potentiels normaux des couples  $\text{Cu}/\text{Cu}(\text{I})$  et  $\text{Cu}(\text{I})/\text{Cu}(\text{II})$ : 70 mV d'après COULTER ET IWAMOTO<sup>5</sup>. La coloration du cuivre(I) est violette. Si l'on ne prend pas la précaution de maintenir la solution à l'abri de l'air, elle prend peu à peu la teinte bleue caractéristique de l'ion cuivrique solvaté. On peut réduire à nouveau le cuivre(II) et reproduire la solution



cuvreuse par action du cuivre métallique sous barbotage d'azote. Nous avons effectué ces réactions. COULTER ET IWAMOTO<sup>5</sup> donnent la valeur approximative 0.1 pour la constante de dismutation des ions cuivre(I) en milieu  $\text{LiClO}_4$  1 M. Selon cette valeur, il est possible d'obtenir, en présence de cuivre métallique, une solution cuivreuse  $10^{-3}$  M ne contenant pas plus de 1% d'ions cuivre(II).

Dans ces conditions, nous avons pu étudier le comportement du cuivre(I) en fonction de l'acidité; les valeurs expérimentales de potentiel d'équilibre d'une électrode de cuivre sont reportées dans les Tableaux II et III.

### *Mercure*

Le mercure est oxydé à l'état d'ion mercure(I) dimérisé<sup>14</sup>. Le couple est réversible polarographiquement. Nos valeurs expérimentales de potentiel d'équilibre sont données dans les Tableaux II et III.

### *Argent*

Il est oxydé à l'état d'argent(I). L'acétate d'argent est peu soluble; sa solubilité a été déterminée par BIRDWHISTELL ET GRISWOLD<sup>20</sup>:  $4.7 \cdot 10^{-8}$  mole  $\text{kg}^{-1}$ . Elle est suffisante pour déterminer les valeurs de potentiel d'équilibre d'une électrode d'argent (Tableaux II et III).

### *Thallium*

Le métal est oxydé à l'état d'ions thallium(I)<sup>21</sup>; le couple amalgame de Tl/Tl(I) a été étudié par chronopotentiométrie<sup>22</sup> et a été montré réversible. Le potentiel d'équilibre d'une électrode de thallium ne montre aucune variation significative, des milieux très acides aux milieux très basiques (Tableaux II et III).

### *Indium*

D'après DAVIDSON ET JIRIK<sup>21</sup>, l'oxydation du métal conduit à un mélange d'indium(I) et d'indium(III). Mais nous avons obtenu, dans toutes nos expériences, de l'indium(I) avec un rendement de 99.5 à 100%.

Les valeurs de potentiel adoptées par une électrode d'indium en présence d'une solution d'indium(I) ne suivent pas la formule de Nernst, impliquant que le couple ne se comporte pas réversiblement. Une étude chronopotentiométrique à une électrode à goutte pendante de mercure a confirmé ce fait; l'équation de Karaoglanoff n'est pas suivie par le chronopotentiogramme expérimental. Il n'a ainsi pas été possible de poursuivre l'étude envisagée sur ce système.

## EXPLOITATION DES RÉSULTATS EXPÉRIMENTAUX

Nous admettons *a priori* que les réactions chimiques qui sont responsables des variations de potentiel des électrodes métalliques ou d'amalgames lorsque l'acidité diminue et la basicité augmente, sont les réactions de formation de complexes acétate successifs des ions en solution correspondant aux métaux considérés. Plus exactement, il s'agit de la substitution progressive des ions  $\text{ClO}_4^-$  du perchlorate métallique par des ions acétate  $\text{AcO}^-$ , et de l'addition éventuelle de ces derniers à l'acétate métallique en milieu très fortement basique. Il faut en effet considérer que les formes prédominantes des espèces chimiques en solution dans ce solvant de faible constante

diélectrique sont des ensembles non chargés, complexes moléculaires ou paires d'ions, ou composés mixtes dans le cas des complexes ioniques. Le perchlorate de lithium concentré (0.5 M) ajouté a d'ailleurs pour rôle essentiel de faire rétrograder la dissociation ionique partielle éventuelle des paires d'ions lorsqu'elles sont à faible concentration, de se comporter comme un "tampon" vis-à-vis des ions  $\text{ClO}_4^-$  et  $\text{Li}^+$  libres dont il maintient constantes les faibles concentrations, et ainsi de simplifier les interprétations des résultats expérimentaux puisqu'il n'est plus nécessaire de tenir compte des fractions dissociées des autres perchlorates ou sels de lithium dilués, maintenues négligeables. La validité de cette hypothèse a été vérifiée dans le cas par exemple du perchlorate de bismuth (*cf.* précédemment).

Le taux de formation des complexes acétate est relié à la concentration de l'acétate de lithium en solution. Nous désignerons par  $[\text{LiOAc}]$  cette concentration. La fraction dissociée en ions  $\text{AcO}^-$  libres peut être négligée, selon les considérations précédentes. En effet, en admettant que les ions  $\text{Li}^+$  libres proviennent en majeure partie de la dissociation de  $\text{LiClO}_4$  0.5 M, on a :

$$[\text{Li}^+] = [\text{ClO}_4^-] = ([\text{LiClO}_4] \cdot 10^{-5.3})^\dagger = 10^{-2.8} \quad (3)$$

D'où :

$$\frac{[\text{AcO}^-]}{[\text{LiOAc}]} = \frac{10^{-6.78}}{[\text{Li}^+]} = 10^{-3.98} \quad (4)$$

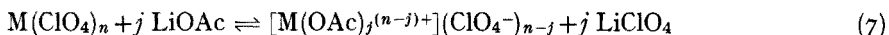
Pour les mesures effectuées en milieu acide perchlorique (considéré également comme une paire d'ions pratiquement pas dissociée, grâce à  $\text{LiClO}_4$  :

$$\left. \frac{[\text{H}^+]}{[\text{HClO}_4]} = \frac{10^{-4.87}}{[\text{ClO}_4^-]} = 10^{-2.07} \right) \quad (5)$$

nous pouvons également faire correspondre à la concentration de  $\text{HClO}_4$  une valeur de  $[\text{LiOAc}]$ , d'après les relations suivantes (valeurs des constantes d'après<sup>7,8,11</sup>) :

$$\begin{aligned} [\text{LiOAc}][\text{HClO}_4] &= 10^{6.78}[\text{Li}^+][\text{AcO}^-] \cdot 10^{4.87}[\text{H}^+][\text{ClO}_4^-] \\ &= 10^{11.65}([\text{H}^+][\text{AcO}^-])([\text{Li}^+][\text{ClO}_4^-]) \\ &= 10^{11.65} \cdot 10^{-14.45} \cdot 10^{-5.31}[\text{LiClO}_4] = 10^{-8.41} \end{aligned} \quad (6)$$

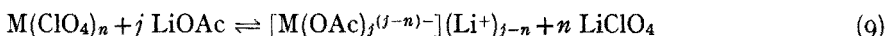
Pour un cation métallique  $\text{M}^{n+}$ , les réactions de formation des complexes acétate en milieu perchlorate vont s'écrire sous la forme générale :



si  $j \leq n$ . Il correspond à cet équilibre la constante de formation cumulative :

$$\beta_j = \frac{[\text{M}(\text{OAc})_j(\text{ClO}_4)_{n-j}][\text{LiClO}_4]^j}{[\text{M}(\text{ClO}_4)_n][\text{LiOAc}]^j} \quad (8)$$

Pour les complexes supérieurs ( $j > n$ ), lorsqu'ils existent, leur formation correspond à l'équilibre :



$$\beta_j = \frac{[\text{M}(\text{OAc})_j \text{Li}_{j-n}][\text{LiClO}_4]^n}{[\text{M}(\text{ClO}_4)_n][\text{LiOAc}]^j} \quad (10)$$

Compte tenu de ce que la concentration de perchlorate de lithium est maintenue constante, nous pouvons définir des constantes apparentes de formation:

$$\beta_j' = \frac{[\text{complexe}]}{[M(\text{ClO}_4)_n][\text{LiOAc}]^j} = \beta_j/[\text{LiClO}_4]^j \text{ ou } n \quad (11)$$

qui sont formellement analogues aux constantes de formation des complexes dans les milieux où les associations ioniques ne se produisent pas (en solution aqueuse notamment).

#### Exploitation des mesures potentiométriques

Le potentiel d'équilibre d'une électrode de métal dans une solution contenant l'ion métallique correspondant à la concentration totale invariable  $c_M$  varie avec l'acidité (c'est-à-dire avec  $[\text{LiOAc}]$ ) lorsqu'une partie au moins de l'ion se trouve à l'état de complexe acétate. Lorsque la forme prédominante est le perchlorate, le potentiel reste invariable, puisqu'il correspond au système:



$$E_{\text{eq}} = E^0_M - 0.058 \log [\text{ClO}_4^-] + \frac{0.058}{n} \log [M(\text{ClO}_4)_n] \quad (13)$$

$$= E^{0'}_M + \frac{0.058}{n} \log [M(\text{ClO}_4)_n] \quad (13')$$

( $E^{0'}$  est une constante puisque  $[\text{ClO}_4^-] = c^{\text{te}}$ , cf. relation (3).) Lorsqu'une partie de l'ion métallique est sous forme de complexe acétate, nous pouvons poser:

$$[M(\text{ClO}_4)_n] = \frac{c_M}{F_0} \quad (14)$$

De sorte que:

$$E_{\text{eq}} = E^{0'}_M + \frac{0.058}{n} \log \frac{c_M}{F_0} \quad (15)$$

et que la variation du potentiel d'équilibre qui en est résultée est:

$$\Delta E_{\text{eq}} = - \frac{0.058}{n} \log F_0 \quad (16)$$

$F_0$  (notation en accord avec la méthode de DEFORD ET HUME) est une fonction dont l'expression est la suivante:

$$F_0 = \sum_{j=0}^{j=m} \beta_j' [\text{LiOAc}]^j \quad (17)$$

( $\beta_0' = 1$ ;  $m$  = nombre maximal d'ions acétate pouvant être liés à l'ion métallique considéré). Une analyse des courbes  $\log F_0 = f(\log [\text{LiOAc}])$ , tirées des valeurs expérimentales de  $\Delta E_{\text{eq}}$  d'après la relation (16), permet donc de déterminer les valeurs des  $\beta_j'$  et par conséquent celles des constantes  $\beta_j$ .

Mais il peut exister des différences non négligeables, dans certains cas, entre les concentrations totales d'acétate de lithium ajouté (ou celles calculées à partir des concentrations de  $\text{HClO}_4$  ajouté), qui sont connues avant expérience, et les concentrations d'acétate libre—désignées par  $[\text{LiOAc}]$ —qui entrent en jeu dans l'expression

(17) de  $F_0$  pour son interprétation correcte. Les corrections à réaliser de ce fait ne peuvent être effectuées que par approximations successives, puisqu'elles nécessitent la connaissance des constantes de formation  $\beta_j'$ .

Pour y arriver commodément, avec le grand nombre de valeurs expérimentales dont nous disposons, nous avons utilisé une méthode de calcul automatique sur programme, au moyen d'une calculatrice EMD-848, qui nous a fourni à la fois les courbes correctes de variation de  $\log F_0$  en fonction de  $\log [\text{LiOAc}]$  (représentées sur les Fig. 3 et 4), les valeurs les plus probables des constantes  $\beta_j'$  rendant compte

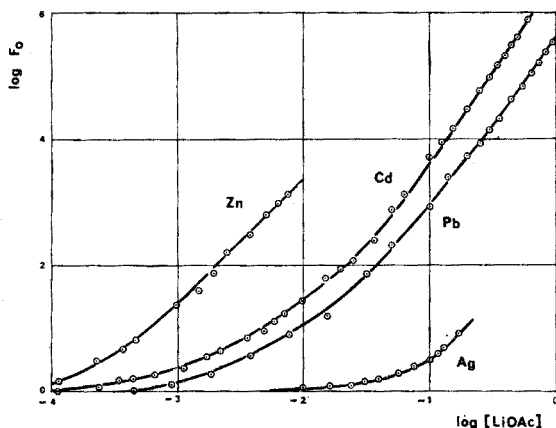


Fig. 3. Courbes de formation des complexes acétate du zinc(II), du cadmium(II), du plomb(II) et de l'argent(I), déduites des valeurs du Tableau III. Tous les points expérimentaux ne sont pas représentés.

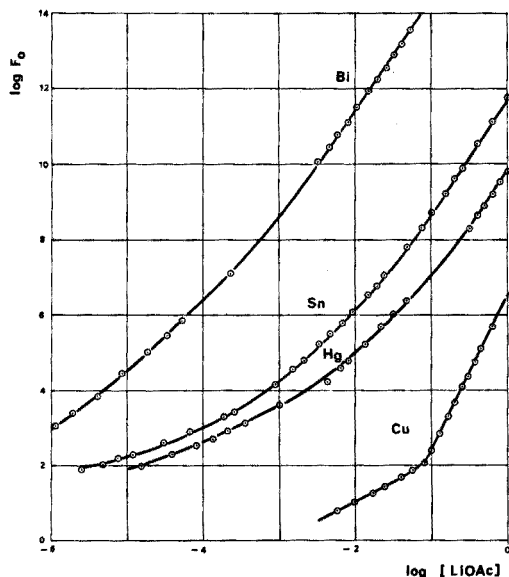


Fig. 4. Courbes de formation des complexes acétate du bismuth(III), de l'étain(II), du cuivre(I) et du mercure(I), déduites des valeurs des Tableaux II et III. Tous les points expérimentaux ne sont pas représentés.

de ces variations expérimentales, et les intervalles de confiance pour les valeurs de constantes obtenues.

Nous avons dû faire appel à deux processus de calcul:

(a) Dans le cas des éléments Ag(I), Cd(II), Pb(II) et Zn(II), les complexes acétate apparaissent dans un domaine de basicité qui n'est pas très étendu; ils se forment d'autre part simultanément car la variation de  $\log F_0$  présente une incurvation continue. Nous avons alors utilisé la méthode de calcul préconisée par INMAN *et al.*<sup>23</sup>. Le principe général en est le suivant. La variation de  $\log F_0$  en fonction de  $\log[\text{LiOAc}]$  correspondant théoriquement à un polynôme dont le degré est  $m$  (expression (17)), elle doit tendre vers une droite de pente  $m$  aux concentrations les plus élevées de LiOAc, lorsque le complexe supérieur (correspondant à cette valeur  $m$ ) devient prédominant. La courbe initiale  $\log F_0 = f(\log [\text{LiOAc} \text{ ajouté}])$  permet généralement de déterminer la valeur de  $m$  à considérer ( $m=3$  pour Cd(II) et Pb(II),  $m=2$  pour Ag(I) et Zn(II)); elle permet d'autre part de déceler l'existence éventuelle de points expérimentaux aberrants que l'on peut rejeter. On calcule alors par la méthode des moindres carrés l'ensemble des valeurs  $\beta_0', \beta_1', \dots, \beta_m'$  qui rendent le mieux compte de l'ensemble des données expérimentales  $F_0$ . Un premier calcul, utilisant les valeurs de concentration de LiOAc ajouté, conduit à une première série de valeurs grossières. Celles-ci permettent de calculer approximativement la fraction d'acétate consommé par la complexation et d'effectuer par suite une première correction des valeurs de  $[\text{LiOAc}]$ . Le calcul de nouvelles valeurs corrigées des  $\beta_j'$  est repris, permettant une nouvelle correction de la concentration  $[\text{LiOAc}]$ , etc. Après un certain nombre de cycles, les corrections à effectuer deviennent inférieures à une limite fixée à l'avance, ce qui permet d'interrompre (automatiquement) le calcul et de rete-

TABLEAU IV

COMPLEXES ACÉTATE DES ÉLÉMENTS Cd(II), Pb(II), Zn(II) ET Ag(I)

(Constantes déduites du calcul automatique sur programme d'après les mesures expérimentales des Tableaux II et III)

|        | Nombre de valeurs<br>expérimentales<br>utilisées | $E^0_M (V)^a$  | $\sigma_{AE}(mV)$ | $\beta_j$<br>( $\beta_3$ , et $\beta_2$ pour Ag, en<br>mole <sup>-1</sup> )   |
|--------|--|----------------|-------------------|---|
| Cd(II) | 80   | -0.690 ± 0.001 | 1                 | ( $\beta_0 = 0.94 \pm 0.04$ )<br>$\beta_1 = 606 \pm 53$<br>$\beta_2 = (339 \pm 37) \cdot 10^2$<br>$\beta_3 = (446 \pm 16) \cdot 10^3$ |
| Pb(II) | 35   | -0.570 ± 0.001 | 1                 | ( $\beta_0 = 0.95 \pm 0.06$ )<br>$\beta_1 = 212 \pm 55$<br>$\beta_2 = (119 \pm 20) \cdot 10^2$<br>$\beta_3 = (455 \pm 33) \cdot 10^2$ |
| Zn(II) | 42   | -0.979 ± 0.001 | 1.8               | ( $\beta_0 = 0.96 \pm 0.11$ )<br>$\beta_1 = 46 \pm 77$<br>$\beta_2 = (580 \pm 47) \cdot 10^2$   |
| Ag(I)  | 28   | +0.355 ± 0.001 | 1.4               | ( $\beta_0 = 1.04 \pm 0.03$ )<br>$\beta_1 = 3.4 \pm 1.6$<br>$\beta_2 = 90 \pm 17$   |

<sup>a</sup> Par rapport à l'électrode de référence Hg/Hg<sub>2</sub>(OAc)<sub>2</sub> saturé/LiOAc saturé + LiClO<sub>4</sub> 0.5 M.

nir les dernières valeurs proposées. En moyenne, dans le cas présent, une dizaine de cycles ont été nécessaires.

Le Tableau IV rassemble les valeurs ainsi déterminées. Les intervalles de confiance correspondent à une probabilité de 95%.  $\sigma_{\Delta E}$  est l'écart-type caractéristique de la précision des mesures de potentiel, calculé en supposant que

$$\sum_1^i \frac{1}{\sigma_{\Delta E}^2} \frac{(\Delta E_{\text{eq}} - \Delta E_{\text{eq}}^*)^2}{i - m} = 1 \quad (18)$$

où  $\Delta E_{\text{eq}}$  représente la mesure et  $\Delta E_{\text{eq}}^*$  la valeur correspondante calculée au moyen des valeurs de  $\beta'$  adoptées;  $i$  est le nombre de mesures utilisées. Cette grandeur est utilisée pour le calcul du coefficient de pondération qu'il faut appliquer aux différentes valeurs expérimentales de  $F_0$  dans la mise en oeuvre de la méthode des moindres carrés, pour tenir compte de ce que  $F_0$  est relié exponentiellement aux valeurs de  $\Delta E_{\text{eq}}$  mesurées avec un écart-type constant (*cf.* 23).

Les valeurs des potentiels formels  $E_M^{0'}$  des couples métal-perchlorate métallique en milieu  $\text{LiClO}_4$  0.5 *M* sont également données, avec leur précision statistique. Les valeurs de  $\beta_j$  qui sont données sont déduites des valeurs  $\beta_j'$ , résultats directs du calcul.

(b) Dans le cas des éléments Bi(III), Sn(II), Cu(I) et Hg(I), le domaine de basicité dans lequel les complexes acétate apparaissent est trop étendu pour que la méthode de calcul général soit commodément applicable. D'autre part, la variation  $\log F_0 = f(\log[\text{LiOAc ajouté}])$  comporte des parties sensiblement linéaires qui indiquent que chacun des complexes devient prédominant dans un domaine de  $[\text{LiOAc}]$  particulier. Il est alors préférable d'effectuer un calcul sur chacune de ces parties, selon le même principe que précédemment—avec correction des valeurs de LiOAc par itération—, conduisant cette fois plus simplement par la méthode des moindres carrés

TABLEAU V

COMPLEXES ACÉTATE DES ÉLÉMENTS Bi(III), Sn(II), Cu(I) ET Hg(I)

|         | Domaines de $-\log[\text{LiOAc}]$ | Nombre de valeurs expérimentales utilisées | $E_M^{0'} (V)$     | $j$             | $\log \beta_j$  |
|---------|-----------------------------------|--|--------------------|-----------------|---|
| Bi(III) | > 6.8                             | 10   | $-0.044 \pm 0.001$ | 0               |   |
|         | 6.8 à 4.8                         | 12   |                    | $1.64 \pm 0.07$ | $(\log \beta_2 = 12.29 \pm 0.38)$                           |
|         | < 4.8                             | 21   |                    | $2.95 \pm 0.04$ | $\log \beta_3 = 16.45 \pm 0.07$                             |
| Sn(II)  | > 6.5                             | 13   | $-0.456 \pm 0.002$ | 0               |   |
|         | 6.5 à 4.3                         | 8  |                    | $0.78 \pm 0.06$ | $(\log \beta_1 = 5.91 \pm 0.31)$                            |
|         | 4.3 à 1.7                         | 12   |                    | $1.94 \pm 0.07$ | $\log \beta_2 = 9.49 \pm 0.18$                              |
|         | < 1.7                             | 12   |                    | $3.00 \pm 0.04$ | $\log \beta_3/\text{mole}^{-1} \text{ l} = 11.11 \pm 0.03$  |
| Cu(I)   | > 3.5                             | 10   | $+0.138 \pm 0.002$ | 0               |   |
|         | 3.5 à 1.2                         | 12   |                    | $1.07 \pm 0.04$ | $\log \beta_1 = 2.91 \pm 0.07$                              |
|         | < 1.2                             | 12   |                    | $4.08 \pm 0.06$ | $\log \beta_4/\text{mole}^{-3} \text{ l}^3 = 6.25 \pm 0.04$ |
| Hg(I)   | > 6.5                             | 6  | $+0.169 \pm 0.001$ | 0               |   |
|         | 6.5 à 3.3                         | 8  |                    | $0.88 \pm 0.06$ | $\log \beta_1 = 5.90 \pm 0.24$                              |
|         | 3.3 à 0.8                         | 11   |                    | $2.07 \pm 0.03$ | $\log \beta_2 = 8.56 \pm 0.06$                              |
|         | < 0.8                             | 12   |                    | $2.98 \pm 0.09$ | $\log \beta_3/\text{mole}^{-1} \text{ l} = 9.21 \pm 0.03$   |
| Tl(I)   | < 6.5                             | 10   | $-0.819 \pm 0.001$ | 0               |   |

appliquée à une droite à la valeur la plus probable de la constante de stabilité du complexe formé dans ce domaine de concentration d'acétate.

Le Tableau V rassemble les valeurs ainsi déterminées. Il y figure également les valeurs les plus probables de  $\beta_1$ , correspondant aux pentes des parties rectilignes après correction de concentration de LiOAc, données par le calcul automatique. Il est à noter que, par suite de la méthode adoptée ici, les intervalles de confiance correspondent aux valeurs de  $\log \beta$  et non aux valeurs de  $\beta$  comme dans le cas de l'autre méthode.

Pour le thallium(I), aucun complexe acétate n'a été mis en évidence. Seule figure donc la valeur du potentiel formel  $E^{0'}_{Tl}$  du couple  $Tl/TlClO_4$ .

#### *Exploitation des courbes polarographiques anodiques*

L'expression théorique des courbes polarographiques réversibles d'oxydation d'un amalgame montre que, lorsque l'acidité varie, ces courbes conservent la même forme et sont seulement déplacées le long de l'échelle de potentiel, à condition que la concentration de LiOAc (ou celle de  $HClO_4$ ) à la surface de l'électrode ne subisse qu'une variation négligeable du fait du courant d'électrolyse. Il faut pour cela que l'intensité reste suffisamment petite et que  $[LiOAc]$  (ou  $[HClO_4]$ ) soit au contraire suffisamment grande. Plusieurs des courbes expérimentales des Figs. 1 et 2 répondent à ces caractéristiques.

Lorsque les courbes polarographiques sont bien "parallèles" entre elles, il suffit de donner une interprétation de leur déplacement le long de l'échelle de potentiel sous l'influence des variations d'acidité, soit pratiquement des variations de la valeur du potentiel d'électrode pour une intensité anodique déterminée. Il y a intérêt à ce que cette dernière soit importante par rapport au courant résiduel, sans être choisie trop grande. Il apparaît alors que cette variation de potentiel est théoriquement similaire à une variation de potentiel d'équilibre et qu'elle est régie par les mêmes lois; elle se trouve donc justiciable des mêmes modes d'exploitation: on tire les valeurs de la fonction  $F_0$  par une formule analogue à la formule (16):

$$\Delta E_{(t=c_1e)} = \frac{0.058}{n} \log F_0 \quad (19)$$

où le premier terme représente la différence de potentiel entre la courbe-limite d'oxydation du métal (amalgamé) à l'état de perchlorate, obtenue en milieu suffisamment acide, et la courbe d'oxydation à l'état de complexe acétate.

Toutefois, il apparaît pratiquement que l'exploitation de ces mesures effectuées sur des courbes polarographiques, sur lesquelles divers phénomènes perturbateurs peuvent intervenir, conduit à des résultats nettement moins précis et moins fiables que ceux tirés des mesures de potentiel d'équilibre. Nous n'en ferons donc pas un état détaillé ici; la Fig. 5 montre seulement la concordance existant entre les deux types de détermination pour le cas du plomb.

#### CONCLUSIONS

1. Une comparaison s'impose immédiatement, entre certaines des constantes exposées ici et celles qui ont été précédemment déterminées selon d'autres méthodes: Pour le cadmium(II), ADLI-BLOCH ET TRÉMILLON<sup>15</sup> ont obtenu par polaro-

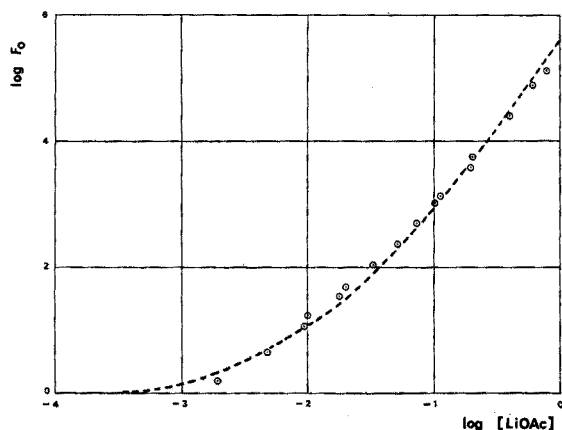


Fig. 5. Comparaison entre les résultats polarographiques ( $\odot$ ) et les résultats potentiométriques (courbe) dans le cas du plomb.

graphie anodique avec une électrode à gouttes d'amalgame de cadmium (en milieu  $\text{NaClO}_4$  0.4 M) et par résolution graphique des résultats:

$$\log \beta_2 = 5.9 \pm 0.1 \quad \log \beta_4 = 7.4 \pm 0.3$$

COULTER<sup>4</sup> a obtenu par polarographie cathodique (en milieu  $\text{LiClO}_4$  0.5 M) et par résolution graphique des résultats:

$$\beta_1' = 1900 \text{ et } 1793 \quad \beta_2' = 39 \cdot 10^4 \text{ et } 34 \cdot 10^4 \quad \beta_3' = 14 \cdot 10^6$$

Pour le plomb(II), BOTTA-CONESA<sup>16</sup> a obtenu par polarographie cathodique (en milieu  $\text{NaClO}_4$  0.5 M) et par résolution graphique:

$$\log \beta_2 = 5.4 \pm 0.1$$

Enfin, pour le mercure(I), DURAND ET TRÉMILLON<sup>14</sup> ont obtenu par polarographie anodique (en milieu  $\text{LiClO}_4$  0.5 M):

$$\log \beta_2 = 8.9 \pm 0.2$$

Pour le cadmium(II) tout particulièrement, la discordance s'avère considérable. Nous pensons que nos résultats présents ont plus de chance d'approcher la réalité, compte tenu de la plus grande fiabilité de la méthode utilisée par rapport aux méthodes polarographiques dans l'acide acétique anhydre et aussi de celle de la méthode d'exploitation des résultats. Des critiques sérieuses ont été formulées à l'encontre des méthodes graphiques<sup>24</sup>, tandis que les avantages des méthodes de calcul statistique programmé au moyen d'un calculateur électronique ont été démontrés et soulignés<sup>23, 25</sup>.

2. Les grandeurs déterminées suffisent pour caractériser, en fonction de l'acidité, le pouvoir réducteur des métaux vis-à-vis des solutions dans l'acide acétique anhydre. Ceci peut être représenté schématiquement au moyen d'un diagramme potentiel-pH, comme ceux utilisés pour les solutions aqueuses.

La grandeur pH a été définie dans l'acide acétique<sup>26</sup> d'une manière analogue au pH en solution aqueuse; mais la formation des paires d'ions dans ce solvant de faible constante diélectrique rend plus délicate son utilisation. Nous avons vu que la formation des complexes acétate était plus directement reliée à la concentration  $[\text{LiOAc}]$ ; nous pouvons cependant établir une relation entre cette dernière et la valeur



de pH. La présence de perchlorate de lithium concentré rend les concentrations  $[\text{LiOAc}]$ ,  $[\text{HClO}_4]$  et celle des ions  $[\text{H}^+]$  libres proportionnelles entre elles (*cf.* relations (3), (4) et (5)). On calcule ainsi:

$$\text{pH} = 2.06 - \log[\text{HClO}_4] = 10.47 + \log[\text{LiOAc}] \quad (20)$$

Cette relation permet de remplacer, en abscisse du diagramme potentiel-acidité des métaux considérés dans le milieu envisagé, le logarithme de la concentration d'acétate par les valeurs de pH. L'échelle de pH est en pratique limitée au domaine 2 à 12 environ.

Le diagramme obtenu avec nos valeurs expérimentales est représenté Fig. 6. Le potentiel d'équilibre du métal varie non seulement avec l'acidité, mais aussi avec la concentration d'ion métallique en solution, et aussi avec celle des ions  $\text{ClO}_4^-$  libres présents (relation (13)); cette concentration peut varier si l'on change la concentration ou la nature du perchlorate utilisé comme électrolyte-support. En ce qui concerne

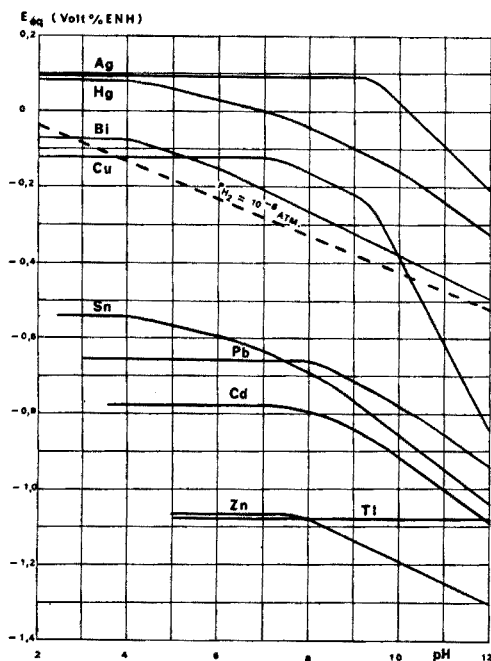


Fig. 6. Diagramme potentiel-pH dans l'acide acétique anhydre: variation en fonction du pH calculé du potentiel d'équilibre du métal en présence de l'ion métallique correspondant à la concentration  $10^{-6} M$ . En trait discontinu, potentiel d'équilibre du couple  $\text{H}^+/\text{H}_2$  pour une pression partielle d'hydrogène égale à  $10^{-6}$  atm.

l'influence de la concentration de l'ion du métal considéré, elle est donnée par la formule (15), et nous n'avons représenté sur la Fig. 6 que les valeurs de  $E_{eq}$  pour une concentration  $c_M = 10^{-6} M$ . Cette valeur est celle adoptée par POURBAIX<sup>27</sup> pour calculer le potentiel de début d'oxydation des métaux, dans le cas de la corrosion par les solutions aqueuses, et nous pensons qu'elle peut aussi servir à caractériser la limite du pouvoir réducteur des métaux (impossibilité de réduire une solution de potentiel inférieur à cette limite).

En ce qui concerne le pouvoir réducteur des amalgames, une correction est à effectuer sur les valeurs de potentiel, pour tenir compte de la diminution d'activité du métal dissous dans le mercure par rapport au métal pur. Si l'on considère les amalgames saturés de métal, la correction est minime, du moins dans le cas des métaux qui nous intéressent. Elle est en principe nulle si l'amalgame saturé est en équilibre avec du métal pur; c'est le cas du zinc. Lorsque l'amalgame liquide saturé est en équilibre avec un alliage solide, il existe une différence de potentiel normal entre les couples  $M(\text{Hg})$  saturé/ $M^{n+}$  et  $M(\text{s})/M^{n+}$ , différence qui s'avère de l'ordre de quelques millivolts seulement pour les métaux considérés ici: Cd, 51 mV; Pb, 6 mV; Tl, 3 mV (valeurs citées par KOLTHOFF ET LINGANE<sup>28</sup>); Cu, 6 mV<sup>29</sup>; en ce qui concerne le bismuth, la valeur n'est pas connue mais elle doit être très petite également, étant donnée la série à laquelle appartient ce métal<sup>30</sup>. On peut donc considérer que le diagramme de la Fig. 6 est approximativement valable aussi bien pour le pouvoir réducteur des métaux purs que pour celui de leurs amalgames saturés.

La variation théorique (représentée en trait discontinu, Fig. 6) du début de réduction des ions  $\text{H}^+$  permet de connaître quels sont les métaux attaqués par les acides—et dans quel domaine de pH—voire par l'acide acétique lui-même. Mais la lenteur de ces réactions, comme en solution aqueuse et surtout dans le cas des amalgames, permet heureusement d'observer des potentiels bien inférieurs à cette limite. Les courbes reportées sont cependant arrêtées dans la zone de pH où le métal commence à être oxydé réellement par les protons.

Il faut remarquer que, contrairement aux solutions aqueuses où les hydroxydes métalliques sont généralement très peu solubles et précipitent à la surface du métal par oxydation de celui-ci, les acétates considérés sont relativement solubles dans l'acide acétique. L'acétate de mercure(I)<sup>14</sup>, l'acétate d'argent<sup>20</sup> sont parmi les moins solubles.

Enfin, il est intéressant de comparer les pouvoirs réducteurs observés dans l'acide acétique avec ceux des mêmes métaux en solution aqueuse. On pourra pour cela se référer aux diagrammes d'équilibres publiés par POURBAIX<sup>27</sup>, ainsi qu'à l'étude expérimentale de l'influence du pH des solutions aqueuses sur le pouvoir réducteur des amalgames effectuée par BRÉANT<sup>31</sup>. Pour établir la corrélation des échelles de potentiel, on peut se servir du couple oxydo-réducteur de référence ferrocène-ferricinium, en admettant pour celui-ci un pouvoir oxydo-réducteur indépendant du solvant<sup>32</sup>; ce couple possède un potentiel normal égal à 0.0 V par rapport à l'électrode normale à hydrogène dans l'acide acétique, d'après les déterminations de DURAND<sup>33</sup>, et égal à 0.40 V par rapport à l'électrode normale à hydrogène en solution aqueuse<sup>34</sup>.

J.C.T. remercie le Commissariat à l'Energie Atomique qui lui a accordé une bourse pour effectuer cette recherche.

#### RÉSUMÉ

Une étude effectuée principalement par mesure de potentiels d'équilibre a permis de déterminer la nature et les constantes de formation des complexes acétate des éléments Bi(III), Cd(II), Pb(II), Zn(II), Sn(II), Ag(I), Cu(I), Hg(I) et Tl(I), en solution dans l'acide acétique anhydre (+  $\text{LiClO}_4$  0.5 M); les complexes de l'indium(I)

n'ont pu être déterminés par suite d'un comportement irréversible de l'électrode de ce métal. Les résultats expérimentaux ont été exploités par une méthode de calcul automatique programmé, avec détermination des intervalles de confiance. Le pouvoir réducteur des métaux et des amalgames correspondants se trouve concrétisé par un diagramme potentiel-pH.

## SUMMARY

A study made principally by measuring equilibrium potentials has enabled determination of the nature and the formation constants of acetate complexes of the elements Bi(III), Cd(II), Pb(II), Zn(II), Sn(II), Ag(I), Cu(I), Hg(I), and Tl(I) in solution in anhydrous acetic acid (+0.5 M LiClO<sub>4</sub>); the complexes of indium(I) could not be established because of the irreversible behavior of the electrode of this metal. The experimental results have been evaluated by computer techniques; the confidence intervals are given. The reducing power of these metals and their corresponding amalgams is represented on a potential-pH diagram.

## ZUSAMMENFASSUNG

Es wurden in wasserfreier Essigsäure (+ 0.5 M LiClO<sub>4</sub>) Gleichgewichtspotentiale untersucht, um die Natur und die Bildungskonstanten der Acetatkomplexe folgender Elemente zu bestimmen. Bi(III), Cd(II), Pb(II), Zn(II), Sn(II), Ag(I), Cu(I), Hg(I), Tl(I). Der Komplex von Indium(I) konnte wegen des irreversiblen Verhaltens der Metallelektrode nicht bestimmt werden. Die experimentellen Ergebnisse wurden mit einem Rechner ausgewertet und die Vertrauensbereiche berechnet. Das Reduktionsvermögen dieser Metalle und ihrer entsprechenden Amalgame wird in einem Potential-pH-Diagramm wiedergegeben.

## BIBLIOGRAPHIE

- 1 G. B. BACHMAN ET M. J. ASTLE, *J. Am. Chem. Soc.*, 64 (1942) 1303, 2177.
- 2 J. CIHALIK ET J. SIMEK, *Chem. Listy*, 51 (1957) 1283, 1663.
- 3 H. E. ULERY, *J. Electrochem. Soc.*, 113 (1966) 479.
- 4 P. D. T. COULTER, *Ph. D.*, Kansas University, 1965.
- 5 P. D. T. COULTER ET R. T. IWAMOTO, *J. Electroanal. Chem.*, 13 (1967) 21.
- 6 I. M. KOLTHOFF ET A. WILLMAN, *J. Am. Chem. Soc.*, 56 (1934) 1007.
- 7 W. O. KOLLING ET J. L. LAMBERT, *Inorg. Chem.*, 3 (1964) 202.
- 8 S. BRUCKENSTEIN ET I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 78 (1956) 2974.
- 9 T. JASINSKI ET H. SMAGOWSKI, *Chem. Anal.*, 10 (1965) 217.
- 10 L. LE PORT, *Thèse Dr. 3ème cycle*, Paris, 1965; Rapport CEA-R-2904, 1966.
- 11 W. O. KOLLING, *Anal. Chem.*, 40 (1968) 956.
- 12 N. PETIT, *Thèse Dr. 3ème cycle*, Paris, 1967; Rapport CEA-R-3643, 1968.
- 13 M. LAPIDUS, M. LUCAS ET B. TRÉMILLON, *Bull. Soc. Chim. France*, (1960) 1949.
- 14 G. DURAND ET B. TRÉMILLON, *Bull. Soc. Chim. France*, (1963) 2855.
- 15 B. ADLI-BLOCH ET B. TRÉMILLON, *Bull. Soc. Chim. France*, (1965) 1683.
- 16 M. C. BOTTA-CONESA, *Diplôme d'Etudes Supérieures*, Paris, 1965.
- 17 W. E. THOMAS, JR., *Ph. D.*, Indiana University, 1966.
- 18 I. M. KOLTHOFF ET S. BRUCKENSTEIN, *J. Am. Chem. Soc.*, 78 (1956) 1.
- 19 G. DURAND, *Thèse Dr. Etat*, Paris, à paraître (communication personnelle).
- 20 R. K. BIRDWHISTELL ET E. GRISWOLD, *J. Am. Chem. Soc.*, 77 (1955) 873.
- 21 A. W. DAVIDSON ET F. JIRIK, *J. Am. Chem. Soc.*, 72 (1950) 1700.
- 22 S. BRUCKENSTEIN, T. O. ROUSE ET S. PRAGER, *Talanta*, 11 (1964) 337.
- 23 D. INMAN, I. REGAN ET B. GIRLING, *J. Chem. Soc.*, (1964) 948.

- 24 J. BRAUNSTEIN, M. BLANDER ET R. M. LINDGREN, *J. Am. Chem. Soc.*, 84 (1962) 1529.
- 25 A. GRESSET, *Thèse Dr. 3ème cycle*, Paris, à paraître (communication personnelle).
- 26 I. M. KOLTHOFF ET S. BRUCKENSTEIN, dans I. M. KOLTHOFF ET P. J. ELVING, *Treatise on Analytical Chemistry*, Partie I, Vol. 1, Interscience, New York, 1959, p. 501.
- 27 M. POURBAIX, *Atlas d'Equilibres Electrochimiques*, Gauthier-Villars, Paris, 1963.
- 28 I. M. KOLTHOFF ET J. J. LINGANE, *Polarography*, 2e Edn., Tome 1, Table XI-2, Interscience, New York, 1952, p. 198.
- 29 F. CHAO, *Thèse Dr. Etat*, Paris, 1967.
- 30 H. HOHN, *Research*, 3 (1950) 16.
- 31 M. BRÉANT, *Thèse Dr. Etat*, Lyon, 1963.
- 32 H. STREHLOW, dans J. J. LAGOWSKI, *The Chemistry of Non-Aqueous Solvents*, Tome 1, Chap. 4, Academic Press, New York, 1966; C. BARRAQUÉ, J. VEDEL ET B. TRÉMILLON, *Bull. Soc. Chim. France*, (1968) 3421.
- 33 G. DURAND, *Bull. Soc. Chim. France*, à paraître.
- 34 J. VEDEL, *Ann. Chim.*, 2 (1967) 335.

*Anal. Chim. Acta*, 49 (1970) 115-134

## ETUDE ELECTROCHIMIQUE DE L'IODE EN SOLUTION DANS L'ACIDE ACETIQUE ANHYDRE

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L'iode a déjà été l'objet de nombreuses études électrochimiques dans divers solvants. Les investigations ont porté principalement sur l'existence d'un complexe  $I_3^-$  entre la molécule d'iode et l'anion iodure. KOLTHOFF ET JORDAN<sup>1</sup> puis TOREN ET DRISCOLL<sup>2</sup> en solution aqueuse, SKELLY<sup>3</sup>, POPOV ET GESKE<sup>4</sup>, NELSON ET IWAMOTO<sup>5</sup>, GUIDELLI ET PICCARDI<sup>6</sup> dans l'acétonitrile, NELSON ET IWAMOTO<sup>5</sup> dans le nitrométhane et l'acétone, PLICHON, BADOZ-LAMBLING ET CHARLOT<sup>7</sup> dans l'anhydride acétique, GIORDANO, BAZAN ET ARVIA<sup>8</sup> dans le diméthylsulfoxyde et enfin IWAMOTO<sup>9</sup> dans quelques autres solvants ont tous réalisé des études voltampérométriques du couple iode-iodure, mettant en évidence dans de nombreux cas le complexe  $I_3^-$ , ou en tenant compte dans leur interprétation; plusieurs valeurs de la constante de formation de ce complexe ont été ainsi déterminées. L'oxydation de l'iode a fait par ailleurs l'objet d'une étude électrochimique en solution aqueuse par KOLTHOFF ET JORDAN<sup>1</sup>, qui ont montré la formation du cation  $I^+$ , de caractère instable mais pouvant être stabilisé par l'addition d'ions chlorure ou de pyridine, d'une base de Lewis de façon plus générale. La même oxydation a été abordée par POPOV ET GESKE<sup>4</sup> dans l'acétonitrile.

En ce qui concerne le comportement électrochimique de l'iode en solution dans l'acide acétique, GUIDELLI ET PICCARDI<sup>10</sup> ont récemment publié un bref mémoire dans lequel ils décrivent la détermination de la constante de formation de  $I_3^-$  en comparant la courbe expérimentale d'oxydation de l'iodure, obtenue en milieu  $NaClO_4$  0.3 M à une micro-électrode tournante de platine poli, aux courbes théoriques calculées pour le système en fonction de la stabilité de  $I_3^-$ . Ce résultat doit, a priori, être accepté avec circonspection, la théorie négligeant l'intervention possible de divers phénomènes électro-cinétiques pouvant rendre erroné ce genre de détermination.

Nous avons nous-mêmes entrepris une étude voltampérométrique (commencée antérieurement à la parution du mémoire de GUIDELLI ET PICCARDI) de l'iode en solution dans l'acide acétique: d'une part, en réduction, où apparaît le complexe  $I_3^-$  puis l'iodure, avec pour objectif la détermination de la stabilité de  $I_3^-$  (par potentiométrie) et l'étude de l'influence de l'acidité du milieu; d'autre part, en oxydation. Les résultats obtenus sont décrits respectivement dans les deux parties suivantes.

### SYSTÈMES IODE-IODURE ET COMPLEXE $I_3^-$

#### *Courbes voltampérométriques*

En premier lieu, nous avons étudié la *réduction de l'iode* dissous dans l'acide

acétique anhydre, en traçant la *courbe intensité-potentiel à une micro-électrode tournante de platine*, dans un milieu comportant du perchlorate de sodium  $0.5 M$  et de l'acétate de sodium  $1 M$  (milieu fortement *basique*). Nous avons constaté que cette courbe comprenait *deux vagues*, la hauteur de la seconde étant sensiblement double de celle de la première (courbe 1, Fig. 1), et nous avons pu vérifier que la valeur de l'intensité-limite globale était proportionnelle à la concentration de l'iode en solution. D'autre

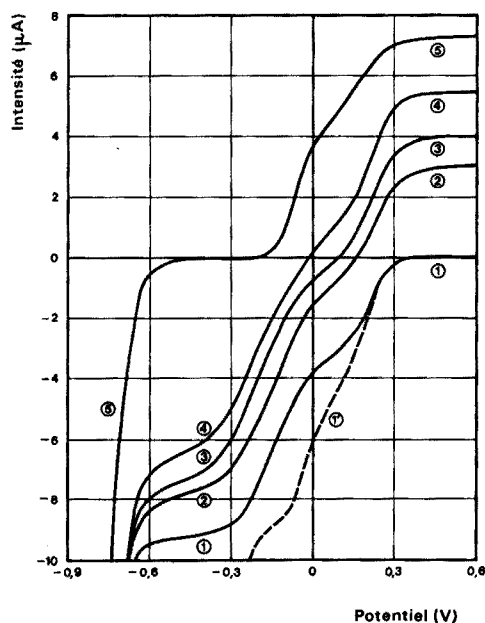


Fig. 1. Courbes voltampérométriques du système iode-iodure à une micro-électrode tournante de platine ( $0.5 \text{ mm}^2$ ,  $600 \text{ r.p.m.}$ ). Milieu  $\text{NaClO}_4 0.5 M + \text{NaOAc } 1 M$ . (1) Iode  $5 \cdot 10^{-3} M$ , (2)  $\text{I}_2 5.0 \cdot 10^{-3} M + \text{NaI } 3.8 \cdot 10^{-3} M$ , (3)  $\text{I}_2 5 \cdot 10^{-3} M + \text{NaI } 5 \cdot 10^{-3} M$ , (4)  $\text{I}_2 5 \cdot 10^{-3} M + \text{NaI } 7.7 \cdot 10^{-3} M$ , (5)  $\text{NaI } 8 \cdot 10^{-3} M$ . Courbe (1')  $\text{I}_2 5 \cdot 10^{-3} M$  en milieu  $\text{NaClO}_4 0.5 M + \text{HClO}_4 1 M$ .

part, nous nous sommes assurés que cette valeur était contrôlée par la diffusion de l'iode: selon la relation de LEVICH<sup>11</sup>, l'intensité-limite de diffusion est proportionnelle à la racine carrée de la vitesse de rotation de l'électrode; les résultats représentés sur la Fig. 2 indiquent ici, effectivement, une bonne linéarité pour la variation du logarithme de l'intensité-limite en fonction de celui de la vitesse de rotation, jusqu'à environ  $1000 \text{ r.p.m.}$ , avec une pente expérimentale de  $0.48$ . A  $600 \text{ r.p.m.}$ , le coefficient de proportionnalité entre l'intensité-limite globale et la concentration de l'iode est égal à  $3.56 \text{ mA mm}^{-2} \text{ mole}^{-1}$ ; dans les mêmes conditions, il est égal à  $3.70$  pour l'iodure.

A titre de vérification et de test de réversibilité des systèmes, nous avons également déterminé la *courbe d'oxydation de l'iodure*, qui se compose de la même manière de deux vagues, la hauteur de la première étant double de celle de la seconde (courbe 5, Fig. 1). Enfin, en ajoutant à une solution initiale d'iode des quantités croissantes d'iodure, la courbe intensité-potentiel évolue comme le montre le faisceau de courbes de la Fig. 1.

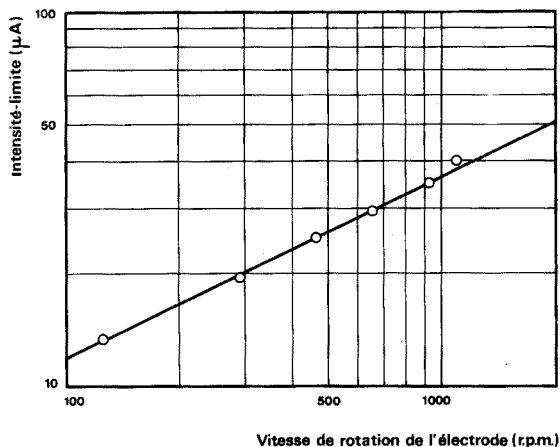


Fig. 2. Influence de la vitesse de rotation de l'électrode sur l'intensité-limite de réduction globale de l'iode (en milieu  $\text{NaClO}_4$  0.5 M +  $\text{NaOAc}$  1 M).

Le rapport des hauteurs des vagues de réduction de l'iode et celui des vagues d'oxydation de l'iodure se trouvent donc en accord avec l'hypothèse de l'existence du complexe  $\text{I}_3^-$ , conduisant à la double réaction électrochimique :



En réalité, la formulation de ces deux réactions n'est pas tout à fait correcte ainsi, compte tenu de la faible dissociation ionique dans l'acide acétique. L'iodure de sodium existe principalement sous forme de paires d'ions  $\text{Na}^+\text{I}^-$ , même en solution diluée en présence du perchlorate de sodium concentré (0.5 M) que nous avons utilisé comme électrolyte-support (*cf.* partie technique expérimentale). De même, le complexe existe principalement sous forme des paires d'ions  $\text{Na}^+\text{I}_3^-$ . On peut alors formuler les réactions électrochimiques :



Les ions  $\text{Na}^+$  nécessaires sont fournis par la dissociation de l'électrolyte-support, ou par celle de l'acétate de sodium.

En milieu *acide* (constitué par un mélange d'acide perchlorique 1 M et de perchlorate de sodium 0.5 M), la courbe intensité-potential de réduction de l'iode à la même micro-électrode tournante de platine présente, par rapport à la courbe obtenue en milieu basique, la différence suivante: si la première vague reste pratiquement inchangée, la seconde se développe à des potentiels moins réducteurs (courbe 1', Fig. 1). Ceci peut être interprété en admettant que la première vague correspond encore à la réaction électrochimique (1'), mais que la seconde correspond ici à la nouvelle réaction :



plus facile à réaliser que (2') si l'acide iodhydrique est moins dissocié que  $\text{NaI}$ , c'est-à-dire s'il s'agit d'un acide relativement faible.

*Remarque.* Il paraît important de souligner l'influence du prétraitement de l'électrode de platine sur les courbes intensité-potential aussi bien de réduction de l'iode que d'oxydation de l'iodeure. La Fig. 3 montre les courbes enregistrées (balayage de potentiel 100 mV/min) pour la réduction de  $I_2$  ou l'oxydation de  $I^-$ , à une électrode de platine d'abord nettoyé par l'acide nitrique, puis poli à l'alumine, rincé à l'eau, à l'alcool et séché (courbe 1). Après avoir maintenu l'électrode 5 à 10 min à un potentiel de +2V avant d'effectuer la réduction de  $I_2$ , ou de -2V avant d'effectuer l'oxydation de

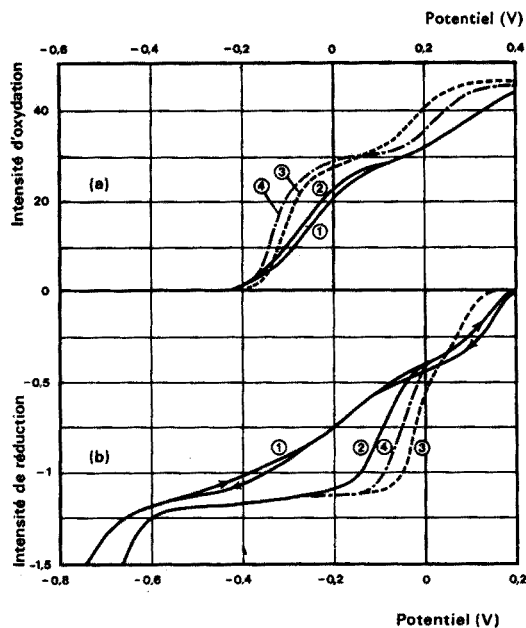


Fig. 3. Influence du pré-traitement de l'électrode sur les courbes voltampérométriques d'oxydation de NaI (a) et de réduction de  $I_2$  (b). (1) Courbe enregistrée avec une électrode non pré-oxydée, (2) courbe enregistrée avec une électrode pré-oxydée à -2 V (a) et +2 V (b), (3) courbe voltampérométrique théorique pour  $\log \beta = 4.4$ , (4) courbe voltampérométrique théorique pour  $\log \beta = 5.24$ .

$I^-$ , nous avons ensuite obtenu les courbes 2, qui s'avèrent alors compatibles avec des équations théoriques comme celles établies par GUIDELLI ET PICCARDI<sup>6</sup>, semblant permettre une détermination de la constante de stabilité de  $I_3^-$  comme ces auteurs l'ont effectué en milieu neutre<sup>10</sup>. Mais nous avons préféré pour cela utiliser la mesure des valeurs de potentiel d'équilibre de l'électrode de platine plongeant dans des solutions contenant  $I_2 + I_3^-$  ou  $I_3^- + I^-$ ; l'allure des courbes intensité-potential justifie pleinement l'emploi de cette méthode, beaucoup plus sûre puisqu'on peut s'assurer de la non-intervention de phénomènes parasites par la vérification de la formule de NERNST.

#### *Détermination potentiométrique de la constante de formation du complexe iode-iodeure*

Nous avons exploité la méthode dite du "logarithme-limite". Dans un premier temps, nous avons mesuré les valeurs de potentiel d'équilibre d'une solution d'iodeure de sodium diluée à laquelle nous avons ajouté des quantités croissantes d'iode en grand excès. Nous pouvons alors admettre que la concentration du complexe  $NaI_3$  formé est à peu près égale à la valeur  $c_1$  de la concentration d'iodeure initial (complexation prati-



quement quantitative) et que celle de l'iode en excès est  $c_2$ . En appliquant la formule de NERNST au système (1') (en utilisant les concentrations des espèces en jeu, la force ionique étant maintenue constante par l'électrolyte-support), il vient :

$$E = E_1^0 + 0.058 \log [\text{Na}^+] + 0.029 \log \frac{(c_2)^3}{(c_1)^2} \quad (3)$$

$c_1$  varie légèrement par suite de la dilution lorsqu'on ajoute l'iode en excès; le potentiel d'équilibre doit varier linéairement en fonction de  $\log [(c_2)^3/(c_1)^2]$  avec une pente de 29 mV/unité de log.

Dans un second temps, nous avons effectué des opérations similaires en renversant les rôles de l'iode et de l'iodure de sodium ( $c_1' > c_2'$ ), de telle sorte que  $[\text{NaI}_3] \neq c_2'$  et  $[\text{NaI}] \neq c_1'$ ; d'où, en appliquant la formule de NERNST au système (2') :

$$E_2 = E_2^0 + 0.058 \log [\text{Na}^+] + 0.029 \log \frac{c_2'}{(c_1')^3} \quad (4)$$

$E$  doit varier linéairement en fonction de  $\log [c_2'/(c_1')^3]$  avec une pente de 29 mV/unité de log.

De ces deux droites, on peut déduire la différence  $E_1^0 - E_2^0$  des deux potentiels formels des systèmes (1') et (2') ( $\log [\text{Na}^+]$  s'élimine par différence), d'où la constante  $\beta$  de l'équilibre de formation du complexe iode-iodure :



$$\log \beta = \log \frac{[\text{NaI}_3]}{[\text{I}_2][\text{NaI}]} = \frac{E_1^0 - E_2^0}{0.087} \quad (6)$$

Sur le Tableau I, figurent les résultats expérimentaux obtenus, d'une part en milieu basique ( $\text{NaOAc } 1 \text{ M} + \text{NaClO}_4 \text{ } 0.5 \text{ M}$ ), d'autre part en milieu neutre ( $\text{NaClO}_4 \text{ } 0.5 \text{ M}$  seul, milieu voisin de celui utilisé par GUIDELLI ET PICCARDI<sup>10</sup>); la détermination n'a pas été possible en milieu acide ( $\text{HClO}_4$ ), en raison d'une oxydation lente de l'iodure par les ions hydrogène, qui fait continuellement varier les concentrations et par conséquent le potentiel d'équilibre. La précision indiquée correspond aux intervalles de confiance à 95 % de probabilité déduits par application de la méthode des moindres carrés aux deux droites expérimentales.

Les valeurs de potentiel figurant dans ce Tableau sont exprimées par rapport au potentiel de l'électrode normale à hydrogène ( $\text{pH} = 0$ ,  $\text{H}_2$  saturé sous  $p = 1 \text{ atm}$ ) pris pour origine, et dont nous avons par ailleurs<sup>12</sup> déterminé la valeur par rapport à l'électrode de référence utilisée dans cette étude :

$$E_{\text{ref}} = E^0_{\text{H}_2/\text{H}^+} + 0.087 \text{ V} \quad (7)$$

Nous avons posé  $E^0_{\text{H}_2/\text{H}^+} = 0$  pour la valeur de potentiel de l'électrode à hydrogène obtenue par extrapolation à  $\text{pH} = 0$ , le calcul du  $\text{pH}$  des solutions étant effectué en admettant que les valeurs des constantes de dissociation de  $\text{HClO}_4$  et de  $\text{NaClO}_4$  sont respectivement<sup>13</sup>  $10^{-4.87}$  et  $10^{-5.48}$ , et que les coefficients d'activité des ions restent voisins de l'unité.

*Remarque.* La valeur de  $\log \beta$  que nous avons obtenue est en désaccord assez net avec celle de GUIDELLI ET PICCARDI, qui est voisine de 4.4. La méthode potentiométrique que nous avons utilisée paraissant tout à fait digne de confiance, il s'avère ainsi

TABLEAU I

DÉTERMINATION POTENTIOMÉTRIQUE DE LA CONSTANCE DE FORMATION DU COMPLEXE  $I_3^-$ 

|                          | Système $I_2/NaI_3$                                   |   |            | Système $NaI_3/NaI$                                 |  |            |
|--------------------------|---|---|------------|---|--|------------|
|                          | $c_1 \cdot 10^3$<br>(mole l <sup>-1</sup> )           | $c_2 \cdot 10^3$<br>(mole l <sup>-1</sup> ) | $E$<br>(V) | $c_1' \cdot 10^3$<br>(mole l <sup>-1</sup> )        | $c_2' \cdot 10^3$<br>(mole l <sup>-1</sup> ) | $E$<br>(V) |
| Milieu basique:          | 1.09  | 0.37  | 0.135      | 3.96  | 0.61   | -0.079     |
| NaOAc 1 M +              | 1.07  | 0.59  | 0.149      | 5.03  | 0.59   | -0.088     |
| NaClO <sub>4</sub> 0.5 M | 1.04  | 0.80  | 0.160      | 6.45  | 0.58   | -0.096     |
|                          | 1.00  | 1.20  | 0.176      | 8.33  | 0.55   | -0.107     |
|                          | 0.95  | 1.57  | 0.188      | 9.72  | 0.53   | -0.115     |
|                          | 0.91  | 1.91  | 0.198      | 11.33   | 0.51   | -0.121     |
|                          | 0.87  | 2.22  | 0.205      | 12.78   | 0.49   | -0.127     |
|                          | 0.85  | 2.51  | 0.212      |   |  |            |
|                          | 0.81  | 2.78  | 0.218      |   |  |            |
|                          | 0.79  | 3.02  | 0.223      |   |  |            |
|                          | $E = f \left[ \log \frac{(c_2)^3}{(c_1)^2} \right] :$ |   |            | $E = f \left[ \log \frac{c_2'}{(c_1')^3} \right] :$ |  |            |
|                          | droite de pente: $0.029 \pm 0.002$ V.                 |   |            | droite de pente: $0.029 \pm 0.002$ V.               |  |            |
|                          | $E_1^0 + 0.058 \log [Na^+] = 0.173 \pm 0.004$ V       |   |            | $E_2^0 + 0.058 \log [Na^+] = -0.283 \pm 0.006$ V    |  |            |
|                          | $E_1^0 = 0.344 \pm 0.004$ V                           |   |            | $E_2^0 = -0.112 \pm 0.006$ V                        |  |            |
|                          | $\log \beta / \text{mole}^{-1} = 5.24 \pm 0.12$       |   |            |   |  |            |
| Milieu neutre:           | 0.75  | 0.23  | 0.106      | 0.48  | 0.45   | -0.016     |
| NaClO <sub>4</sub> 0.5 M | 0.75  | 0.35  | 0.119      | 1.08  | 0.44   | -0.047     |
|                          | 0.74  | 0.46  | 0.130      | 1.68  | 0.44   | -0.065     |
|                          | 0.74  | 0.57  | 0.139      | 2.25  | 0.43   | -0.076     |
|                          | 0.72  | 0.69  | 0.146      | 2.82  | 0.43   | -0.085     |
|                          | 0.72  | 0.79  | 0.152      | 3.37  | 0.42   | -0.092     |
|                          | 0.70  | 0.91  | 0.158      | 3.90  | 0.42   | -0.097     |
|                          | 0.70  | 0.99  | 0.163      | 4.43  | 0.41   | -0.102     |
|                          | 0.69  | 1.09  | 0.167      | 4.94  | 0.41   | -0.106     |
|                          | 0.69  | 1.20  | 0.172      | 5.44  | 0.40   | -0.109     |
|                          | 0.67  | 1.28  | 0.175      | 5.94  | 0.40   | -0.113     |
|                          | 0.67  | 1.38  | 0.179      | 6.41  | 0.39   | -0.116     |
|                          | 0.66  | 1.47  | 0.182      | 6.88  | 0.39   | -0.118     |
|                          | 0.66  | 1.58  | 0.185      | 7.34  | 0.38   | -0.120     |
|                          | 0.64  | 1.65  | 0.188      | 7.79  | 0.38   | -0.123     |
|                          | 0.64  | 1.73  | 0.191      | 8.23  | 0.38   | -0.125     |
|                          | 0.64  | 1.81  | 0.193      | 8.66  | 0.37   | -0.126     |
|                          | 0.63  | 1.90  | 0.195      | 9.09  | 0.37   | -0.128     |
|                          | 0.63  | 1.99  | 0.198      | 9.50  | 0.36   | -0.130     |
|                          | 0.61  | 2.08  | 0.200      | 9.90  | 0.36   | -0.131     |
|                          | 0.61  | 2.13  | 0.202      | 10.30   | 0.36   | -0.133     |
|                          | 0.60  | 2.23  | 0.204      | 11.07   | 0.35   | -0.135     |
|                          | 0.60  | 2.29  | 0.206      | 11.81   | 0.34   | -0.138     |
|                          | 0.58  | 2.39  | 0.207      | 12.53   | 0.34   | -0.140     |
|                          | 0.58  | 2.45  | 0.209      | 13.21   | 0.33   | -0.142     |
|                          | 0.58  | 2.51  | 0.211      | 13.87   | 0.32   | -0.144     |
|                          | 0.57  | 2.57  | 0.212      | 14.51   | 0.32   | -0.145     |
|                          | 0.56  | 2.69  | 0.215      | 15.13   | 0.31   | -0.147     |
|                          | 0.56  | 2.81  | 0.218      | 15.72   | 0.31   | -0.148     |
|                          | 0.54  | 2.95  | 0.221      | 16.30   | 0.30   | -0.149     |
|                          | 0.53  | 3.09  | 0.223      | 16.85   | 0.30   | -0.150     |
|                          | 0.52  | 3.23  | 0.226      |   |  |            |
|                          | 0.52  | 3.31  | 0.228      |   |  |            |
|                          | 0.51  | 3.46  | 0.230      |   |  |            |
|                          | $E = f \left[ \log \frac{(c_2)^3}{(c_1)^2} \right] :$ |   |            | $E = f \left[ \log \frac{c_2'}{(c_1')^3} \right] :$ |  |            |
|                          | droite de pente: $0.33 \pm 0.001$ V.                  |   |            | droite de pente: $0.027 \pm 0.001$ V.               |  |            |
|                          | $E_1^0 + 0.058 \log [Na^+] = 0.168 \pm 0.001$ V       |   |            | $E_2^0 + 0.058 \log [Na^+] = -0.289 \pm 0.001$ V    |  |            |
|                          | $E_1^0 = 0.339 \pm 0.001$ V                           |   |            | $E_2^0 = -0.118 \pm 0.001$ V                        |  |            |
|                          | $\log \beta / \text{mole}^{-1} = 5.25 \pm 0.02$       |   |            |   |  |            |

que la méthode préconisée par ces auteurs, s'appuyant sur l'interprétation quantitative des courbes voltampérométriques à une micro-électrode solide, n'est pas suffisamment fiable pour déterminer des constantes d'équilibres chimiques en solution.

#### OXYDATION DE L'IODE

Les courbes voltampérométriques d'une solution d'iode dans l'acide acétique font apparaître non seulement des phénomènes de réduction de cette espèce en  $I_3^-$  puis  $I^-$  — comme il vient d'être décrit — mais aussi des phénomènes d'oxydation, qui se traduisent par une double vague précédée d'un pic de courant, avant la limite d'électro-activité correspondant à l'oxydation de l'acide acétique lui-même. Les courbes obtenues à une micro-électrode tournante de platine poli sont celles représentées sur la Fig. 4.

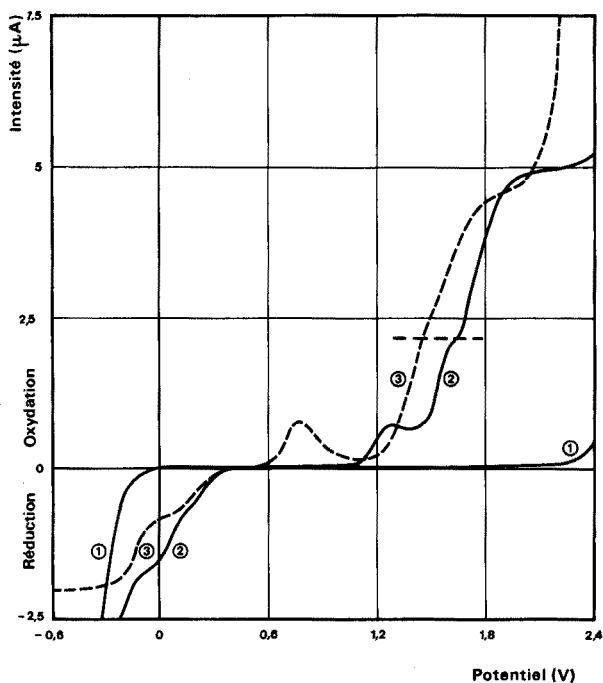


Fig. 4. Courbes voltampérométriques de l'iode à une micro-électrode tournante de platine (0.5 mm<sup>2</sup>, 600 r.p.m.). Milieu NaClO<sub>4</sub> 0.5 M + HClO<sub>4</sub> 1 M. (1) Courant résiduel, (2) I<sub>2</sub> 1.1 · 10<sup>-3</sup> M, (3) I<sub>2</sub> 1.1 · 10<sup>-3</sup> M en milieu NaClO<sub>4</sub> 0.5 M + NaOAc 1 M.

Les phénomènes se présentent d'une façon similaire en milieu acide et en milieu basique, l'oxydation apparaissant un peu plus facile en milieu basique (courbe 3, Fig. 4). Les deux vagues sont mieux définies en milieu acide. Les phénomènes étant vraisemblablement les mêmes dans les deux cas, nous avons cherché à en donner une interprétation au moyen de l'étude expérimentale en milieu acide (HClO<sub>4</sub> 1 M + NaClO<sub>4</sub> 0.5 M) uniquement.

Les essais expérimentaux dont la description suit nous ont amenés à la conclu-

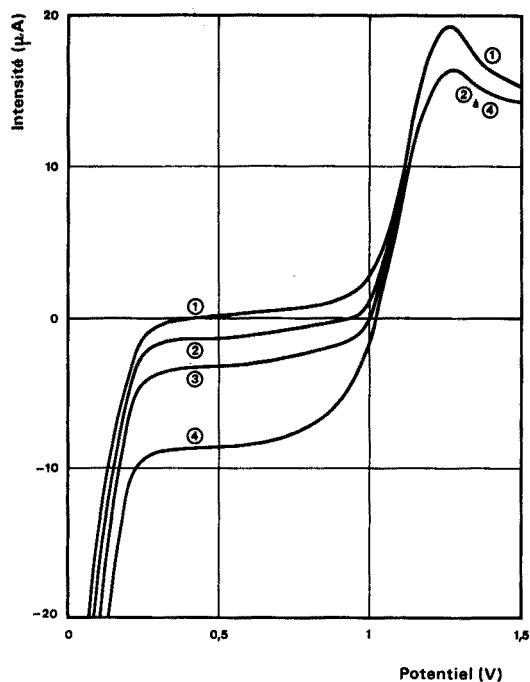


Fig. 5. Courbes voltampérométriques de l'iode tracées à l'anneau d'une électrode disque-anneau (disque 2 mm<sup>2</sup>, anneau 7 mm<sup>2</sup>, 600 r.p.m.). Milieu NaClO<sub>4</sub> 0.5 M + HClO<sub>4</sub> 1 M. (1) Potentiel nul au disque, (2) potentiel de + 1.29 V imposé au disque, (3) + 1.74 V, (4) + 2.09 V.

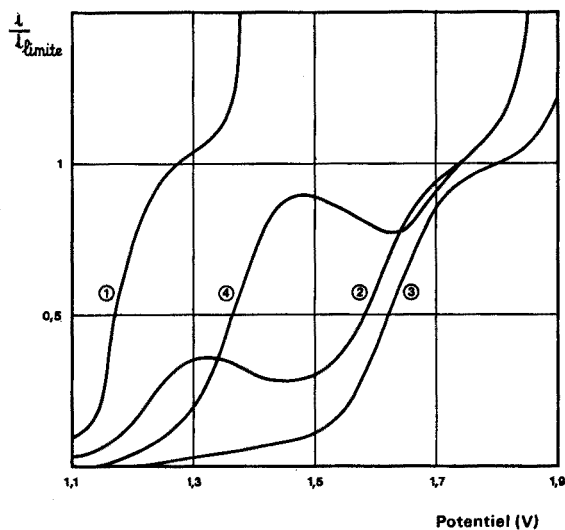


Fig. 6. Influence de la nature de l'électrode sur l'allure de la courbe voltampérométrique d'oxydation de l'iode en milieu NaClO<sub>4</sub> 0.5 M + HClO<sub>4</sub> 1 M (électrodes 0.5 mm<sup>2</sup>, 600 r.p.m.). (1) Electrode de platine platiné, (2) électrode de platine poli, (3) électrode de platine poli pré-oxydé à + 2.7 V, (4) électrode d'or.

sion que l'ensemble de la première vague et du pic étaient représentatifs de la même réaction électrochimique globale, le pic devant correspondre à un processus mettant en jeu l'adsorption de l'iode sur le platine; la seconde vague est représentative d'une autre réaction électrochimique.

#### *Etude de la première vague et du pic*

La hauteur de la première vague d'oxydation étant peu différente de celle de la double vague de réduction, il est tout de suite suggéré que le nombre d'électrons globalement échangés par molécule d'iode oxydée est 2 comme dans la réduction à l'état d'iodure. L'oxydation de l'iode conduirait donc d'abord à l'iode (+I), c'est-à-dire au cation  $I^+$ .

(a) En effectuant une coulométrie d'une solution d'iode ( $3 \cdot 10^{-5} M$  lors d'un premier essai et  $4.25 \cdot 10^{-5} M$  lors d'un second) à potentiel constant +1.74 V, c'est-à-dire au palier de la vague, nous avons trouvé une quantité d'électricité en accord à moins de 5% près avec ce degré d'oxydation supposé formé. La même opération effectuée à un potentiel constant moins élevé, +1.29 V, c'est-à-dire au pic qui précède la vague, nous a donné le même résultat (sur deux essais).

(b) Après oxydation pratiquement quantitative de l'iode dans ces conditions, le pic et la première vague ont disparu; il ne subsiste que la seconde vague d'oxydation. Il n'apparaît plus aucune vague en réduction, ce qui implique que le produit final d'oxydation de l'iode n'est pas électro-réductible.

Néanmoins, nous avons pu mettre en évidence qu'il se forme *transitoirement* à l'électrode, lors de l'oxydation de l'iode, une espèce qui est électro-réductible. Nous avons pour cela utilisé une électrode *disque-anneau*, dont l'emploi pour ce genre d'expérience a été maintes fois recommandé, depuis l'idée originale de FRUMKIN ET NEKRASOV<sup>14</sup>. En imposant au disque central un potentiel constant correspondant soit au palier de la 1ère vague (+1.74 V), soit au pic (+1.29 V), nous avons déterminé la courbe intensité-potentiel, en oxydation et en réduction, à l'anneau concentrique. Il apparaît alors une vague de réduction précédant celle de l'iode, dont le potentiel correspond au pic d'oxydation. Seule la hauteur de cette vague diffère lorsqu'on fait varier le potentiel du disque de celui du pic à celui du palier (Fig. 5).

(c) Le pic de la courbe voltampérométrique est manifestement lié à des phénomènes d'ordre électrocinétique, probablement à l'adsorption de l'iode à la surface du platine—phénomène déjà mis en évidence et ayant fait l'objet de plusieurs études en solution aqueuse<sup>15-18</sup>. A l'appui de cette hypothèse, nous pouvons en effet invoquer l'influence de la nature de l'électrode, de son pré-traitement et celle de la présence d'anions iodure, eux-mêmes fortement adsorbés sur le platine.

En ce qui concerne l'influence du pré-traitement de l'électrode de platine poli, nous avons constaté que le pic signalé dans la Fig. 4 était obtenu avec une électrode nettoyée et polie comme indiqué dans la première partie et non pré-oxydée. La pré-oxydation de l'électrode—ou tout simplement lors d'une seconde détermination de la courbe voltampérométrique sans ramener le potentiel de l'électrode en-dessous de 0.8 V—fait disparaître le pic et ne laisse subsister que la double vague d'oxydation (courbe 3, Fig. 6). Le pic réapparaît après avoir tracé une vague de réduction complète de l'iode. Il semble ainsi que l'apparition du pic soit liée à l'état de surface du platine, l'absorption de l'iode ne se produisant plus lorsque la surface est oxydée.

A l'opposé, la formation de platine divisé, par platinage de l'électrode, doit

rendre l'adsorption plus intense et accentuer le pic de courant. Effectivement, la courbe obtenue à une électrode de platine platiné, représentée en 1, Fig. 6, montre, à la place du pic de la courbe 2, non plus un pic mais une vague de hauteur correspondant à celle des courbes 2 ou 3.

L'existence d'un film d'oxydation à la surface du platine est manifestée par l'apparition d'un accroissement du courant résiduel enregistré à une électrode pré-réduite, lorsque le potentiel arrive au-dessus de  $+0.5$  V; à une électrode pré-oxydée, un accroissement du courant résiduel apparaît lorsque le potentiel arrive au-dessous de  $+0.3$  V (balayage en sens inverse).

Avec une électrode d'or, nous avons obtenu un pic similaire à celui obtenu sur le platine, mais à un potentiel légèrement plus élevé (courbe 4, Fig. 6).

L'influence de l'addition d'iodure de sodium est représentée Fig. 7. Il apparaît d'abord, naturellement, une vague d'oxydation du complexe  $I_3^-$  formé. Le pic d'oxydation demeure ensuite, à la même valeur de potentiel, mais son amplitude diminue au fur et à mesure de l'addition d'iodure, jusqu'à ce qu'il disparaisse lorsque l'iodure est en excès par rapport à l'iode; il semble que le pic ne puisse avoir de hauteur supérieure à celle observée en l'absence d'iodure. Le pic n'apparaît pas sur la courbe d'oxydation de l'iodure de sodium seul.

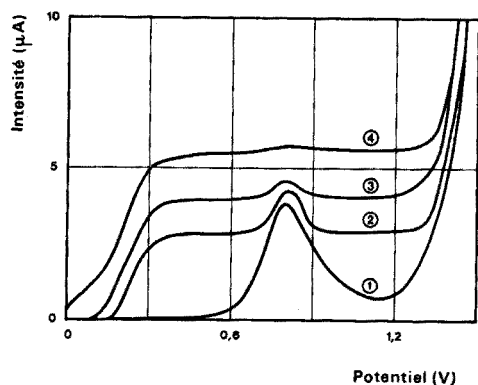


Fig. 7. Influence de l'iodure de sodium en solution sur la présence d'un pic de courant lors du tracé de la courbe voltampérométrique d'oxydation de l'iode à une micro-électrode tournante de platine ( $0.5$  mm<sup>2</sup>, 600 r.p.m.). Milieu  $\text{NaClO}_4$   $0.5$  M +  $\text{NaOAc}$   $1$  M. (1)  $I_2$   $5 \cdot 10^{-3}$  M, (2)  $I_2$   $5 \cdot 10^{-3}$  M +  $\text{NaI}$   $3.8 \cdot 10^{-3}$  M, (3)  $I_2$   $5 \cdot 10^{-3}$  M +  $\text{NaI}$   $5 \cdot 10^{-3}$  M, (4)  $I_2$   $5 \cdot 10^{-3}$  M +  $\text{NaI}$   $7.7 \cdot 10^{-3}$  M.

Enfin, avec une électrode disque-anneau, nous avons constaté que le pic d'oxydation de l'iode était indépendant de la présence préalable du produit d'oxydation (formé à la surface du disque et envoyé par rotation à la surface de l'anneau).

(d) Nous avons vérifié que la hauteur de la première vague était contrôlée par la diffusion: nous avons obtenu, pour la variation du logarithme de cette hauteur (mesurée à  $1.74$  V) en fonction du logarithme de la vitesse de rotation de l'électrode, une droite de pente égale à  $0.42$ , critère satisfaisant compte tenu de l'imprécision sur la détermination du palier mal défini.

#### Etude de la seconde vague

La hauteur de la seconde vague d'oxydation de l'iode, voisine de celle de la

première, est compatible avec un échange d'un électron supplémentaire par atome d'iode. Mais il ne nous a pas semblé, à la suite des essais effectués, que la formation d'iode (+ II) puisse être retenue comme probable. Nous avons envisagé un autre processus d'oxydation impliquant l'iode présent en solution.

(a) Nous avons constaté que la *seconde vague d'oxydation de l'iode se confond avec celle de l'acide mono-iodoacétique*. La solution de celui-ci est incolore, comme celle du produit final d'oxydation électrochimique de l'iode obtenu par coulométrie à +1.74 V; comme ce dernier, l'acide iodoacétique donne une vague d'oxydation mais n'est pas électroréductible.

(b) Nous avons constaté un comportement également identique du produit d'oxydation de l'iode et de l'acide iodoacétique lors d'*oxydations coulométriques à potentiel constant*, égal à +2.09 V (correspondant au palier de la vague d'oxydation de l'acide iodoacétique). Supposant que l'oxydation de l'acide iodoacétique devait être une réaction du type de la réaction de KOLBE, il doit alors apparaître des ions hydrogène (à raison d'un  $H^+$  par molécule d'acide oxydée). Nous avons donc effectué des oxydations coulométriques de solutions d'acide iodoacétique + perchlorate de sodium 0.5 M, puis dosé l'acide perchlorique apparu, pour une quantité d'électricité consommée déterminée, à l'aide d'une solution titrée d'acétate de pyridinium. Nous avons alors constaté que la quantité d'acide perchlorique produit était considérablement plus grande que celle d'acide iodoacétique consommé (environ 7 à 8 fois plus pour des solutions initiales d'acide iodoacétique  $2 \cdot 10^{-3} M$  et  $8 \cdot 10^{-4} M$ ). D'autre part, le courant d'oxydation de l'acide iodoacétique mesuré au cours de l'électrolyse variait assez rapidement tout au début de celle-ci, mais tendait ensuite vers une valeur très supérieure à celle du courant résiduel (Fig. 8). Ceci suggère qu'il se produit une régénération de l'acide iodoacétique, à une vitesse telle qu'il y a, après un certain temps, compensation de la consommation par électrolyse et établissement d'un courant stationnaire.

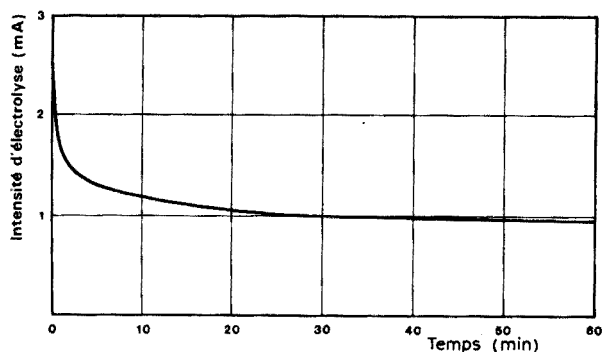


Fig. 8. Variation du courant d'électrolyse en fonction du temps lors de l'oxydation d'acide mono-iodoacétique (concentration  $10^{-3} M$ ) à une électrode de platine poli de grande surface, au potentiel de +2.09 V.

(c) Cependant, l'intensité-limite d'oxydation de l'acide iodoacétique à une micro-électrode de platine (courbe voltampérométrique) nous est apparue proportionnelle à la concentration de cet acide (de  $4 \cdot 10^{-4}$  à  $4 \cdot 10^{-3} M$ ) et contrôlée par la diffusion, la variation de son logarithme en fonction du logarithme de la vitesse de rotation de l'électrode étant une droite de pente 0.45 (entre 200 et 1500 r.p.m.). La régénération

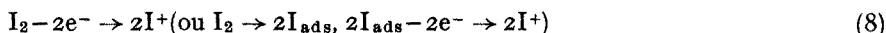
de l'acide iodoacétique doit donc être suffisamment lente pour expliquer les deux observations des paragraphes (b) et (c).

(d) En utilisant l'électrode disque-anneau, le disque étant porté à un potentiel constant tel que l'acide iodoacétique soit oxydé (+2.09 V), la courbe voltampérométrique déterminée à l'anneau fait apparaître la même vague de réduction que celle observée en portant le disque seulement à 1.29 V ou à 1.74 V. Cette espèce électro-réductible ainsi détectée est une espèce transitoire puisque le résultat de l'oxydation coulométrique de l'acide ne fournit aucune espèce réductible (la courbe voltampérométrique ne présente aucune vague de réduction). Nous admettons qu'il s'agit de la même espèce que lors de l'oxydation de l'iode, c'est-à-dire le cation  $I^+$ .

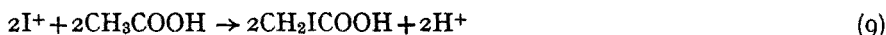
#### Interprétation et conclusion

L'ensemble de ces résultats expérimentaux nous conduit à donner des phénomènes d'oxydation de l'iode dans l'acide acétique l'interprétation suivante.

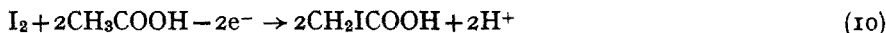
*L'iode serait d'abord oxydé à l'état de cation  $I^+$ : celui-ci pourrait ensuite réagir—rapidement mais non instantanément puisqu'on peut le mettre en évidence à l'électrode disque-anneau—sur l'acide acétique, en formant de l'acide mono-iodoacétique.* Le processus serait:



suivi de:



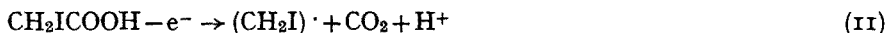
soit globalement:



(Il est à remarquer qu'en laissant vieillir une solution d'iode dans l'acide acétique, au contact de l'air sec, on observe une décoloration progressive, très lente, et au bout de plusieurs jours la disparition complète de l'iode et l'apparition d'acide iodoacétique.)

Le processus (8) serait réversible lorsqu'il met en jeu l'iode adsorbé à l'état atomique, et les potentiels à intensité nulle obtenus à l'anneau de l'électrode disque-anneau lorsqu'on produit  $I^+$  sur le disque seraient voisins du potentiel d'équilibre du couple iode/ $I^+$ . La vague qui suit le pic serait la vague irréversible d'oxydation de l'iode, qui deviendrait réversible lorsqu'on utilise une électrode de platine platiné.

*La seconde vague d'oxydation de l'iode correspondrait à l'oxydation de l'acide mono-iodoacétique formé lors de la première réaction (10), le processus primaire de la réaction de KOLBE s'écrivant:*



Pour expliquer l'apparition transitoire de  $I^+$  et la régénération de l'acide iodoacétique lors de l'électrolyse à potentiel constant, avec production excessive d'ions hydrogène, nous invoquerons la possibilité des processus suivants:



suivi du processus (9) ci-dessus (d'autre part, à partir du radical  $CH_3 \cdot$ , formation de divers hydrocarbures, comme cela est bien connu pour l'oxydation de l'acide acétique).

Si l'on fait la somme des processus (11), (12) et (9), on voit que, globalement,



l'acide iodoacétique est régénéré et que c'est l'acide acétique lui-même qui se trouve consommé par la réaction de KOLBE. Autrement dit, on aurait affaire à un processus d'oxydation catalytique de l'acide acétique par l'intermédiaire de l'acide iodoacétique plus sensible à l'oxydation du point de vue cinétique.

Nous avons retenu ces hypothèses comme étant les plus vraisemblables et les plus compatibles avec les faits expérimentaux observés. Des confirmations seraient souhaitables, en mettant en jeu d'autres méthodes expérimentales que celles utilisées pour cette étude.

#### TECHNIQUE EXPÉRIMENTALE

##### *Solutions utilisées*

La déshydratation de l'acide acétique et des solutions d'acide perchlorique, de perchlorate de sodium ou d'acétate de sodium, a été réalisée au moyen d'anhydride acétique selon les techniques classiques déjà décrites. La concentration d'eau résiduelle a été déterminée selon la méthode de KARL FISCHER, réalisée par coulométrie à intensité constante; elle était toujours inférieure à 10 mg/l. Les produits utilisés étaient les produits commerciaux les plus purs, sans traitement préalable.

##### *Appareillage*

Les courbes intensité-potential ont été déterminées au moyen d'un montage classique à trois électrodes, comprenant: potentiostat Tacussel PRT 500 associé à un élément-pilote du potentiel type Servovit Tacussel, millivoltmètre électronique Tacussel S 6 ER, enregistreur galvanométrique XY Sefram. Pour les coulométries à potentiel constant, nous avons utilisé un potentiostat PRT 20 et un enregistreur galvanométrique Sefram type Graphirack BS.

Les micro-électrodes indicatrices étaient constituées par un disque rotatif de 0.5 mm<sup>2</sup> (section droite d'un fil de 0.8 mm de diamètre). L'électrode de référence était constituée par le système mercure-acétate de mercure(I) saturé-acétate de sodium saturé + perchlorate de sodium 0.5 M (solvant: acide acétique anhydre).

L'électrode disque-anneau était identique à celle décrite par CAVALIER, DEZAELE ET JACQ\*<sup>19</sup>: disque de platine de 2 mm<sup>2</sup> et anneau concentrique de platine de 7 mm<sup>2</sup>, séparés par un anneau de polythène de très faible épaisseur (section droite d'un ensemble fil de platine + gaine de polythène introduits à force dans un tube de platine). Dans les deux montages électriques nécessaires à son utilisation, l'électrode de référence et l'électrode auxiliaire étaient communes.

#### RÉSUMÉ

L'étude voltampérométrique de la réduction de l'iode en solution dans l'acide acétique anhydre, à une électrode de platine, et la détermination des valeurs de potentiel d'équilibre des mélanges iode-iodure de sodium en milieux NaClO<sub>4</sub> 0.5 M et NaOAc 1 M + NaClO<sub>4</sub> 0.5 M, ont permis de déterminer la valeur de la constante de formation du complexe iode-iodure dans l'acide acétique:  $\text{NaI} + \text{I}_2 \rightleftharpoons \text{NaI}_3$ ,  $\log \beta / \text{mole}^{-1} =$

\* Nous remercions vivement M. JACQ de nous avoir gracieusement fourni cette électrode et initié à son fonctionnement.

$5.24 \pm 0.12$ . Cette valeur est plus élevée que celle donnée par GUIDELLI ET PICCARDI (4.4).

L'oxydation de l'iode a été étudiée par voltampérométrie, coulométrie à potentiel constant et au moyen de l'électrode disque-anneau. L'interprétation suivante a été avancée pour rendre compte des faits observés: l'iode serait oxydé à l'état de cations  $I^+$ , qui réagiraient ensuite sur l'acide acétique en formant de l'acide mono-iodoacétique. Ce dernier serait à son tour oxydable selon un processus dérivé de la réaction de KOLBE, avec consommation d'acide acétique et régénération de l'acide iodoacétique.

#### SUMMARY

A voltammetric study, with a platinum electrode, of the reduction of iodine in anhydrous acetic acid media and measurements of equilibrium potentials of iodine/iodide mixtures in  $0.5 M NaClO_4$  and  $1 M NaOAc + 0.5 M NaClO_4$  media, have allowed the determination of the formation constant of the iodine-iodide complex in acetic acid:  $NaI + I_2 \rightleftharpoons NaI_3$ ,  $\log \beta / \text{mole}^{-1} l = 5.24 \pm 0.12$ . This value is greater than that given by GUIDELLI AND PICCARDI (4.4).

The oxidation of iodine has been studied by voltammetry, constant potential coulometry and also with a ring-disk electrode. The observed phenomena can be explained as follows: iodine is oxidized to  $I^+$  cations, which then react with the acetic acid to form mono-iodoacetic acid. This acid is then oxidized in the same way as for the KOLBE reaction with consumption of acetic acid and regeneration of iodoacetic acid.

#### ZUSAMMENFASSUNG

Die voltametrische Untersuchung der Reduktion von Jod mit einer Platinelektrode in wasserfreier Essigsäure und die Messungen der Gleichgewichtspotentiale von Jod-Jodid-Mischungen in  $0.5 M NaClO_4$  und  $1 M NaOAc + 0.5 M NaClO_4$  erlauben die Bestimmung der Bildungskonstante des Jod-Jodid-Komplexes in Essigsäure. Sie beträgt  $5.24 \pm 0.12$  und ist damit grösser als der von GUIDELLI UND PICCARDI angegebene Wert. Die Oxydation des Jods wurde durch voltametrische Coulometrie bei konstanten Potentialen unter Verwendung einer Ringscheibenelektrode untersucht. Es ergab sich, dass das Jod zu  $J^+$ -Kationen oxydiert wird und dann mit der Essigsäure Monojodoessigsäure bildet. Diese Säure wird in gleicher Weise wie bei der Kolbe-Reaktion oxydiert unter Verbrauch der Essigsäure und Regeneration der Jodoessigsäure.

#### BIBLIOGRAPHIE

- 1 I. M. KOLTHOFF ET J. JORDAN, *J. Am. Chem. Soc.*, 75 (1953) 1571.
- 2 E. C. TOREN ET C. P. DRISCOLL, *Anal. Chem.*, 38 (1966) 872.
- 3 N. E. SKELLY, *Diss. Abstr.*, 15 (1955) 958.
- 4 A. I. POPOV ET D. H. GESKE, *J. Am. Chem. Soc.*, 80 (1958) 1340.
- 5 I. V. NELSON ET R. T. IWAMOTO, *J. Electroanal. Chem.*, 7 (1964) 218.
- 6 R. GUIDELLI ET G. PICCARDI, *Electrochim. Acta*, 12 (1967) 1085.
- 7 V. PLICHON, J. BADOZ-LAMBLING ET G. CHARLOT, *Bull. Soc. Chim. France*, (1964) 287.
- 8 M. C. GIORDANO, J. C. BAZAN ET A. J. ARVIA, *Electrochim. Acta*, 11 (1966) 741.

- 9 R. T. IWAMOTO, *Anal. Chem.*, 31 (1959) 955.
- 10 R. GUIDELLI ET G. PICCARDI, *Anal. Letters*, 1 (1968) 779.
- 11 V. G. LEVICH, *Physicochemical Hydrodynamics*, Prentice-Hall, New York, N.Y., 1962.
- 12 G. DURAND, *Bull. Soc. Chim. France*, à paraître.
- 13 I. M. KOLTHOFF ET S. BRUCKENSTEIN, *J. Am. Chem. Soc.*, 78 (1956) 1; S. BRUCKENSTEIN ET I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 78 (1956) 10, 2974; I. M. KOLTHOFF ET S. BRUCKENSTEIN, dans I. M. KOLTHOFF ET P. J. ELVING (Rédacteurs), dans *Treatise on Analytical Chemistry*, Chap. 13, Interscience, New York, N.Y., 1959.
- 14 A. N. FRUMKIN ET L. I. NEKRASOV, *Dokl. Akad. Nauk SSSR (Phys. Chem.)*, 126 (1959) 115.
- 15 R. A. OSTERYOUNG, *Anal. Chem.*, 35 (1963) 1100.
- 16 R. A. OSTERYOUNG ET F. C. ANSON, *Anal. Chem.*, 36 (1964) 975.
- 17 A. T. HUBARD, R. A. OSTERYOUNG ET F. C. ANSON, *Anal. Chem.*, 38 (1966) 692.
- 18 H. JANKOWSKA, *Przemysl Chem.*, 44 (1965) 295.
- 19 B. CAVALIER, C. DEZAEI ET J. JACQ, *Bull. Soc. Chim. France*, (1966) 3210.

*Anal. Chim. Acta*, 49 (1970) 135-149

## TRACE ELEMENT ANALYSIS OF SOLUTIONS BY HOLLOW-CATHODE EXCITATION

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The principle and operation of hollow-cathode tubes have been well known to physicists involved in spectroscopy<sup>1-3</sup>. The operation and discharge characteristics of the tube with different filler gases have been investigated by various workers<sup>4-9</sup>. Determination of halogens by means of hollow-cathode excitation had been a primary object of attack<sup>10-13</sup>. MILAZZO AND SOPRANZI<sup>12</sup> reported the use of a demountable hollow cathode for qualitative and quantitative analysis in the vacuum ultraviolet region. The hollow-cathode source has also been used successfully for the analysis of refractory oxides<sup>14,15</sup> as well as arsenic and phosphorus<sup>16</sup>. RUDNEVSKI<sup>17</sup> reported analysis of white cast iron for bismuth, boron and aluminum with a carrier salt. Some work of exploratory nature with organic and inorganic phosphates has been reported by ROBINSON *et al.*<sup>18</sup>.

It was shown by McNALLY *et al.*<sup>11</sup> that quantitative relationships could be obtained between the amount of material placed in the hollow cathode and the resultant emission intensity. MANDELSTAM AND NEDLER<sup>19</sup> later calculated that the theoretical ultimate sensitivity obtainable from hollow-cathode excitation was greater than for conventional emission spectrographic analysis.

Compared to conventional arc and spark emission spectrography, hollow-cathode excitation can be expected to have several advantages, including (a) less selective volatilization owing to the "sputtering" process; (b) excellent discharge stability when properly shielded; (c) very good sensitivity for many metals and non-metals; (d) elimination by the inert gas atmosphere of refractory oxide formation, atmospheric contamination, and interfering bands such as cyanogen; (e) production of extremely sharp spectral lines because of the small temperature and pressure broadening effects; (f) a simple, inexpensive means of exciting elements with very high excitation potentials; and (g) relatively good precision and accuracy ( $\pm 3-5\%$ ).

The main object of the present investigation was to utilize the highly energetic and controllable source of hollow-cathode excitation for emission spectrometric analysis of solutions. Although most previous investigations had involved the analysis of solid samples, the deposition and evaporation of a solution on a hollow-cathode surface results in a sample film which can then be excited by the discharge in the conventional manner. Recently, BÜGER AND FINK<sup>20</sup> demonstrated the feasibility of using the hollow cathode for obtaining emission spectra of aqueous solutions containing a dissolved salt.

## EXPERIMENTAL

*Hollow-cathode source*

Most quantitative emission analyses reported with a hollow-cathode excitation source have been carried out with an unshielded design very similar to the original SCHÜLER tube<sup>3</sup>. This design is inefficient, produces a rather unstable output intensity, and requires considerable warm-up time for stable operation. Enhancement in stability and intensity can be achieved by shielding the cathode so that only the cathode cavity is exposed to the discharge, which is concentrated between the cathode-anode interface, resulting in a highly localized plasma and a very efficient utilization of tube current. The advantages of the shielded design were early recognized for commercial hollow-cathode tubes used as line sources<sup>21</sup> for atomic absorption spectrometry. ROSSI AND OMENETTO<sup>22</sup> used a shielded hollow-cathode tube as an excitation source for atomic fluorescence analysis.

The hollow-cathode tube designed for the present investigation is modelled after the shielded design with several modifications. The demountable design permits the tube to be used as a versatile line source for many elements for atomic absorption analysis or for emission spectroscopic analysis of solutions and solids. The tube design is shown in Fig. 1. The main body of the tube is mounted on a 500-cm triangular steel optical bench which also supports a quartz lens system, focussing the hollow-cathode output radiation onto the spectrometer entrance slit. A special tube holder was fabricated, with rack and pinion gears to provide for fine movement along three axes, thus allowing fine focussing and optimal alignment of the hollow-cathode tube with the spectrometer.

For a stable discharge, the cathode glass shield (Fig. 1) should be positioned to leave an annular space of 0.5 mm or less between the cathode and the shield. An adjustable stainless steel anode enabled rapid change in cathode-anode distance for selection of optimum distance, usually about 10 mm. A distance much shorter

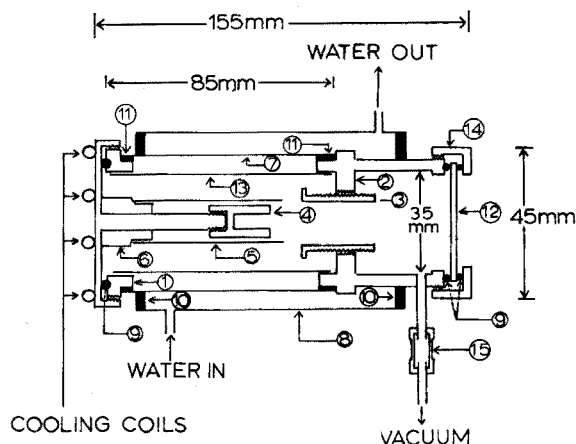


Fig. 1. Demountable hollow-cathode excitation source showing (1) cathode block, (2) anode block, (3) adjustable anode, (4) stainless steel hollow cathode, (5) glass cathode shield, (6) Teflon shield support, (7) glass connecting tube, (8) cooling jacket, (9) Neoprene O-ring gaskets, (10), (11) glass-to-metal epoxy seals, (12) quartz disc window, (13) inner glass sleeve, (14) window support, and (15) vacuum connection.

resulted in an unstable diffuse discharge glow across the interface, whereas a much larger distance caused prolonged scintillations before the attainment of a steady stable discharge. For graphite electrodes, a bayonet friction fit mounting was used to join the cathode to the cathode support.

#### *Vacuum system*

The vacuum system ( $10^{-5}$  mm) consisted of a two-stage mercury diffusion pump backed by an oil rotary pump, along with the associated traps, vacuum monitors, and a gas inlet manifold. The hollow-cathode tube was attached to the vacuum system by a stainless steel flexible bellows coupling with a glass-to-metal seal on each end. The filler gas pressure was read on a differential oil manometer filled with Apiezon oil. Fine adjustment of the filler gas pressure was accomplished by a controlled leak through a capillary.

Static operation was chosen for the hollow cathode, rather than a circulatory system<sup>13</sup>, as the tube was designed for solution samples which require short term operation only. With pure metal hollow cathodes, however, stable output radiation over an extended period could be achieved with currents up to 30 mA. Operation of the tube in this mode provided a stable line source for atomic absorption spectrometry. In the case of solution samples, individual runs of the hollow cathode lasted for only a few minutes. The precision and accuracy obtained with the static gas-filled system was quite satisfactory.

#### *Measurement system*

The radiation from the hollow-cathode source was directed to a Hitachi-Perkin Elmer Model 139 spectrometer, producing an output signal which was fed into a Sargent Model SRG recorder. The hollow-cathode tube was powered by a Kepco model BHK 2000 power supply which can provide regulated current up to 200 mA with an operating maximum of 1000 V.

#### *Reagents*

Reagent-grade chemicals were used throughout the investigation. Graphite electrodes were fabricated from "Ultra Purity" spectroscopic electrodes (Ultra Carbon Corporation, Bay City, Michigan). Standard stock solutions were prepared by appropriate dilution of Fisher atomic absorption standards. Distilled water was further purified by passing it through a mixed bed ion-exchange column and used for making up all standard solutions and for rinsing.

#### *Procedure*

Standard solutions of the test element were prepared, containing a suitable carrier salt which was in the concentration range of 10–50 p.p.m., depending upon the particular carrier salt and the test element. For stainless steel hollow cathodes, 0.45 ml of the test solution was transferred to the electrode cavity by pipette, evaporated to dryness at 100° in an oven, and then heated in a small muffle furnace to 300–350° for about 2–3 min to expel all traces of water. With graphite electrodes, which were used for work with highly acidic solutions, the test solution had a tendency during evaporation to diffuse into the graphite, resulting in a reduced quantity of sample film coating the electrode cavity with subsequently lower emission intensity. To compensate,

the graphite electrode was placed in a vial of slightly greater diameter than the electrode and 2 ml of the test solution were added to fill the vial, immersing the graphite electrode. This was evaporated to dryness and heated as before.

The hollow-cathode tube was assembled, evacuated, and filled to the desired pressure with an appropriate rare gas, after which the discharge was initiated at a low current. The current was then gradually, over 30–60 sec, increased to the desired operating value. The spectrometer, set to the desired wavelength and slit width (0.02–0.06 mm), produced in conjunction with the recording potentiometer a display of emission intensity as a function of time. Owing to the very small amount of the test element actually present, this recording trace took the form of a rise in emission intensity to a peak value followed then by a decrease. The peak value was taken in each case. Blanks were run for each sample, involving measurements taken for the cathode and carrier salt put through the entire analysis procedure as described.

The slit width, current and filler gas pressure were selected after preliminary studies with stainless steel hollow cathodes (or graphite electrodes impregnated with an appropriate salt). The stainless steel hollow cathodes were reused after soaking in aqua regia for 2 min and then polished with fine emery paper. Traces of grease were removed by soaking the electrodes in alcoholic potassium hydroxide and were finally washed with hot distilled deionized water. The anode was also cleaned in this manner. The graphite electrodes were discarded after each run.

## RESULTS AND DISCUSSION

### *Cathode material*

Excitation of a salt deposited in the hollow-cathode cavity involves decomposition of the salt into its constituent atoms before excitation. To equal the intensity obtainable from a hollow cathode constructed of a pure test metal, the current required with a salt of the test element deposited in the cathode cavity is 10–30 times higher<sup>23</sup>. Therefore, the sputtering characteristics of the hollow-cathode material containing the salt deposit can be expected to play an important role in the sensitivity and precision of the quantitative analysis. To obtain reasonable intensities for test solutions in the sub-p.p.m. range, currents of the order of 50–100 mA are required. Copper and aluminum, in spite of their fairly simple emission spectra, were found to be quite unsuitable as cathodes, because of the extreme ease with which they undergo sputtering, resulting in a correspondingly rapid escape of the deposited salt from the hollow-cathode cavity. Resistance to atmospheric oxidation, high melting point, and the ability to withstand the action of slightly acidic and alkaline solutions are other important factors which should be taken into account in selecting the hollow-cathode material for the analysis of solutions. Metals which are easily oxidized by air tend to form a non-conducting oxide layer on the surface resulting in unstable discharge, outgassing, and frequent difficulty in initiating the discharge. Stainless steel, though showing a fairly complex emission spectrum, was found to exhibit a number of advantages. The very low sputtering rate of stainless steel, as well as its resistance both to atmospheric oxidation and the action of the test solutions, resulted in very good discharge stability and a high intensity-to-background ratio in the quantitative analysis of aqueous solutions of a number of metallic salts. A smooth, flat bottom cavity was found to give the best reproducibility.

### *Carrier salt*

Initial experiments were done with simple aqueous solutions of the analysis element in the electrode cavity. However, as the current used to excite the sample film sputters the cathode material, it creates a very rapid and erratic escape of the trace quantities of the test element from the excitation zone. Measurement of emission intensities showed poor reproducibility. A decrease in current could improve precision but at the expense of sensitivity.

This problem was overcome by the addition to the sample of a "carrier salt", a compound present in quantities 20–50 times the concentrations of the analyte. The salt acted as a matrix to prevent too rapid escape of the analysis element from the discharge plasma and by forming a more uniform deposit also improved precision. Inter-element effects may also be reduced by proper selection of a carrier salt which could act as a spectroscopic buffer. The carrier salt selected for hollow-cathode excitation should have a fairly high ionization potential to prevent energy loss in the discharge, be of relatively low volatility, exhibit high thermal stability, and be available in high purity.

A considerable number of potential carrier salts were examined; magnesium sulphate was found to give satisfactory results for currents up to 80 mA, whereas for higher currents, lithium sulphate was found to be more suitable.

Hollow-cathode excitation was investigated in this laboratory with the thought of its development as a complementary analytical method to the more conventional techniques, such as atomic absorption. Therefore, the elements which have been examined are those which have not exhibited high sensitivity by other methods or those elements for which hollow-cathode excitation seemed to offer a significant increase in sensitivity. For each element studied, it was necessary to optimize a number of parameters, such as analytical wavelength, tube current, choice of filler gas, pressure of filler gas, carrier salt, and cathode type. The particular parameters shown for each element to be discussed reflect the results of many experiments and data tabulations which are not listed here.

### *Lead*

This element was selected for preliminary studies because lead is of interest in various biological systems. For dilute solutions of lead in the sub-p.p.m. range, magnesium sulphate carrier salt was added to obtain a concentration of 20 p.p.m. magnesium in the solution. A graphite electrode impregnated with 0.1% lead chloride solution was used for the selection of the most sensitive line for analytical purposes. The strongest emission line of lead was listed as 4057.8 Å by one source<sup>24</sup> and 2393.8 Å by another<sup>25</sup>. In the hollow-cathode discharge spectrum, the 4057.8 Å line was found to be more intense than the 2393.8 Å line and was not subject to spectral interference from the stainless steel hollow cathode.

The emission response of the 4057.8 Å line of lead for a 0.5 p.p.m. solution is shown in Fig. 2. Also shown is a typical plot for the blank solution containing the carrier salt, which is used to correct peak height for background. The blank readings were quite consistent for the same cathode, gas fill, carrier salt, and tube current. The use of argon at a pressure of 35 mm of oil (16 mm oil = 1 mm Hg) resulted in the highest intensity-to-background ratio. Initiation of the discharge was easier with helium but resulted in poor sensitivity for lead. A neon discharge tended to be rather erratic



and unstable compared to other two gases. The effect of filler gas on the lead  $4057.8 \text{ \AA}$  emission intensity is shown in Fig. 3, which indicates the linearity and overall sensitivity obtainable by this method. A stainless steel hollow cathode containing magnesium sulphate carrier salt gave the most satisfactory results for lead at sub-p.p.m. levels with a tube current of 80 mA. Precision of individual intensity measurements was in the range of  $\pm 3\text{--}5\%$ .

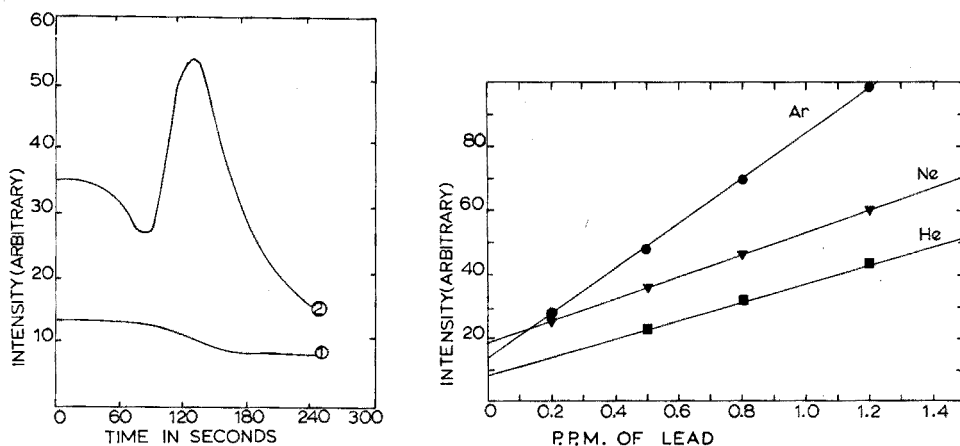


Fig. 2. Recorder tracing of  $4057.8 \text{ \AA}$  lead emission line as a function of time for (1) background from cathode and carrier salt and (2) a  $0.5 \text{ p.p.m.}$  standard lead solution containing magnesium sulphate carrier salt ( $20 \text{ p.p.m.}$  magnesium in solution). Filler gas, argon at  $35 \text{ mm oil}$  ( $16 \text{ mm oil} = 1 \text{ mm Hg}$ ); slit width,  $0.06 \text{ mm}$ ; tube current,  $80 \text{ mA}$ .

Fig. 3. Working curves for lead, showing the effect of argon ( $35 \text{ mm oil}$ ), neon ( $35 \text{ mm}$ ), and helium ( $65 \text{ mm}$ ), each at optimum pressure for maximum lead intensity. Other conditions as in Fig. 4.

### Copper

Copper was investigated as an element also of interest in biological materials<sup>26</sup>. Standard aqueous solutions of copper were used to study the emission intensity of the copper discharge spectrum, with stainless steel hollow cathodes. The  $3247.5 \text{ \AA}$  resonance line was selected as the most intense and was free from spectral interference. The best sensitivity, precision, and discharge stability were obtained with helium as the filler gas at a pressure of  $65 \text{ mm oil}$  with a tube current of  $80 \text{ mA}$ . A typical working curve for copper is shown in Fig. 4. Copper solutions evaluated from a routine  $0\text{--}5 \text{ p.p.m.}$  atomic absorption working curve were diluted ten fold and analyzed by hollow-cathode excitation with results which agreed within  $4\%$  of the atomic absorption values. A small copper contamination in the magnesium sulphate carrier salt showed up in the blank as a weak but sharp line at  $3247.5 \text{ \AA}$ .

### Boron

Boron was selected as one of the typical elements which shows poor sensitivity by atomic absorption and emission techniques. Improvement in flame sensitivity can be achieved by using a nitrous oxide-acetylene flame, but overall sensitivity is still only of the order of  $20\text{--}30 \text{ p.p.m.}$ <sup>27</sup> and working concentrations are, of course, much higher<sup>28</sup>. More sensitive spectrophotometric<sup>29</sup> and fluorescence<sup>30</sup> methods have been

described for the determination of boron, but these procedures usually involve lengthy separations and use of masking agents. The extremely simple emission spectrum of boron suggested use of the inert high-energy, hollow-cathode discharge.

The most intense lines of boron<sup>25</sup> are 2496.8 Å and 2497.7 Å, which were unresolved by the spectrometer used. Investigations with both boron-impregnated graphite electrodes and stainless steel hollow cathodes showed that the use of argon at 35 mm oil pressure resulted in the optimum intensity-to-background ratio at a given current.

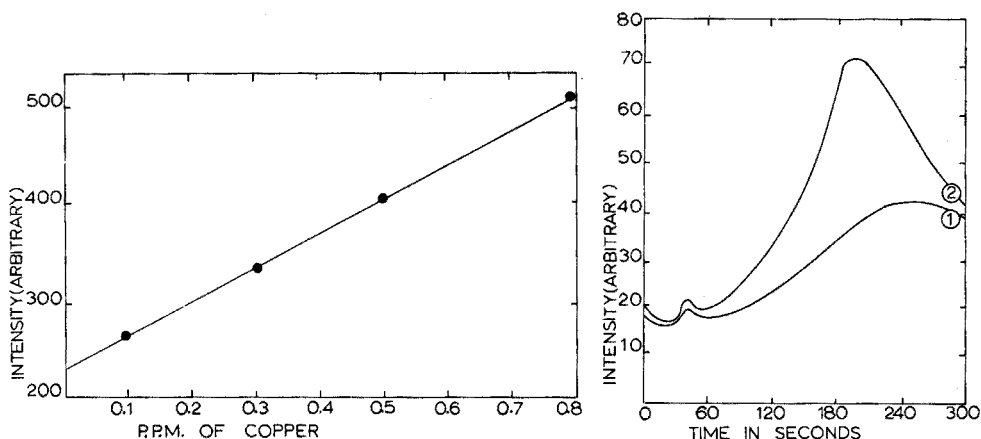


Fig. 4. Working curve for copper by hollow-cathode excitation at 3247.5 Å. Filler gas, helium at 65 mm oil; tube current, 80 mA; slit width, 0.04 mm; carrier salt, magnesium sulphate (20 p.p.m. magnesium in solution).

Fig. 5. Recorder tracing of boron 2497.7 Å emission line as a function of time for (1) background from cathode and carrier salt and (2) 0.1 p.p.m. standard boron solution containing lithium sulphate carrier salt (50 p.p.m. lithium in solution). Slit width, 0.03 mm; tube current, 120 mA; filler gas, argon at 35 mm oil.

Initial studies were carried out with stainless steel hollow cathodes and standard boron solutions containing magnesium sulphate carrier salt. Owing to the very low background, currents as high as 120 mA could be used for excitation. At these high current levels, lithium sulphate was preferred over magnesium sulphate as the carrier salt. The better discharge stability and precision attainable with lithium sulphate at higher currents could be due to its higher thermal stability (larger  $\Delta H$ ), resulting in a smoother evaporation of the carrier salt. Figure 5 shows the 2497 Å emission response for a 0.1 p.p.m. boron solution. The extreme sensitivity shown for boron by this technique allows for analyses at the sub-p.p.m. level with ease. The slight peak in the blank indicated a trace boron contamination either from the carrier salt or from the stainless steel hollow cathode. Working curves (0.1–0.5 p.p.m. range) obtained by plotting peak height against concentrations were linear as in the case of copper and lead.

#### *Tin, with graphite hollow cathodes*

Several elements like Bi, Sn, Zr, Hf, and Ta tend to hydrolyze in aqueous solutions unless the solutions are highly acidic (4–6 M hydrochloric acid) which would attack the stainless steel hollow cathodes. Graphite, possessing relatively high resistance

to the action of acids and alkalis at ordinary temperatures and also showing a simple emission spectrum, is very suitable for work with such highly acidic solutions. Tin was selected for preliminary studies with the graphite electrodes because of its relatively poor sensitivity by flame spectrometric methods.

The 3262.3 Å line was selected for analytical purposes after initial studies with a graphite electrode impregnated with tin(II) chloride solution. Argon at a pressure of 35 mm oil appeared to be the best filler gas. The working curve obtained by plotting the peak intensity against concentration was linear in the concentration range tested of 0–5 p.p.m.; 4 ml of the tin solution were used for each individual run, 2 ml of the solution being first evaporated to dryness as previously described and the procedure then repeated with a second 2-ml portion. A carrier salt was not necessary for the graphite electrodes since the sample was present throughout the electrode and not merely as a thin sample film on the surface.

#### CONCLUSION

The results reported here for the several elements are designed to demonstrate the potential of hollow-cathode excitation as a trace analysis technique and certainly do not represent the ultimate sensitivity attainable. Further optimization of equipment and parameters will no doubt improve analytical results. Currently under investigation in this laboratory are inter-element effects, other carrier salts, and several instrumental modifications. Based on these experiments, it would appear that hollow-cathode excitation, as a complementary technique to other analytical trace analysis procedures, can be quite useful in the case of certain elements for which it shows particularly advantageous properties.

This work was supported by Grant No. GM-14569, USPHS.

#### SUMMARY

Construction and operation of a shielded hollow-cathode tube for emission spectrometric trace element analysis of solution is described. The demountable tube design also permits the tube to be used as a versatile line source in atomic absorption spectrometry. Quantitative analysis of solutions can be performed after evaporation of a small portion of the test solution containing a suitable carrier salt in the cavity of the hollow cathode. Both stainless steel and graphite have been studied as cathodes. The effects of cathode material, filler gas, lamp current, and carrier salt were investigated for solutions of lead, copper, boron, and tin. The precision attainable in quantitative analysis is of the order of  $\pm 3-5\%$ .

#### RÉSUMÉ

On décrit les caractéristiques d'un tube à cathode creuse pour l'analyse spectrométrique par émission d'éléments en traces. La partie démontable du tube permet son utilisation pour la spectrométrie par absorption atomique. Une analyse quantitative des solutions peut être effectuée évaporation, en présence d'un sel entraîneur dans la cavité de la cathode creuse. On a examiné les possibilités d'utilisation de l'acier

inoxydable et du graphite comme cathodes. On a étudié l'influence de la nature de la cathode du gaz, du courant de lampe et du sel entraîneur pour le dosage du plomb du cuivre, du bore et de l'étain. La précision est de l'ordre de  $\pm 3-5\%$ .

## ZUSAMMENFASSUNG

Es wird die Konstruktion und Arbeitsweise einer abgeschirmten Hohlkathodenröhre zur emissionsspektralanalytischen Spurenbestimmung von Lösungen beschrieben. Die demontierbare Anordnung der Röhre erlaubt es, dass sie als wandelbare Quelle von Linien bei der Atomabsorption verwendet werden kann. Die quantitative Analyse von Lösungen kann durchgeführt werden, nachdem ein kleiner Anteil der Testlösung, welche ein geeignetes Trägersalz enthält in den Raum der Hohlkathode verdampft ist. Sowohl rostfreier Stahl als auch Graphit wurden als Kathoden untersucht. Die Einflüsse des Kathodenmaterials des Füllgases, des Lampenstromes und des Trägersalzes wurden für Lösungen von Blei, Kupfer, Bor und Zinn untersucht. Die Genauigkeit bei quantitativen Analysen liegt bei etwa  $\pm 3-5\%$ .

## REFERENCES

- 1 H. SCHÜLER AND H. GOLLNOW, *Z. Physik*, 93 (1935) 611.
- 2 A. G. SHENSTONE, *Trans. Roy. Soc. (London)*, A 235 (1936) 195.
- 3 H. SCHÜLER, *Z. Physik*, 85 (1926) 323.
- 4 C. C. VAN VOORHES AND A. G. SHENSTONE, *Rev. Sci. Instr.*, 12 (1941) 257.
- 5 K. B. MITCHELL, *J. Opt. Soc. Am.*, 51 (1961) 846.
- 6 I. A. BEREZIN, *Opt. Spectry (USSR) (English Transl.)*, 13 (1962) 483.
- 7 H. M. CROSSWHITE, G. H. DIEKE AND C. S. LEGAGNEUR, *J. Opt. Soc. Am.*, 45 (1955) 270.
- 8 P. A. BÜGER AND W. FINK, *Fresenius' Z. Anal. Chem.*, 244 (1969) 121.
- 9 A. N. STEINBERG, *Opt. Spectry (USSR) (English Transl.)*, 18 (1965) 7.
- 10 M. P. CHAIKA, *Opt. Spectry (USSR) (English Transl.)*, 2 (1957) 421.
- 11 J. R. McNALLY, G. R. HARRISON AND E. ROWE, *J. Opt. Soc. Am.*, 37 (1947) 93.
- 12 G. MILAZZO AND N. SOPRANZI, *Appl. Spectry.*, 21 (4) (1967) 256.
- 13 G. MILAZZO AND N. SOPRANZI, *Appl. Spectry.*, 21 (3) (1967) 185.
- 14 G. A. PEVSTOV AND V. Z. KRASILSCHIK, *Zh. Analit. Khim.*, 19 (1964) 1106.
- 15 J. S. MATIC AND D. S. PESIC, *Appl. Spectry.*, 22 (1968) 63.
- 16 KH. I. ZILBESHTAIN, *Izv. Sibirsk. Otd. Akad. Nauk, Ser. Khim. Nauk*, 4 (1967) 87.
- 17 L. V. RUDNEVSKII, A. N. TUMANOVA, L. V. KUTERGINA AND N. A. POZDNYAKOVA, *Zh. Prikl. Spektrosk.*, 8 (4) (1968) 571.
- 18 J. W. ROBINSON, H. P. LOFTIN, JR. AND D. TRUTT, *Anal. Chim. Acta*, 40 (1968) 24.
- 19 S. L. MANDELSTAM AND V. V. NEDLER, *Spectrochim. Acta*, 17 (1961) 855.
- 20 P. A. BÜGER AND W. FINK, *Z. Anal. Chem.*, 244 (1969) 314.
- 21 J. C. BÜGER, W. GILLS AND G. YAMASAKI, *Westinghouse Product Engineering Memo*, ETD-6702, 1967.
- 22 G. ROSSI AND N. OMENETTO, *Talanta*, 16 (1969) 263.
- 23 M. S. KASHTAN, E. V. SOBOTOVICH AND T. N. KHOLPINA, *Opt. Spectry (USSR) (English Transl.)*, 8 (1960) 1.
- 24 *Tables of Spectral Lines*, N.B.S. Monograph 32, Part 1, U.S. Government Printing Office, Washington, D.C., 1961.
- 25 W. R. BRODE, *Chemical Spectroscopy*, 2nd Edn., John Wiley, New York, 1949.
- 26 W. HARRISON, J. P. YURACHEK AND C. A. BENSON, *Clin. Chim. Acta*, 23 (1969) 83.
- 27 D. C. MANNING, *At. Absorption Newsletter*, 6 (1967) 35.
- 28 H. BADER AND H. BRANDENBERGER, *At. Absorption Newsletter*, 7 (1968) 1.
- 29 W. W. MEINKE AND B. F. SCRIBNER (Editors), *National Bureau of Standards Monograph 100*, U.S. Government Printing Office, Washington, D. C., 1967.
- 30 W. E. CLARKE AND R. NORBURY, *Brit. Cast Iron Res. Assoc. J.*, 12 (1964) 787.

## ULTRAVIOLET EMISSION AND ABSORPTION SPECTRA PRODUCED BY ORGANIC COMPOUNDS IN OXYHYDROGEN FLAMES

### PART II. ABSORPTION SPECTRA. CONTINUOUS SOURCE<sup>1</sup>

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The purpose of the present investigation<sup>2</sup> is three-fold: (a) to indicate sources of spectral interferences in flame photometry and atomic absorption, (b) to add to the knowledge of physical and chemical processes in flames employed for analytical work, and (c) to study the development of analytical methods for the determination of organic compounds by flame spectroscopy.

Spectral interferences are produced in atomic absorption by intense flame emission<sup>3-9</sup> and by scattering and/or absorption of light by droplets, solid particles, flame gases, solvents, and other species formed from flame and sample constituents<sup>3-7,10-24</sup>. Interferences produced by scattering and absorption are particularly severe at low wavelengths and when the path length through the flame is extended by the use of a multipass system or of a horizontal tube.

Absorption by the OH radical has been observed in the 2600-3300 Å region<sup>3,4,11,12,17,25-27</sup>. Absorption of the bismuth 3068 Å line by OH radicals has been reported<sup>4,12,17</sup>.

KNISELEY AND FASSEL *et al.*<sup>6,28</sup> observed absorption by C<sub>2</sub> and CN radicals in fuel-rich oxyacetylene and nitrous oxide-acetylene flames. FUWA AND VALLEE<sup>29</sup> observed a detection limit of 10 μg of sulfur dioxide by measuring molecular absorption spectra produced by compounds containing sulfur in air-hydrogen flames.

#### EXPERIMENTAL CONDITIONS

The experimental conditions were the same as those used to obtain the data reported in Part I<sup>2</sup>.

Two continuous light sources were used, a hydrogen lamp with the Beckman Power Supply Serial No. PS454-Model A and tungsten lamp.

In order to obtain detailed band spectra of organic fragments, it was necessary to decrease the cross-section of the beam from the hydrogen or tungsten lamp. An aperture 0.1-0.6 cm in diameter was placed between the lamp and the lens focussing the beam in the flame. The necessity of using a beam of small diameter indicates that the species absorbing are concentrated in a relatively small region of the flame. A similar effect has been described by RANN AND HAMBLY<sup>26</sup>.

Absorption spectra were obtained for organic solvent sprays as well as for flames by aspirating the solvents into the light path with oxygen. The hydrogen flow rate was zero, and there was no flame burning.

In order to determine whether any emission was detected from the unmodulated flames, the light from the lamp was blocked and any signal from the flames was recorded.

## RESULTS AND DISCUSSION

### *Wavelengths of band maxima and identification of the species absorbing*

The prominent absorption bands that were observed are listed in Table I by wavelength and absorbing species. The 3064 Å OH system was observed in absorption spectra from the oxyhydrogen flame<sup>30</sup>.

When compounds containing carbon, hydrogen, and/or oxygen atoms were aspirated into the flame, absorption bands of the 3900 Å CH, 4300 Å CH, and Swan C<sub>2</sub> systems were produced<sup>6,30,31</sup>, as shown in Fig. 14.

When solvents containing nitrogen atoms were aspirated into the flame, the 3360 Å NH system<sup>30</sup>, the violet CN system (some absorption from the CH fragment was possibly detected in this region also)<sup>6,30</sup>, and a band at 4500 Å, which was probably due to NH<sup>30</sup>, were observed, as shown in Figs. 1, 2, 5 and 15.

When tributyl or triethyl phosphate was introduced into the flame, the β and γ systems of PO and a band at 3400 Å, which was probably the 3400 Å PH system (some absorption by PO was possibly detected in this region also), were observed in the absorption spectra<sup>30</sup>, as shown in Figs. 3 and 7.

Solvents containing sulfur produced absorption bands of the CS fragment and a band at 3280 Å, which was part of the 3237 Å SH system (some absorption by SO was possibly detected in this region also)<sup>30</sup>, as shown in Fig. 8.

TABLE I

ABSORPTION BANDS PRODUCED BY OXYHYDROGEN FLAMES INTO WHICH ORGANIC COMPOUNDS WERE INTRODUCED

| <i>Wavelength of band maxima (Å)<sup>a</sup></i> | <i>Absorbing species</i> | <i>Wavelength of band maxima (Å)<sup>a</sup></i> | <i>Absorbing species</i> | <i>Wavelength of band maxima (Å)<sup>a</sup></i> | <i>Absorbing species</i> | <i>Wavelength of band maxima (Å)<sup>a</sup></i> | <i>Absorbing species</i> |
|--|--------------------------|--|--------------------------|--|--------------------------|--|--------------------------|
| 2370   | PO                       | 3150   | OH                       | 3860   | CN                       | 4680   | C <sub>2</sub>           |
| 2460   | PO                       | 3190   | OH                       | 3870   | CN                       | 4700   | C <sub>2</sub>           |
| 2530   | PO                       | 3250   | PO                       | 3870   | CH                       | 4720   | C <sub>2</sub>           |
| 2580   | CCl                      | 3260   | PO                       | 3880   | CN                       | 4740   | C <sub>2</sub>           |
| 2580   | CS                       | 3270   | PO                       | 3890   | CH                       | 5100   | C <sub>2</sub>           |
| 2600   | CS                       | 3280   | SH                       | 4150   | CN                       | 5130   | C <sub>2</sub>           |
| 2620   | OH                       | 3360   | NH                       | 4170   | CN                       | 5160   | C <sub>2</sub>           |
| 2690   | OH                       | 3370   | NH                       | 4180   | CN                       | 5500   | C <sub>2</sub>           |
| 2820   | OH                       | 3400   | PH                       | 4200   | CN                       | 5540   | C <sub>2</sub>           |
| 2840   | OH                       | 3430   | OH                       | 4220   | CN                       | 5580   | C <sub>2</sub>           |
| 3070   | OH                       | 3480   | OH                       | 4310   | CH                       | 5640   | C <sub>2</sub>           |
| 3090   | OH                       | 3590   | CN                       | 4370   | CH                       | 5900   | Na                       |
| 3120   | OH                       | 3850   | CN                       | 4500   | NH                       |  |                          |

<sup>a</sup>Wavelengths were measured to ± 30 Å.

Solvents containing chlorine produced an absorption band at 2580 Å which was attributed to the CCl radical<sup>30</sup>.

Absorption at 5900 Å by sodium impurity was frequently observed.

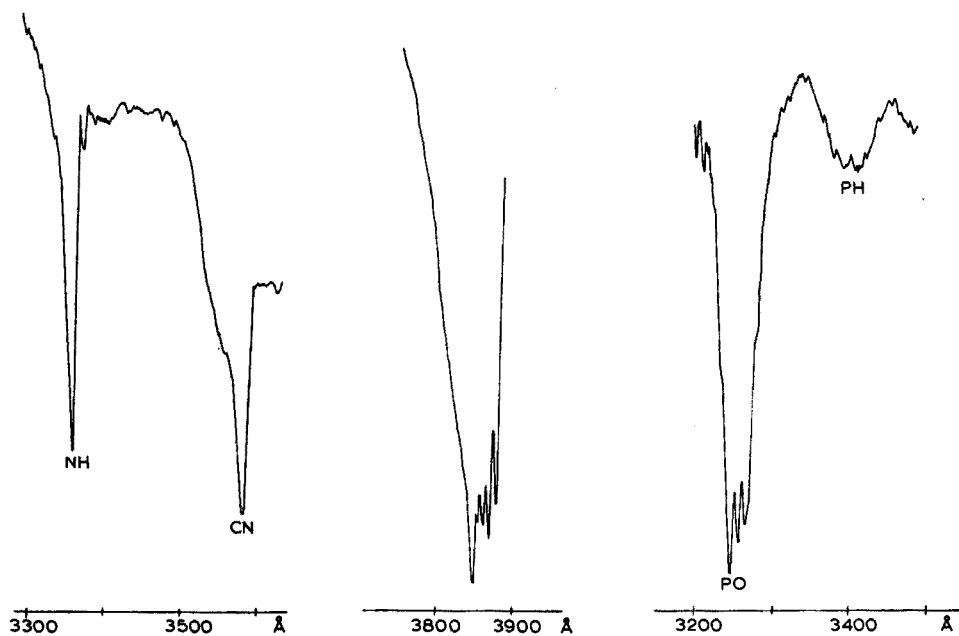


Fig. 1. Absorption bands produced by NH and CN fragments. Pyridine was sprayed into the flame. Flame height: 0.75 cm.

Fig. 2. Absorption bands produced by CN fragments. Pyridine was sprayed into the flame. Flame height: 0.75 cm.

Fig. 3. Absorption bands produced by PO and PH fragments. Triethyl phosphate was sprayed into the flame. Flame height: 0.75 cm.

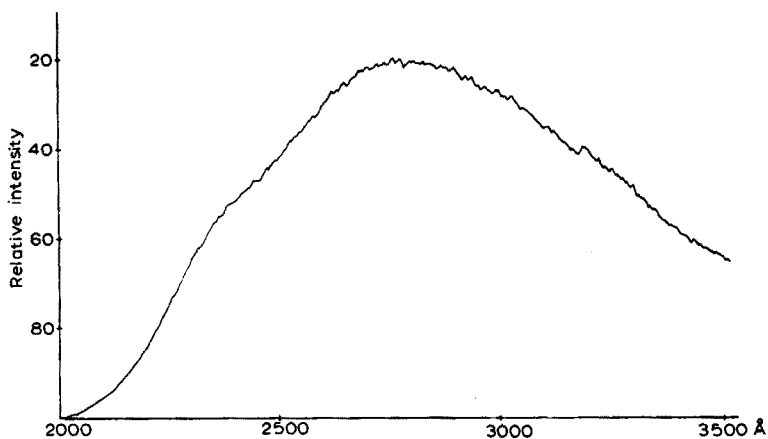


Fig. 4. Hydrogen lamp. No flame. Slit 0.40 mm. Gain 6.3.

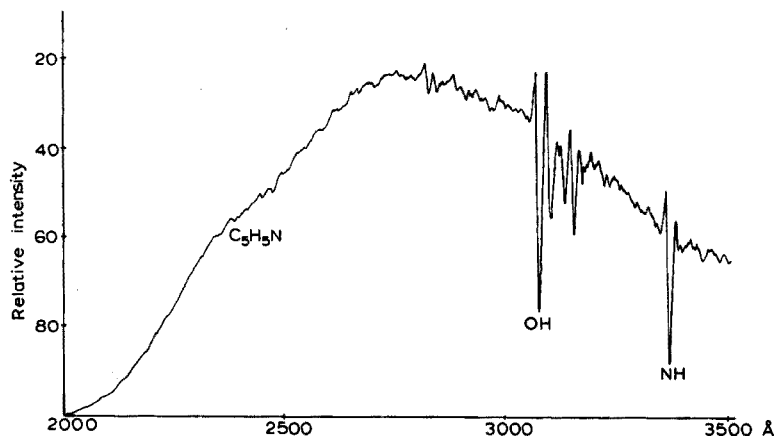


Fig. 5. Flame absorption spectrum of pyridine 0.75 cm above the burner. Slit 0.40 mm. Gain 6.3. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

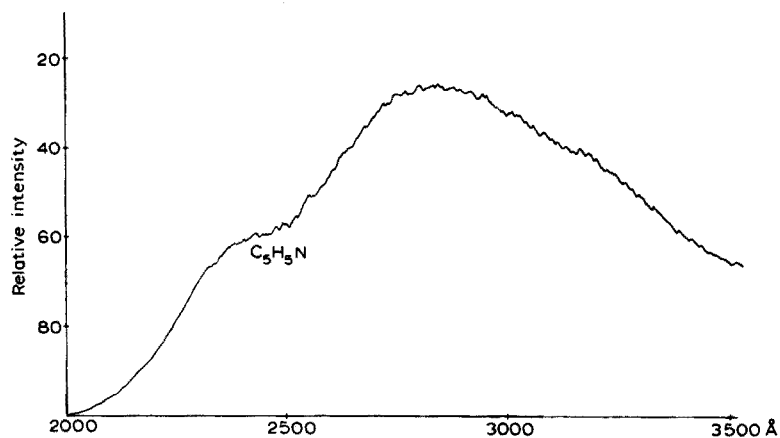


Fig. 6. Absorption spectrum of pyridine 0.75 cm above the burner. No flame. Slit 0.40 mm. Gain 6.3. Oxygen: 3.5 l/min.

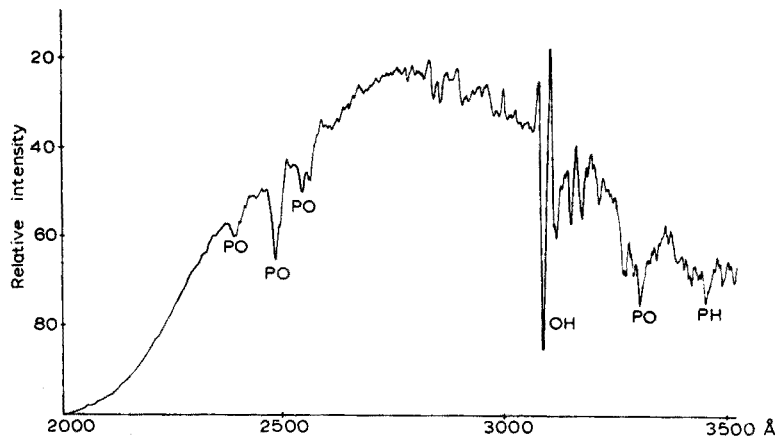


Fig. 7. Flame absorption spectrum of tributyl phosphate 0.75 cm above the burner. Slit 0.40 mm. Gain 6.3. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.



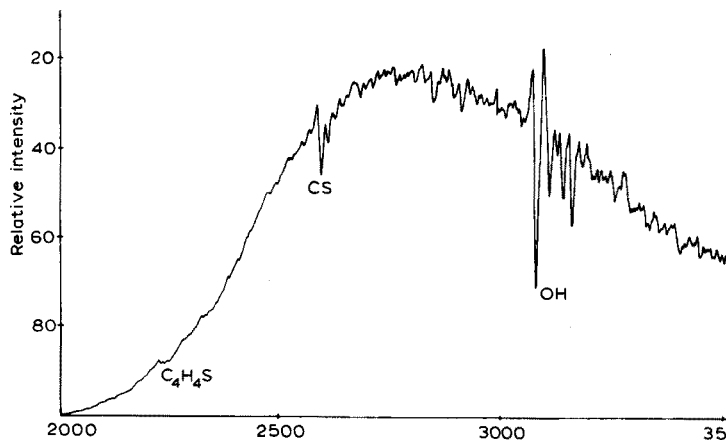


Fig. 8. Flame absorption spectrum of thiophene 0.75 cm above the burner. Slit 0.40 mm. Gain 6.3. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

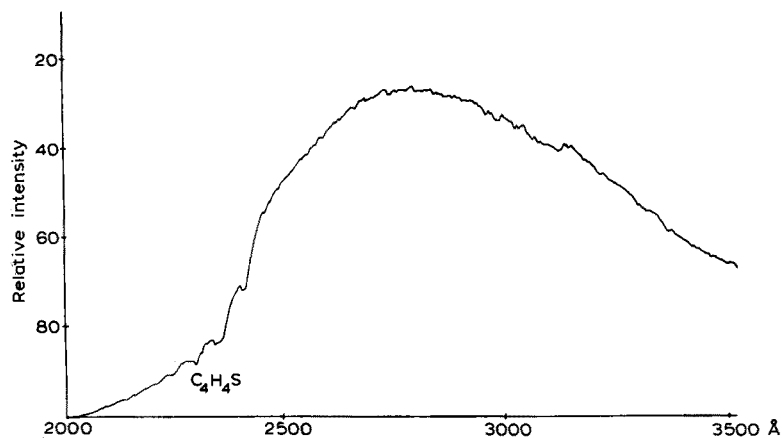


Fig. 9. Absorption spectrum of thiophene 0.75 cm above the burner. No flame. Slit 0.40 mm. Gain 6.3. Oxygen: 3.5 l/min.

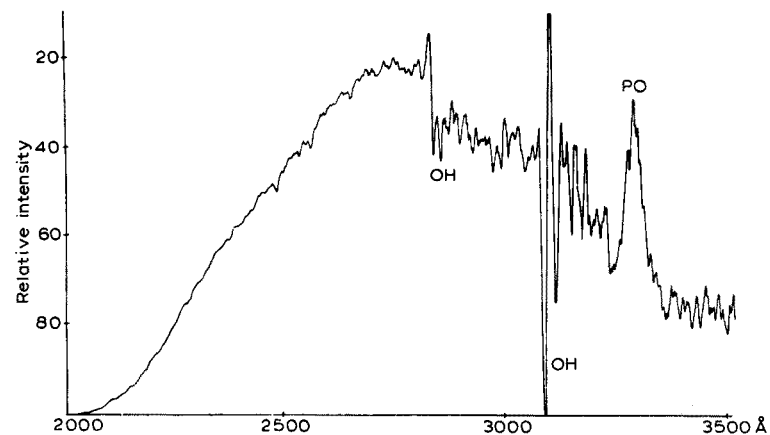


Fig. 10. Flame absorption spectrum of pyridine 2 cm above the burner. Slit 0.40 mm. Gain 6.3. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

*Comparisons between absorption spectra produced by different compounds*

Figures 4–22 show absorption spectra obtained at flame heights of (a) 0.75 and (b) 2.0 cm when benzene, pyridine, tributyl phosphate, thiophene and dimethyl sulfoxide were introduced into the flame. The diameter above the burner of the beam from the hydrogen or tungsten lamp was 0.1–0.2 cm. Emission spectra from the unmodulated flames were obtained by blocking the beam from the lamp and recording any signal that was detected. At sensitive instrument settings, *i.e.* wide slits and high gains, appreciable emission was detected, as shown in Figs. 11 (PO), 15 (CN), and 18. Absorption spectra were obtained for whole organic molecules by aspirating the

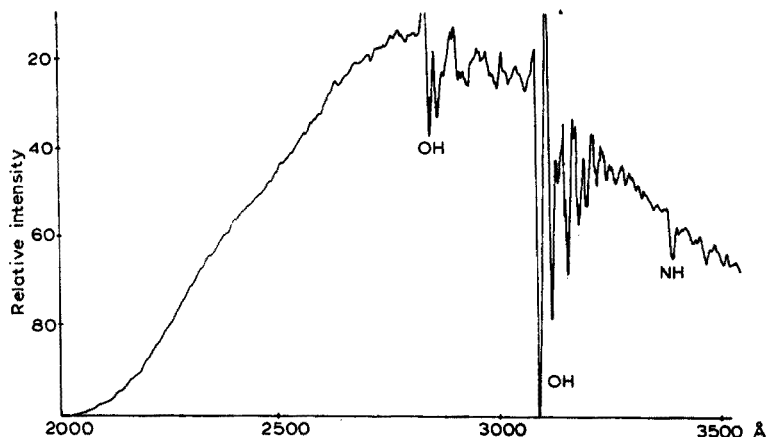


Fig. 11. Flame absorption spectrum of tributyl phosphate 2 cm above the burner. Slit 0.40 mm. Gain 6.3. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

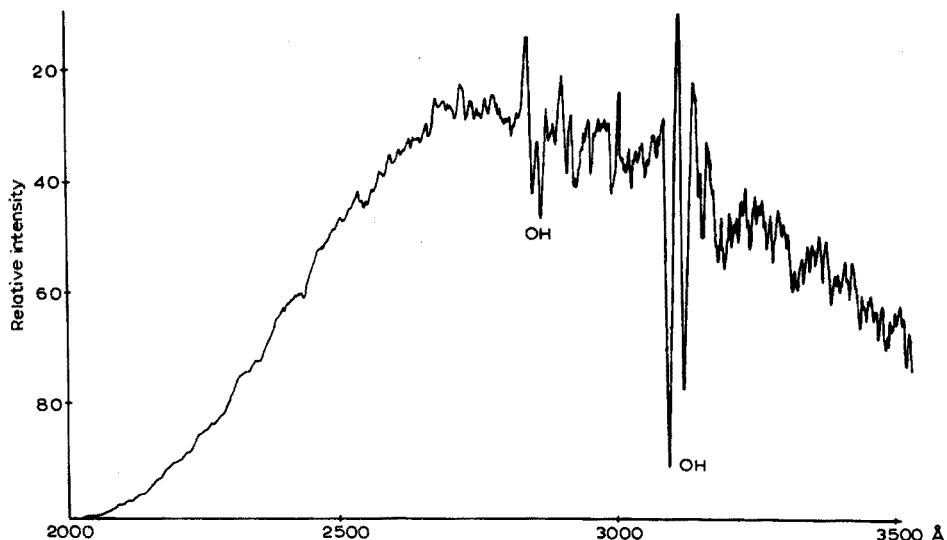


Fig. 12. Flame absorption spectrum of thiophene 2 cm above the burner. Slit 0.40 mm. Gain 6.3. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

sample into the light path with no flame burning. The oxygen flow rate was 3.5 l/min and the hydrogen flow rate was zero.

Figures 4-12 show spectra obtained with the hydrogen lamp in the 2000-3500 Å region. Absorption by the OH fragment was more intense at a flame height of 2 cm than at a flame height of 0.75 cm. However, absorption by the other fragments examined was more intense at a flame height of 0.75 cm, which was within the reaction zone. Figure 11 shows emission between 3200 and 3400 Å detected from excited PO fragments in the flame.

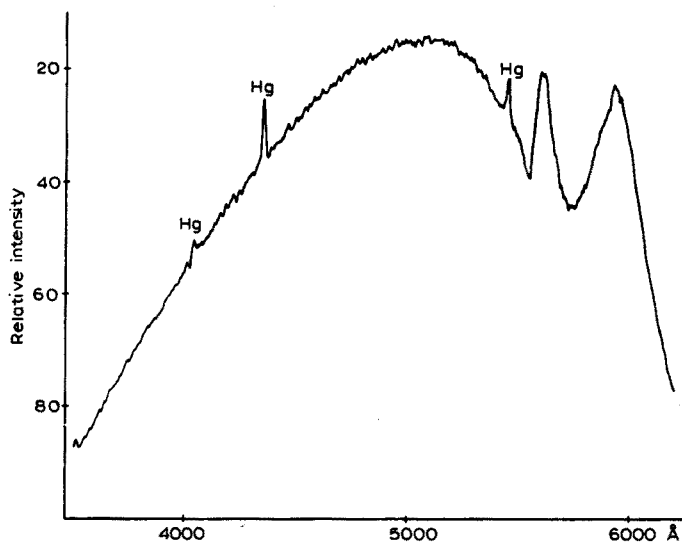


Fig. 13. Tungsten lamp. No flame. Slit 0.50 mm. Gain 7.4.

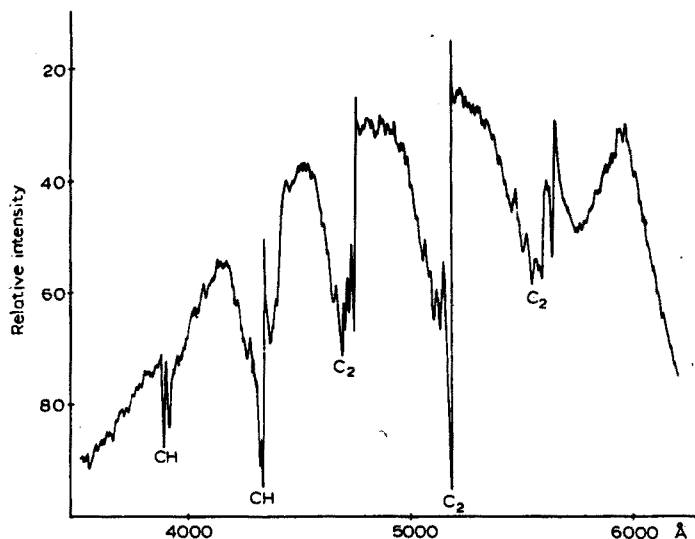


Fig. 14. Flame absorption spectrum of benzene 0.75 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

When pyridine or thiophene was aspirated into the flame absorption was observed in the 2300–2800 Å and 2000–25000 Å regions, respectively. Strong absorption was produced in the same regions by the pyridine and thiophene sprays with no flame burning, as shown in Figs. 6 and 9. Absorption at these wavelengths agrees with the Sadtler u.v. spectra<sup>32</sup> for pyridine and thiophene. There was less absorption by pyridine and thiophene molecules in the flame at a height of 2 cm than at 0.75 cm, presumably

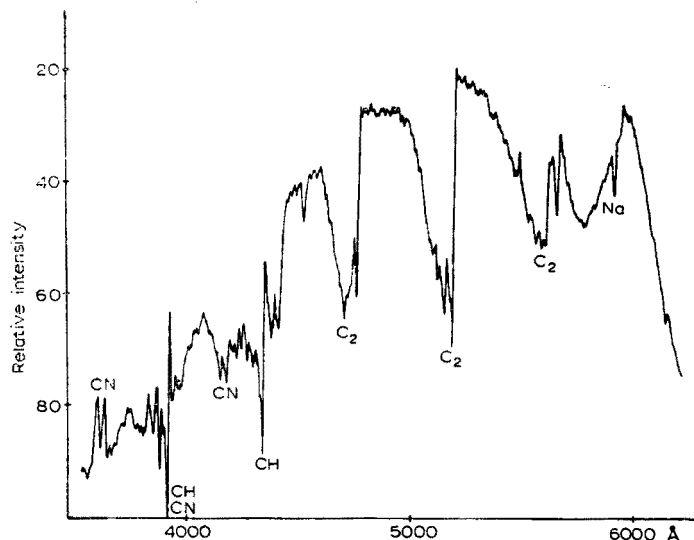


Fig. 15. Flame absorption spectrum of pyridine 0.75 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

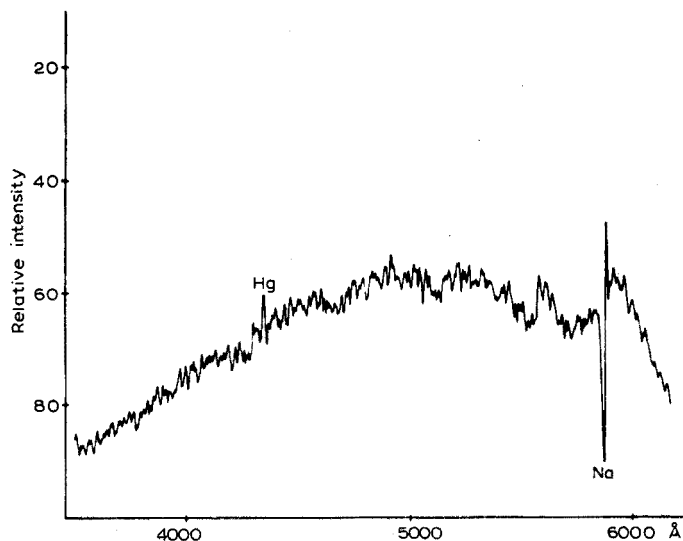


Fig. 16. Flame absorption spectrum of tributyl phosphate 0.75 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

because more of the solvent had been burned. No significant absorption was observed for benzene, tributyl phosphate, or dimethyl sulfoxide sprays.

In Figs. 13–22 are shown absorption spectra obtained with the tungsten lamp in the 3500–6200 Å region. No absorption was observed for the oxyhydrogen flame by itself or for the solvent sprays. Figure 15 shows emission in the 3590 Å region from excited CN radicals in the flame. Figure 18 shows emission detected from the un-

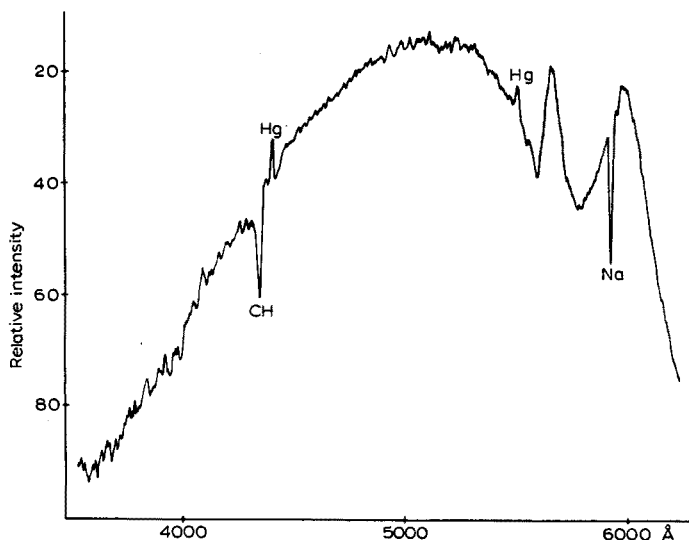


Fig. 17. Flame absorption spectrum of dimethyl sulfoxide 0.75 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

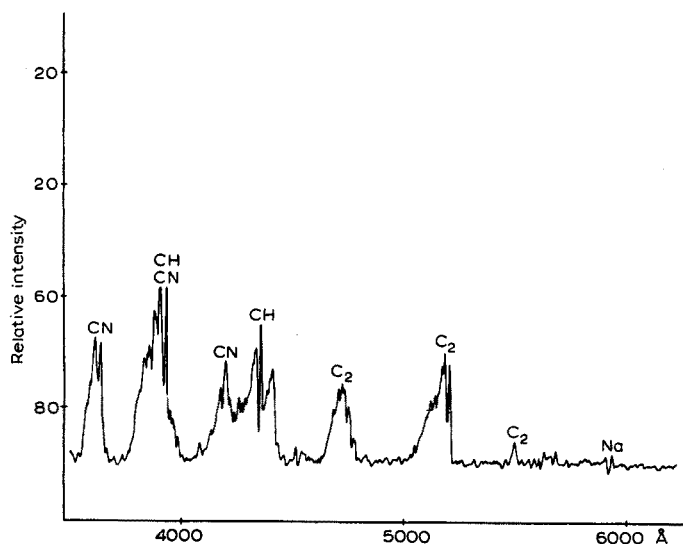


Fig. 18. Emission spectrum of pyridine from the unmodulated flame 0.75 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

modulated flame when pyridine was introduced and the beam from the lamp was blocked.

Absorption over a relatively wide spectral region produced by solvents containing phosphorus or sulfur was attributed to PO and SO<sub>2</sub> fragments<sup>29,30,33</sup>.

### Absorption profiles

Absorption profiles were obtained at several wavelengths by measuring in-

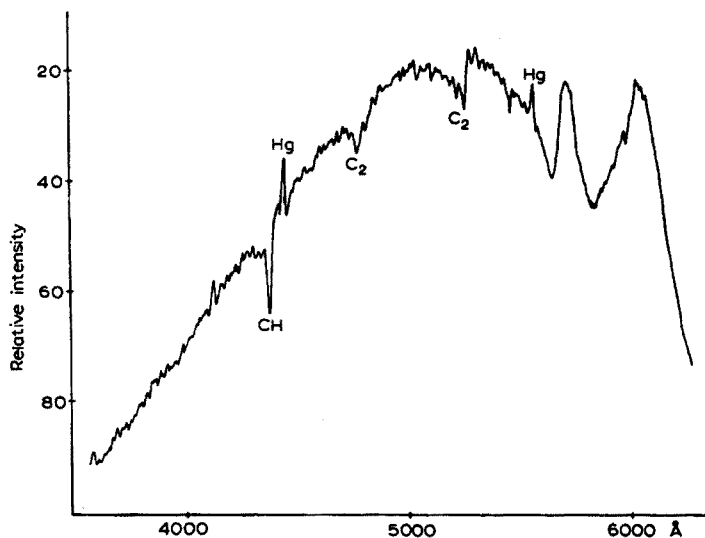


Fig. 19. Flame absorption spectrum of benzene 2 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

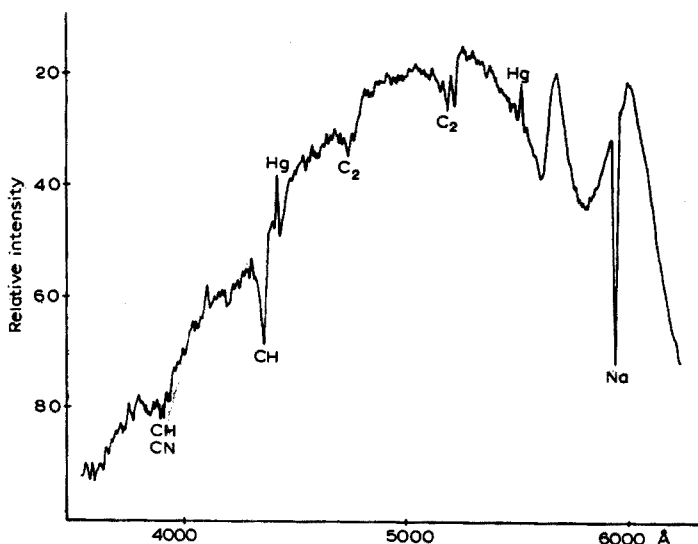


Fig. 20. Flame absorption spectrum of pyridine 2 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

tensities of absorption at selected flame heights. The diameter of the beam in the flame from the hydrogen or tungsten lamp was 0.1–0.2 cm. The emission signal detected from the unmodulated flame was also recorded. Absorption and emission signals obtained from the flame by itself were subtracted from emission and absorption signals produced when the compound was introduced. The resulting emission and absorption values were attributed to the compound and were summed. The sum was plotted as a function of flame height, as shown in Figs. 23–27.

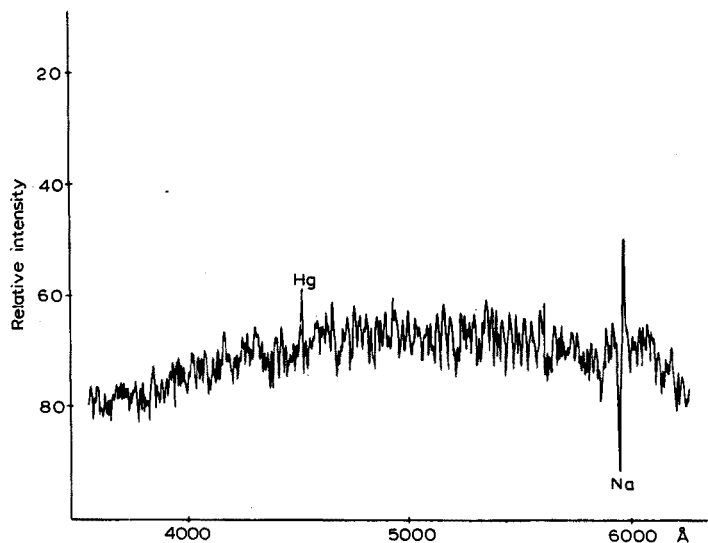


Fig. 21. Flame absorption spectrum of tributyl phosphate 2 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

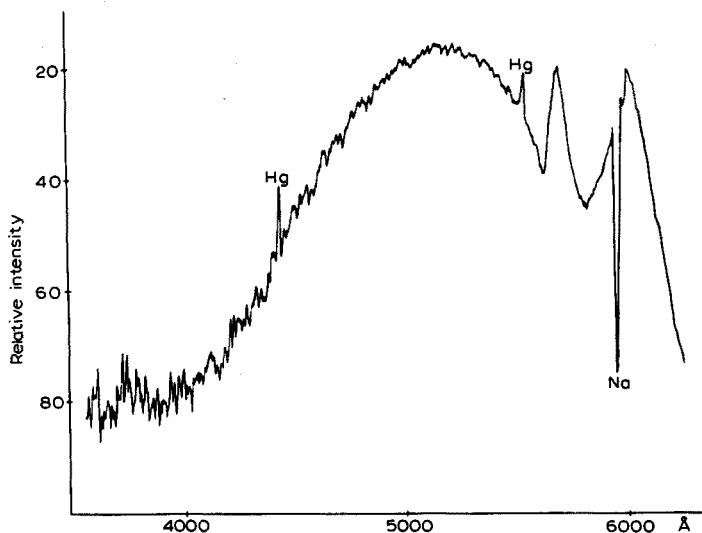


Fig. 22. Flame absorption spectrum of dimethyl sulfoxide 2 cm above the burner. Slit 0.50 mm. Gain 7.4. Oxygen: 3.5 l/min. Hydrogen: 10 l/min.

Maximum absorption by OH fragments occurred between flame heights of 1 and 3.5 cm, as shown in Fig. 23. The absorption profile for OH fragments agrees with spectra obtained at various flame heights, as shown in Figs. 4-12. A comparison of the emission profile<sup>2</sup> and the absorption profile for OH fragments shows that maximum emission and maximum absorption occurred approximately within the same region of the flame, that is, between 2 and 3.5 cm above the tip of the burner.

Maximum absorption by CH, C<sub>2</sub>, CN, NH, PO (2460 Å), and CS fragments occurred between 0.5 and 2.0 cm above the burner, as shown in Figs. 24-26. This was within the reaction zone of the flame. The absorption profiles agree with spectra obtained at different flame heights, as shown in Figs. 4-22. Absorption profiles and emission profiles<sup>2</sup> for CH, C<sub>2</sub>, CN, and NH fragments are similar. Maximum emission and absorption occurred within the reaction zone. Absorption profiles at 2460 Å (PO) and 2590 Å (CS, SO<sub>2</sub>) are not as similar to emission profiles<sup>2</sup> at the same wavelengths; however both maximum emission and maximum absorption occurred in the reaction zone.

Absorption profiles (Fig. 27) at 3270 Å (PO) and 3280 Å (SH, SO<sub>2</sub>) for solvents containing phosphorus and sulfur show maximum absorption between 0.5 and 3 cm above the tip of the burner. The corresponding emission profiles<sup>2</sup> exhibit maxima slightly higher in the flame.

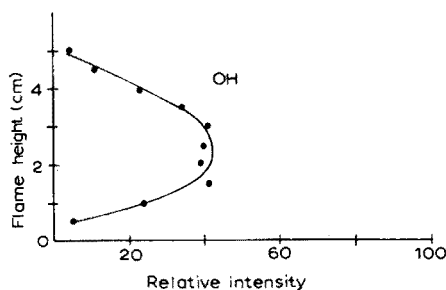


Fig. 23. Flame absorption profile at 3090 Å. No solvent. Slit 0.50 mm. Gain 5.9.

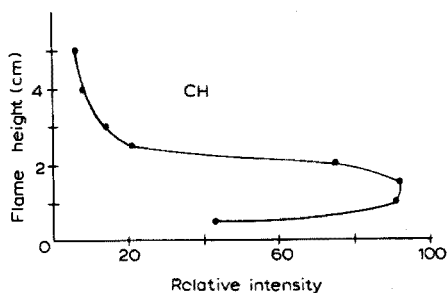


Fig. 24. Flame absorption profile at 4310 Å. Benzene was sprayed into the flame. Slit 1.25 mm. Gain 6.1.

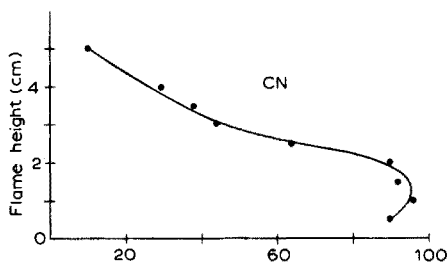


Fig. 25. Flame absorption profile at 3860 Å. Pyridine was sprayed into the flame. Slit 0.75 mm. Gain 7.2.

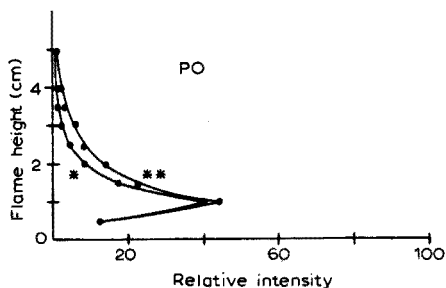


Fig. 26. Flame absorption profile at 2460 Å. Tributyl\* phosphate and triethyl\*\* phosphate were sprayed into the flame. Slit 0.75 mm. Gain 5.8.



Some differences in emission and absorption profiles might be attributed to the different experimental conditions involved. In the absorption studies the source beam was concentrated in a very small area of the flame, whereas a relatively wide section of the flame was observed in the emission profile studies, possibly allowing appreciable background, or continuous, emission to be detected. Background absorption may have been detected at 3270 and 3280 Å in the studies of the phosphorus and sulfur compounds.

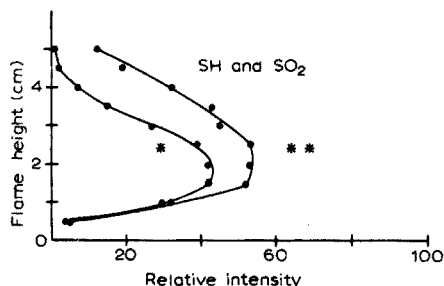


Fig. 27. Flame absorption profile at 3280 Å. Dimethyl sulfoxide\* and thiophene\*\* were sprayed into the flame. Slit 0.75 mm. Gain 5.8.

#### SUMMARY

Ultraviolet absorption spectra produced by aspirating organic compounds into oxyhydrogen flames have been investigated. Spectra are presented and compared. The prominent bands observed are listed by wavelength and absorbing species. Flame absorption profiles for organic and inorganic fragments are presented. Maximum absorption by organic fragments occurred in the reaction zone of the flame. Absorption by OH fragments and by fragments containing phosphorus or sulfur was intense above and within the reaction zone of the flame. Absorption by whole solvent molecules in the flame was observed.

#### RÉSUMÉ

On a examiné les spectres d'absorption dans l'ultra-violet de composés organiques aspirés dans des flammes oxyhydrogène. L'absorption maximum de particules organiques se produit dans la zone de réaction de la flamme. L'absorption par OH et par particules renfermant phosphore et soufre est intense au-dessus et dans la zone de réaction. On examine également l'absorption par des molécules de solvants.

#### ZUSAMMENFASSUNG

Es wurden ultraviolette Absorptionsspektren, welche durch organische Verbindungen in der Sauerstoff-Wasserstoff-Flamme erzeugt werden, untersucht. Die Spektren werden angegeben und verglichen. Die Hauptbanden, welche beobachtet wurden, werden unter Angabe der Wellenlänge und der absorbierenden Spezies tabelliert. Die Profile der Flammenabsorption für organische und anorganische Fragmente

werden aufgeführt. Eine maximale Absorption durch organische Fragmente tritt in der Reaktionszone der Flamme in Erscheinung. Die Absorption durch OH-Fragmente und durch solche, die Phosphor oder Schwefel enthalten, war besonders intensiv oberhalb oder innerhalb der Reaktionszone der Flamme. Absorption durch ganze Lösungsmittelmoleküle in der Flamme wurden beobachtet.

## REFERENCES

- 1 Taken in part from the *Ph.D. Dissertation* of V. J. SMITH, Louisiana State University, Baton Rouge, 1969.
- 2 V. J. SMITH AND J. W. ROBINSON, *Anal. Chim. Acta*, 48 (1969) 391.
- 3 J. W. ROBINSON, *Atomic Absorption Spectroscopy*, Marcel Dekker, New York, 1966.
- 4 W. T. ELWELL AND J. A. F. GIDLEY, *Atomic-Absorption Spectrophotometry*, 2nd rev. Edn., Pergamon Press, Oxford, 1966.
- 5 C. L. CHAKRABARTI, *Appl. Spectry.*, 21 (1967) 160.
- 6 J. A. FIORINO, R. N. KNISELEY AND V. A. FASSEL, *Spectrochim. Acta*, 23B (1968) 413.
- 7 W. SLAVIN, *Atomic Absorption Spectroscopy*, Interscience, New York, 1968.
- 8 G. F. KIRKBRIGHT, M. K. PETERS AND T. S. WEST, *Talanta*, 14 (1967) 789.
- 9 J. D. WINEFORDNER AND C. VEILLON, *Anal. Chem.*, 36 (1964) 943.
- 10 C. L. CHAKRABARTI, J. W. ROBINSON AND P. W. WEST, *Anal. Chim. Acta*, 34 (1966) 269.
- 11 G. F. KIRKBRIGHT AND T. S. WEST, *Appl. Opt.*, 7 (1968) 1305.
- 12 R. M. DAGNALL, K. C. THOMPSON AND T. S. WEST, *Talanta*, 14 (1967) 1467.
- 13 J. B. WILLIS, in *Methods of Biochemical Analysis*, Vol. 11, Interscience, New York, 1963, p. 1.
- 14 J. E. SCHALLIS AND H. L. KAHN, *At. Absorption Newsletter*, 7 (1968) 75.
- 15 M. D. AMOS, *The Element-Technical News Notes from Aztec Instruments, Inc.*, No. 16.
- 16 J. E. ALLAN, *Spectrochim. Acta*, 17 (1961) 467.
- 17 S. R. KOIRTYOHANN AND C. FELDMAN, *Develop. Appl. Spectry.*, 3 (1964) 180.
- 18 I. RUBESKA AND B. MOLDAN, *Appl. Opt.*, 7 (1968) 1341.
- 19 J. A. DEAN, *Develop. Appl. Spectry.*, 5 (1966) 317.
- 20 R. A. G. RAWSON, *Analyst*, 91 (1966) 630.
- 21 C. L. CHAKRABARTI, *Anal. Chim. Acta*, 39 (1967) 293.
- 22 C. S. RANN AND A. N. HAMBLY, *Anal. Chim. Acta*, 32 (1965) 346.
- 23 J. RAMÍREZ-MUÑOZ, *Atomic-Absorption Spectroscopy*, Elsevier, Amsterdam, 1968.
- 24 G. F. KIRKBRIGHT, M. SARGENT AND T. S. WEST, *At. Absorption Newsletter*, 8 (1969) 34.
- 25 D. J. HALLS AND E. PUNGOR, *Anal. Chim. Acta*, 44 (1969) 40.
- 26 C. S. RANN AND A. N. HAMBLY, *Anal. Chem.*, 37 (1965) 879.
- 27 I. RUBESKA AND B. MOLDAN, *Analyst*, 93 (1968) 148.
- 28 T. G. COWLEY, V. A. FASSEL AND R. N. KNISELEY, *Spectrochim. Acta*, 23B (1968) 771.
- 29 K. FUWA AND B. L. VALLEE, *Anal. Chem.*, 41 (1969) 188.
- 30 R. W. B. PEARSE AND A. G. GAYDON, *The Identification of Molecular Spectra*, 3rd Edn., Chapman and Hall, London, 1963.
- 31 P. F. JESSEN AND A. G. GAYDON, *Combust. Flame*, 11 (1967) 11.
- 32 *Ultra Violet Spectra*, Sadtler Research Laboratories, Philadelphia.
- 33 A. G. GAYDON, *The Spectroscopy of Flames*, John Wiley, New York, 1957.

## DETERMINATION OF GOLD BY ATOMIC FLUORESCENCE SPECTROSCOPY IN PREMIXED FLAMES\*

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The determination of gold by atomic fluorescence spectroscopy has been investigated mostly in turbulent flames. WINEFORDNER *et al.*<sup>1-3</sup> excited atomic fluorescence of gold both with a 150-W xenon arc and an electrodeless discharge tube in a turbulent oxy-hydrogen flame; they obtained detection limits of 3.5 p.p.m. for the continuous and 0.2 p.p.m. for the line excitation source. The best detection limit of 0.05 p.p.m. at the gold line 2676.0 Å has been reported by DINNIN<sup>4</sup> who used a demountable hot hollow-cathode lamp and a turbulent air-hydrogen flame. In premixed air-hydrogen flames, MANNING AND HENEAGE<sup>5</sup> found relatively poorer detection limits when they excited the fluorescence with a 150-W xenon arc or a shielded hollow-cathode lamp.

The purpose of this study was to increase the sensitivity of the determination, by means of a more intense excitation source and flames with a lower noise level and lower quenching efficiency.

### EXPERIMENTAL

#### *Apparatus*

A Techtron AA-4 atomic absorption spectrophotometer equipped with an A.S.L. high-intensity gold hollow-cathode lamp and an HTV R 106 photomultiplier was coupled to an Hitachi Perkin-Elmer, Model 165 recorder. The lamp and amplifier were square-wave modulated at 285 Hz. The lamp was situated as closely as possible to the flame and the fluorescence emission was focussed with a condensing quartz lens behind the entrance slit of the monochromator. A spherical aluminum mirror in the optical path of the exciting beam increased the fluorescence emission by approximately 100%. The mirror in the optical path of the fluorescence radiation enhanced the measured fluorescence signal by 70%.

The high-intensity hollow-cathode lamp was operated at the maximum currents recommended by the manufacturers, 20 mA for the primary and 500 mA for the secondary discharge. The monochromator slit-width was set to its maximum value of 300  $\mu$ , which corresponds to a band-width of 9.9 Å.

The instrument settings used for atomic absorption measurements were: primary lamp current, 4 mA; booster current, 500 mA; slit-width, 100  $\mu$  (1.7 Å); 10-cm air-acetylene burner.

\* Presented at the International Atomic Absorption Symposium, Sheffield, July, 1969.

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### Reagents

Gold metal, analytical grade. A 1000 p.p.m. gold stock solution was prepared by dissolving 0.2500 g of metal in the minimal amount of *aqua regia* and diluting to 250 ml with water. More dilute solutions were prepared, as required, by appropriate dilution of the stock. Addition of *ca.* 10 ml of *aqua regia* per l of dilute solutions containing 0.05–100 p.p.m. of gold was found to be necessary. All other solutions were prepared from analytical-reagent-grade chemicals.

### Flame conditions

Nitrogen-separated air–acetylene and air–hydrogen flames, and oxy–hydrogen flame diluted with argon were used. For the separated air–acetylene flame, the Techtron FE-1 emission burner head for the air–acetylene flame was fitted with a chamber with five concentric rows of holes and tangential nitrogen inlet to enable separation of the flame. For the air–hydrogen and hydrogen–oxygen–argon flames, a specially manufactured Meker-type brass burner head was also fitted with this chamber.

The dependence of background emission of the flames and of the fluorescence signal on the fuel-to-oxidant ratio was investigated to find the optimum gas flow rates. The fluorescence signal of gold in the air–hydrogen and air–acetylene flames at the optimum air flow rate decreased slowly with increasing fuel flow rate. The fluorescence signal in the hydrogen–oxygen–argon flame at the optimum oxygen flow rate strongly depended on the hydrogen flow rate and the dependence exhibited a maximum.

The height of measurement in the flame was not a critical factor with regard to the fluorescence signal. To avoid emission of the primary reaction zone, measurements for all flames were performed 15–25 mm above the burner top.

## RESULTS AND DISCUSSION

### Atomic fluorescence lines

The relative intensities of lines emitted by the high-intensity gold hollow-cathode lamp and of corresponding fluorescence lines were determined to choose the most sensitive fluorescence lines and to evaluate quantum efficiencies of the fluorescence process. The results for the hydrogen–oxygen–argon flame corrected for detector response are listed in Table I. Four lines exhibit atomic fluorescence, the two resonance lines being the most intense. For the resonance doublet it can be seen that the quantum efficiency of the fluorescence process for the 2428.0 Å line is practically two-fold the quantum efficiency for the 2676.0 Å line. This is in contrast to the observation of

TABLE I

RELATIVE EMISSION AND FLUORESCENCE INTENSITIES OF GOLD LINES

| Line (Å) | Energy levels (eV) | Relative emission intensity | Relative fluorescence intensity |
|----------|--------------------|-----------------------------|---------------------------------|
| 2428.0   | 0–5.105            | 100                         | 100                             |
| 2676.0   | 0–4.632            | 96                          | 52                              |
| 3029.2   | 1.136–5.227        | 42                          | 1                               |
| 3122.8   | 1.136–5.105        | 12                          | 5                               |

WEST AND WILLIAMS<sup>6</sup> who found the same quantum efficiency for both components of the resonance doublet of silver. This can be partly explained by the fact that the separation of the two components of the  $6p\ ^2P^0$  term of gold is greater than that of the two components of the  $5p\ ^2P^0$  term of silver. The separation is 0.47 eV for gold against 0.11 eV for silver.

The 3122.8 Å line is due to direct-line fluorescence: excitation with the 2428.0 Å line to the  $6p\ ^2P^0_{1/2}$  state followed by a radiative transition to the metastable  $6s^2\ ^2D_{3/2}$  state. For the 3029.2 Å line, the upper energy level lies 0.122 eV higher than the upper energy level of the 2428.0 Å resonance line (Table I). In this case, thermally assisted direct-line fluorescence, postulated by DAGNALL *et al.*<sup>7,8</sup> for the explanation of some fluorescence transitions of antimony and bismuth, must be assumed. Radiational excitation with the 2428.0 Å line combines with the thermal excitation. The upper energy levels for the other possible transitions lie too high and therefore no fluorescence emission was observed at corresponding wavelengths.

#### Analytical working curves and detection limits

In Fig. 1, analytical working curves are shown for the most sensitive gold resonance line at 2428.0 Å in the three flames. The starting points of the three curves correspond to the detection limits in the given flames. The detection limit is considered as the concentration for which the signal-to-noise ratio is equal to 2. The shapes of the working curves are in very good agreement with those derived by HOOYMAYERS<sup>9</sup> for the case when the source-line half-width is narrow compared to the absorption line half-width and for the  $a$ -parameter between 0 and 1.0.

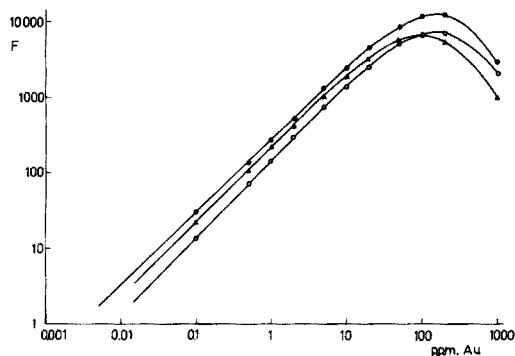


Fig. 1. Analytical working curves for gold resonance line 2428.0 Å with various flames. (○) Air-hydrogen, (●) hydrogen-oxygen-argon, (Δ) air-acetylene.

From the theoretical results<sup>9</sup> it is apparent that differences in the shapes and positions of the analytical curves for the same line excited in various flames by the same spectral source and with the same optical arrangement, are caused by differences in the ground-state atom concentration, fluorescence yield factor and  $a$ -parameter. For the 2428.0 Å line, the fluorescence signal in the separated air-acetylene flame is higher than the corresponding fluorescence signal in the air-hydrogen flame for the linear portion of the curves. This is caused by the higher efficiency of atomization in the hotter air-acetylene flame. This assumption is confirmed by the fact that the

maximum signal obtained is practically the same in both flames. For the air-acetylene flame the total absorption is reached at lower concentrations of gold in solution than for the air-hydrogen flame. The highest signal was obtained in the oxy-hydrogen flame diluted with argon because of the smaller quenching cross-section of argon than of nitrogen. This lower quenching efficiency of argon is the main factor causing the differences in the analytical curves for the air-hydrogen and hydrogen-oxygen-argon flames because the maxima of the curves lie at the same concentration of gold in solution.

An approximately 2.5-fold increase in the fluorescence signal with the hydrogen-oxygen-argon flame compared to the air-hydrogen flame, was observed for the 2428.0, 2676.0 and 3122.8 Å lines. Since the noise of measurement for both flames is practically the same, the higher signal in the hydrogen-oxygen-argon flame results in lower detection limits. The use of the nitrogen sheath makes both air-hydrogen and hydrogen-oxygen-argon flames steadier and enables improvement in the detection limits. For the 3122.8 Å line, of course, it is necessary to use the separated air-hydrogen flame because the line lies in the OH band region. It would not be necessary to separate the hydrogen-oxygen-argon flame, because at the optimum gas flow rates the emission of the OH bands is very low.

In Table II, a comparison is made between detection limits for atomic fluorescence with various flames, and atomic absorption with the same instrument, the same spectral source and a 10-cm air-acetylene flame. The best detection limits were

TABLE II

SENSITIVITIES FOR GOLD BY ATOMIC FLUORESCENCE AND ATOMIC ABSORPTION SPECTROSCOPY

| Line<br>(Å) | Detection limit (p.p.m.)           |                    |                                   |                                   |
|-------------|------------------------------------|--------------------|-----------------------------------|-----------------------------------|
|             | A.F.S.                             |                    |                                   | A.A.S.                            |
|             | H <sub>2</sub> -O <sub>2</sub> -Ar | Air-H <sub>2</sub> | Air-C <sub>2</sub> H <sub>2</sub> | Air-C <sub>2</sub> H <sub>2</sub> |
| 2428.0      | 0.005                              | 0.015              | 0.015                             | 0.06                              |
| 2676.0      | 0.02                               | 0.07               | 0.07                              | 0.1                               |
| 3122.8      | 2.5                                | 4.5                | 2.0                               | 80                                |

obtained for the resonance line at 2428.0 Å. Even though the fluorescence signal in the separated air-acetylene flame is higher than that in the air-hydrogen flame, the relatively higher noise of measurement for the separated air-acetylene flame causes levelling of the detection limits for both resonance lines in both flames. The best detection limit of 0.005 p.p.m. obtained for the resonance line at 2428.0 Å in the hydrogen-oxygen-argon flame is practically 10 times better than the detection limit for the determination by atomic absorption spectroscopy. In the case of the 3122.8 Å line, there is a great difference between the sensitivity of the determination by atomic fluorescence and atomic absorption spectroscopy. Direct-line fluorescence, which has already been discussed above, is responsible for this fact.

### Extraction

To increase the sensitivity of the determination further, the extraction procedure which is commonly used in atomic absorption spectroscopy was employed. Gold was extracted as its bromide complex from 1 M hydrobromic acid<sup>10</sup> or its chloride

complex from 3 *M* hydrochloric acid<sup>11</sup> into methyl isobutyl ketone. Both methods gave practically the same results. The extracts gave fluorescence signals 5 times greater than those obtained with aqueous solutions of the same concentration. The detection limits were found to be 0.0002 p.p.m. in the nitrogen-sheathed air-hydrogen flame and 0.00007 p.p.m. in the nitrogen-sheathed hydrogen-oxygen-argon flame. Use of the nitrogen sheath decreases the noise of measurement approximately two-fold. When the extraction procedure was used, linear calibration curves were obtained over the concentration range 0.001–0.1 p.p.m.

### Chemical interferences

A study of interferences which could be expected to be present in practical analyses by atomic fluorescence spectroscopy was carried out. The effect of inorganic acids in concentrations of 0.01–0.5 *M* and of 100-fold amounts of 18 cations on the fluorescence signal produced by 5 p.p.m. of gold was investigated. The results are listed in Table III. Errors greater than 5% and more are considered as an interference. The

TABLE III

CHEMICAL INTERFERENCES OF INORGANIC ACIDS AND OF 100-FOLD AMOUNTS OF OTHER ELEMENTS

(5 p.p.m. of gold taken)

| <i>Acid or element</i>                       | <i>Error (%)</i>         |                                       |                                       |
|--|--------------------------|---------------------------------------|---------------------------------------|
|  | <i>Air-H<sub>2</sub></i> | <i>H<sub>2</sub>-O<sub>2</sub>-Ar</i> | <i>Air-C<sub>2</sub>H<sub>2</sub></i> |
| H <sub>2</sub> SO <sub>4</sub> 0.5 <i>M</i>  | –8                       | —                                     | —                                     |
| H <sub>3</sub> PO <sub>4</sub> 0.01 <i>M</i> | –10                      | –5                                    | —                                     |
|  | –14                      | –8                                    | –5                                    |
| 0.5 <i>M</i>                                 | –15                      | –10                                   | –7                                    |
|  | –15                      | —                                     | —                                     |
| HF 0.01 <i>M</i>                             | –73                      | –79                                   | –34                                   |
|  | –43                      | –41                                   | –29                                   |
| 0.5 <i>M</i>                                 | –16                      | —                                     | —                                     |
| Zn   | –9                       | —                                     | —                                     |
| Bi   | —                        | —                                     | –55                                   |
| Pd   | –9                       | —                                     | —                                     |
| Rh   | –5                       | —                                     | —                                     |
| Al   | –6                       | —                                     | —                                     |
| W  | —                        | —                                     | —                                     |

interferences of sulphuric, phosphoric and hydrofluoric acids were more pronounced in the air-hydrogen flame than in the other two flames. The effects of zinc, bismuth, rhodium, aluminum and tungsten observed in the air-hydrogen flame were practically eliminated in the hydrogen-oxygen-argon or air-acetylene flames; in contrast, palladium strongly decreased the fluorescence signal in the air-acetylene flame but had no effect in the air-hydrogen and hydrogen-oxygen-argon flames. This behaviour is in agreement with observations on the fluorescence determination of palladium<sup>12</sup>; more pronounced interferences in the air-acetylene flame were found than in the cooler air-hydrogen flame. The chemical interferences of the acids and cations were eliminated by addition of lanthanum to a final concentration of 0.1%.

Similar interferences were found for gold with atomic absorption in the same circular flames used in the fluorescence arrangement and in a 10-cm air-acetylene flame. Only palladium was an exception. A strong decrease in absorption signal in the

circular air-acetylene flame caused by the presence of palladium completely disappears in the long-path flame. Probably, this is a new type of interference which involves the spatial distribution of the sample within the flame, such as has been recently described by KOIRTYOHANN AND PICKETT<sup>13</sup>.

#### *Practical applications*

The high sensitivity of the gold determination in the hydrogen-oxygen-argon flame and freedom of interferences in this flame permitted the direct determination of gold in mine water containing 0.045 p.p.m. of gold. With the extraction procedure described by BUTLER *et al.*<sup>14</sup>, gold can be determined in mine waters down to a level of  $10^{-5}$  p.p.m.

#### SUMMARY

The atomic fluorescence of gold in premixed air-hydrogen, separated air-acetylene and oxy-hydrogen-argon flames, excited with a high-intensity hollow-cathode lamp was studied. Fluorescence of the gold resonance lines at 2428.0 and 2676.0 Å was observed and also direct-line fluorescence at 3122.8 Å. The emission at 3029.2 Å appears to arise from thermally assisted direct-line fluorescence. The most intense line at 2428.0 Å permits atomic fluorescence determination to be made with a detection limit of 0.005 p.p.m. in the oxy-hydrogen flame diluted with argon; the fluorescence signal in this flame is *ca.* 2.5-fold stronger than that in the air-hydrogen flame. The detection limit by atomic absorption (with the same instrument and source but 10-cm air-acetylene flame) is 10 times greater. With an extraction procedure, detection limits of 0.0002 and 0.00007 p.p.m. were obtained in the nitrogen-sheathed air-hydrogen and hydrogen-oxygen-argon flames, respectively. The method was used for the determination of gold in mine waters.

#### RÉSUMÉ

Les auteurs ont effectué une étude sur le dosage de l'or par spectroscopie de fluorescence atomique, à l'aide d'une lampe à cathode creuse de haute intensité, avec flammes air-hydrogène, air-acétylène, et oxy-hydrogène-argon. La ligne de résonance la plus intense, à 2428.0 Å permet un dosage par fluorescence atomique, offrant une limite de détection de 0.005 p.p.m. dans une flamme oxy-hydrogène diluée avec argon. La limite de détection correspondante par absorption atomique (avec le même appareil et la même source, mais flamme air-acétylène) est 10 fois plus grande. On peut améliorer encore ces limites de détection (respectivement 0.0002 et 0.00007 p.p.m.) en procédant par extraction. Cette méthode est utilisée pour le dosage de l'or dans les eaux des mines.

#### ZUSAMMENFASSUNG

Es wurde die Atomabsorption von mit einer hochintensiven Hohlkathodenlampe angeregten Gold untersucht. Dabei wurde eine vorgemischte Luft-Wasserstoff-Flamme, eine getrennte Luft-Acetylen-Flamme und eine Sauerstoff-Wasserstoff-Argon-Flamme verwendet. Die Fluoreszenz der Goldresonanzlinien wurden bei 2428.0 und 2676.0



Å beobachtet. Die direkte Fluoreszenz bei 3122.8 Å. Die Emission bei 3029.2 Å scheint durch die thermisch unterstützte direkte Fluoreszenz anzusteigen. Die intensivste Linie bei 2428.0 Å erlaubt in der Sauerstoff-Wasserstoff-Argon-Flamme eine Nachweisgrenze von 0.005 p.p.m. Das Signal dieser Flamme ist etwa 2.5 mal so stark wie das der Luft-Wasserstoff-Flamme. Die Nachweisgrenze bei der Atomabsorption ist 10 mal grösser. Mit einem Extraktionsverfahren und entsprechender Flammenwahl erreicht man Nachweisgrenzen von 0.0002 bzw. 0.00007 p.p.m. Die Methode wurde zur Bestimmung von Gold in Grubenwässern verwendet.

## REFERENCES

- 1 C. VEILLON, J. M. MANSFIELD, M. L. PARSONS AND J. D. WINEFORDNER, *Anal. Chem.*, 38 (1966) 204.
- 2 M. P. BRATZEL, JR. AND J. D. WINEFORDNER, *Anal. Letters*, 1 (1967) 43.
- 3 K. E. ZACHA, M. P. BRATZEL, JR., J. D. WINEFORDNER AND J. M. MANSFIELD, JR., *Anal. Chem.*, 40 (1968) 1733.
- 4 J. I. DINNIN, *Anal. Chem.*, 39 (1967) 1491.
- 5 D. C. MANNING AND P. HENEAGE, *Atomic Absorption Newsletter*, 7 (1968) 80.
- 6 T. S. WEST AND X. K. WILLIAMS, *Anal. Chem.*, 40 (1968) 335.
- 7 R. M. DAGNALL, K. C. THOMPSON AND T. S. WEST, *Talanta*, 14 (1967) 1151.
- 8 R. M. DAGNALL, K. C. THOMPSON AND T. S. WEST, *Talanta*, 14 (1967) 1467.
- 9 H. P. HOOYMAYERS, *Spectrochim. Acta*, 23B (1968) 567.
- 10 M. C. GREAVES, *Nature*, 199 (1963) 552.
- 11 F. W. E. STRELOW, E. C. FEAST, P. M. MATHEWS, C. J. C. BOTHMA AND C. R. VAN ZYL, *Anal. Chem.*, 38 (1966) 115.
- 12 J. MATOUŠEK AND V. SYCHRA, unpublished results.
- 13 S. R. KOIRTYOHANN AND E. PICKETT, *Anal. Chem.*, 40 (1968) 2068.
- 14 L. R. P. BUTLER, A. STRASHEIM, F. W. E. STRELOW, P. M. MATHEWS AND E. C. FEAST, *Colloq. Spectros. Intern.*, 12th, Exeter, 1965.

## SHORT COMMUNICATIONS

## Location method for amino acids and some amines on chromatograms and electropherograms

In previous work, 7,7,8,8-tetracyanoquinodimethan (TCNQ) was used in the analysis of free radical precursors, mercaptans, prolines, carbazoles, acridines, thiosemicarbazones, and polynuclear aromatic hydrocarbons<sup>1</sup>. The reagent was valuable in the location of these various compounds on thin-layer and paper chromatograms. Only a few amino acids were investigated; since these gave brilliant visible colors, and some gave fluorescent colors, it was decided to investigate a larger number of compounds with the amino functional group, *e.g.* amino acids, aliphatic amines, and amino acid derivatives.

*Reagents and apparatus*

All of the amino acids, proteins, and other amines were obtained from commercial sources in the purest form available. 7,7,8,8-Tetracyanoquinodimethan (TCNQ) was obtained from E. I. DuPont de Nemours and Co., Wilmington, Delaware. Pyridine and dimethylsulfoxide were obtained in pure form and used directly.

A 0.3% (w/v) solution of TCNQ in pyridine-acetone (1:1) was used.

An Aminco-Bowman spectrophotofluorimeter was used with the following settings: sensitivity 50, slit arrangement No. 2, and phototube RCA type 1P21.

*Location procedure for various chemicals on a chromatogram*

Spray the chromatogram (Whatman 3 MM paper and silica gel plates) with dimethylsulfoxide. Dry the chromatogram with gentle heat with a hair dryer. Next spray the chromatogram with the TCNQ solution. Let the chromatogram air-dry for 15 min at room temperature. Record the visible colors, and then put the chromatogram under ultraviolet light for 5 min. Record the fluorescent colors at the end of the 5-min period. The visible and fluorescent colors obtained with various amines are shown in Table I.

TABLE I

LOCATION OF AMINO ACIDS AND ANALOGOUS COMPOUNDS ON CHROMATOGRAMS AND ELECTRO-PHEROGRAMS

| Compounds <sup>a</sup>            | Color <sup>b</sup> (det. limits)<br>( $\mu\text{g}/\text{cm}^2$ ) |                      | Fluor. (det. limits)<br>( $\mu\text{g}/\text{cm}^2$ ) |                |
|-----------------------------------|---|----------------------|---|----------------|
|                                   | Si Gel  | Paper                | Si Gel  | Paper          |
| Alanine                           | G (5)   | Br (2)               | O (20)  | — <sup>c</sup> |
| Cystathionine                     | Br (20)   | G (3)                | O (10)  | O (10)         |
| <i>o</i> -Aminoacetophenone       | O (10)  | — <sup>d</sup>       | P (20)  | —              |
| $\gamma$ -Aminobutyric acid       | G (2)   | Y (2)                | O (2)   | O (2)          |
| DL- $\beta$ -Aminoisobutyric acid | G (3)   | G (5)                | Y (3)   | Y (10)         |
| 2-Aminoethanol                    | G (3) <sup>e</sup>  | G (2.5) <sup>e</sup> | O (2)   | O (2)          |
| Arginine                          | O (20)  | B (2)                | O (10)  | O (10)         |

TABLE I (continued)

| Compounds <sup>a</sup>        | Color <sup>b</sup> (det. limits)<br>( $\mu\text{g}/\text{cm}^2$ ) |                    | Fluor. (det. limits)<br>( $\mu\text{g}/\text{cm}^2$ ) |        |
|-------------------------------|---|--------------------|---|--------|
|                               | Si Gel  | Paper              | Si Gel  | Paper  |
| L-Arterenol bitartrate        | G (10)  | G (1)              | —   | —      |
| Asparagine                    | P (2)   | Br (20)            | O (20)  | —      |
| Aspartic acid                 | BrP (20)  | BrP (10)           | —   | —      |
| D-Azetidine-2-carboxylic acid | G (3)   | G (3)              | P (3)   | P (10) |
| n-Butylamine                  | G (10)  | —                  | O (10)  | —      |
| Canavanine                    | P (1)   | BrP (2)            | —   | —      |
| Carbazole                     | —   | P (10)             | —   | —      |
| Carnosine                     | G (3)   | G (3)              | YG (10)   | Y (10) |
| Chymotrypsin                  | G (20)  | G (10)             | O (10)  | O (10) |
| Cysteic acid                  | G (20)  | G (2)              | O (20)  | —      |
| Cytochrome C                  | G (10)  | G (10)             | O (10)  | —      |
| L-Djenkolic acid              | Br (3)  | BrP (3)            | O (20)  | O (3)  |
| Ethylenediamine               | G (1)   | Y (20)             | O (1)   | O (3)  |
| Gamma globulin (human)        | —   | G (10)             | —   | Y (20) |
| D-Glucosamine                 | YG (10)   | YG (10)            | Y (10)  | Y (1)  |
| Glutamic acid                 | O (20)  | Br (10)            | —   | O (10) |
| Glutamine                     | Br (10)   | Br (2)             | O (10)  | O (2)  |
| Glycine                       | P (2)   | P (2)              | —   | —      |
| Hemoglobin (human)            | G (20)  | G (10)             | O (20)  | —      |
| Histidine                     | G (3)   | G (3)              | O (10)  | O (20) |
| Hydroxylysine                 | G (3)   | G (3)              | O (20)  | —      |
| Hydroxyproline                | G (10)  | G (3)              | YO (3)  | Y (20) |
| 2,2'-Iminodiethanol           | Y (10)  | G (10)             | Y (10)  | G (10) |
| Indole                        | G (20) <sup>f</sup>   | G (3) <sup>f</sup> | —   | —      |
| Isoleucine                    | Br (3)  | Br (5)             | YO (10)   | O (2)  |
| Leucine                       | O (10)  | Br (2)             | O (10)  | O (10) |
| Lysine                        | G (2)   | Br (5)             | O (2)   | O (2)  |
| Methionine                    | O (20)  | Br (2)             | O (10)  | O (20) |
| L-1-Methylhistidine           | Br (10)   | BrP (10)           | O (10)  | O (10) |
| N(1-Naphthyl)ethylene-diamine | YG (10)   | G (10)             | P (10)  | O (1)  |
| DL-Norleucine                 | O (20)  | Br (2)             | O (10)  | O (10) |
| Phenylalanine                 | Br (10)   | Br (2)             | O (10)  | O (20) |
| Pipelicolic acid              | G (3)   | Br (2)             | Y (20)  | O (2)  |
| Piperazine                    | W (10) <sup>g</sup>   | G (1) <sup>g</sup> | Y (10)  | —      |
| Proline                       | G (2)   | G (2)              | B (2)   | O (2)  |
| Ribonuclease A                | G (20)  | G (10)             | —   | O (20) |
| Serine                        | G (5)   | Br (5)             | O (20)  | —      |
| Taurine                       | G (5)   | G (20)             | O (2)   | OY (2) |
| L-2-Thiohistidine             | G (3)   | G (2)              | —   | —      |
| Thiourea                      | B (1)   | B (1)              | —   | —      |
| Threonine                     | P (2)   | Br (2)             | G (20)  | —      |
| Trypsin                       | G (10)  | G (10)             | O (10)  | O (10) |
| Tryptamine                    | Y (10)  | G (10)             | Y (10)  | Y (10) |
| Tryptophan                    | P (10)  | P (10)             | —   | —      |
| Tyrosine                      | G (2)   | Br (20)            | O (20)  | —      |
| Valine                        | Br (3)  | Br (2)             | YO (10)   | O (10) |

<sup>a</sup> Negative results with betaine, cytosine, diethylamine, glycoyamine, pepsin, pyrrol, *p*-tosylglycine, and urea.

<sup>b</sup> B = blue, Br = brown, G = green, O = orange, P = purple, Y = yellow, and W = white.

<sup>c</sup> — = negative at 20  $\mu\text{g}$ .

<sup>d</sup> Turns brown purple after 10 min under ultraviolet light.

<sup>e</sup> Gives a green visible color without the dimethylsulfoxide, and with the TCNQ reagent only; color fades after 15 min.

<sup>f</sup> Turns blue after 5 min under ultraviolet light.

<sup>g</sup> Turns orange after 10 min under ultraviolet light.

### Results and remarks

The preliminary spraying with dimethylsulfoxide helps in development of fluorescent colors from the reaction of TCNQ with various amino acids, ethylenediamine, and ethanolamine. Most compounds gave an orange fluorescence and a green or brown visible color on paper or silica gel. In a few cases the spot was extracted with acetone, the acetone was evaporated to a small volume, and a fluorescence spectrum was obtained for this solution. Examples of the spectra obtained are shown in Fig. 1. An excitation wavelength maximum at 460 nm and an emission

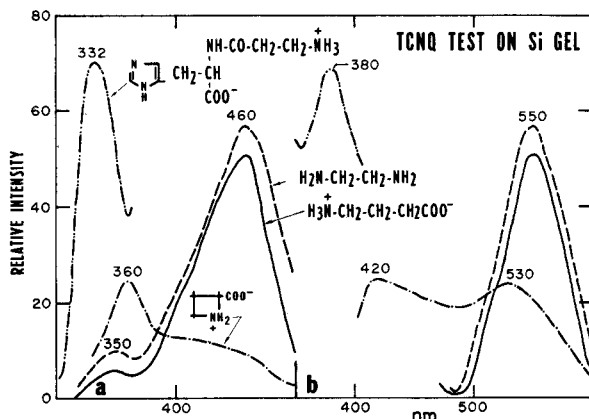


Fig. 1. Fluorescence excitation (a) and emission (b) spectra.  $\gamma$ -Aminobutyric acid (—) at F 460/550 and MM 0.01. Ethylenediamine (---) at F 460/550 and MM 0.01. Azetidine-2-carboxylic acid (-·-·) at F 360/530 and MM 0.003. Carnosine (-·-·-·) at F 332/380 and MM 0.003. All concentrations at 20  $\mu\text{g}/0.5$  or 1 ml acetone. MM is the meter multiplier reading.

wavelength maximum at 550 nm were obtained for the compounds having orange fluorescence. Examination of many of these spectra indicated that another compound was present in addition to the one absorbing at 460 nm. For example, the eluted orange spot obtained with ethylenediamine also gave an emission band at 395 nm when excited at 350 nm. These bands are derived from a second compound present in the spot. The procedure should be useful in locating and characterizing the amino acids isolated from various atmospheres.

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1 E. SAWICKI, C. R. ENGEL AND W. C. ELBERT, *Talanta*, 14 (1967) 1169.

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## Convenient data presentation for thermogravimetric analysis

The usual manner of data presentation in thermogravimetric analysis (TGA) is mass-change *versus* temperature or time<sup>1</sup>. Most commercial thermobalances, with one exception, record the change in sample mass rather than the percent mass-change, the latter being a more convenient form of presentation. From direct mass-change data, the sample mass must be known in order to calculate the percent mass-change and/or other stoichiometry calculations. In the percent mass-change data recording, the data are readily available for stoichiometry calculations of various types.

We have found that by the proper choice of recorder, the percent mass-change of the sample can be recorded directly. There is also no need to determine accurately the exact sample mass, hence a saving of time is possible in preparing a sample for analysis on the thermobalance. By the simple addition of a retransmitting potentiometer to the recorder, percent mass-change data can be recorded *versus* furnace temperature on an auxiliary X-Y recorder, or it can be converted to digital form for digital recording.

### Experimental

**Apparatus.** The thermobalance<sup>2</sup> consisted of a Cahn Model RG balance, a small Nichrome wire wound furnace, furnace temperature programmer<sup>3</sup>, and a Sargent Model SRG recorder. The sample was contained in shallow platinum cup of 4 mm diameter suspended by a platinum wire into the furnace zone. A 10-k $\Omega$  three-turn potentiometer was connected to the recorder balancing motor by means of a small idler gear and bracket. The voltage applied to the potentiometer (Fig. 1) was from a 3-25 V d.c. regulated power supply. Zero adjust in the circuit was provided by bucking the potentiometer output voltage by means of the voltage across a 100  $\Omega$  resistor. Output voltage from the retransmitting potentiometer was from 0 to 1.000 V and this was led into a Moseley Model 3S X-Y recorder and a Hewlett-Packard Model 2210 voltage-to-

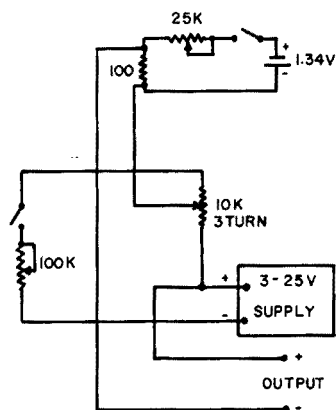


Fig. 1. Retransmitting potentiometer circuit.

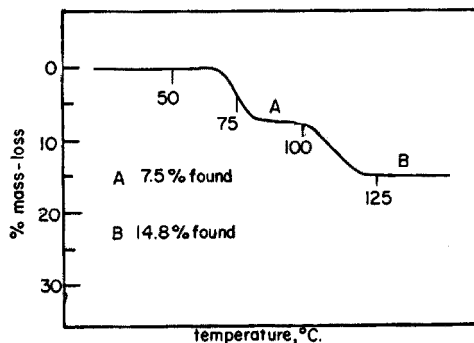


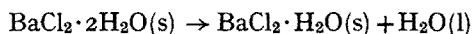
Fig. 2. Percent mass-loss curve for  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . Heating rate  $7^\circ/\text{min}$ , static air atmosphere, sample size *ca.* 9 mg. Theoretical values: (A) 7.38%; (B) 14.75%.

frequency converter. The frequency output from the latter was counted for 1-sec intervals by a Hewlett-Packard Model 521 A/D counter which triggered a Hewlett-Packard Model 560AR digital printer. The print-out of the digital data ranged from 0.0 to  $100.0 \pm 0.1\%$ . Simultaneously, the data were displayed on the strip-chart recorder (% mass-change *versus* time), the X-Y recorder (% mass-change *versus* temperature) and on the digital printer (% mass-change).

*Procedure.* A small amount of sample (4–10 mg) was placed in the sample container. It was not necessary to determine the exact amount, only that it be within this range (10 mg full scale deflection) on the recorder. Then, by means of the variable span control on the recorder, the pen was positioned on the extreme left position of the scale (0%). Any mass-loss of the sample will now be recorded as direct percent mass-loss. For stoichiometry calculations, it is not necessary to know the sample mass since the percent mass-loss is read directly from the recorder chart. For other mass ranges, 0–4, 0–2, and 0–1 mg, the procedure is identical except that a smaller amount of sample is employed.

### Results

The percent mass-loss curve for barium chloride 2-hydrate is illustrated in Fig. 2. The percent mass-loss *versus* time (temperature) is shown, indicating that the dehydration reaction is:



Although this is a rather simple dehydration reaction, there is a pronounced saving in calculation time in this system and in more complicated systems.

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1 W. W. WENDLANDT, *Thermal Methods of Analysis*, J. Wiley-Interscience, New York, 1964, Chapt. 2.

2 Reference 1, p. 58.

3 W. W. WENDLANDT, *J. Chem. Educ.*, 38 (1961) 571.

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## A capillary tube sample holder for differential scanning calorimetry

It is frequently necessary to study the thermal dissociation or other thermal behavior of substances which react with the conventional aluminum sample cups employed in differential scanning calorimetry (DSC). We have found that glass capillary melting-point tubes (1.6–1.8 mm in diameter  $\times$  90 mm long), contained in the metal holder illustrated in Fig. 1, may be employed as an inexpensive sample holder for such substances. The sample (1–10 mg) is placed in the tube, tamped gently into place, and the tube cut off to a length of 1.0–1.5 cm. The tube is then placed in the aluminum metal holder whose base is 7.0 mm in diameter, 1.0 mm thick, and 9.0 mm in height. Two such metal holders are employed; one for the sample tube, the other containing an empty tube which is used for the reference cup of the calorimeter.

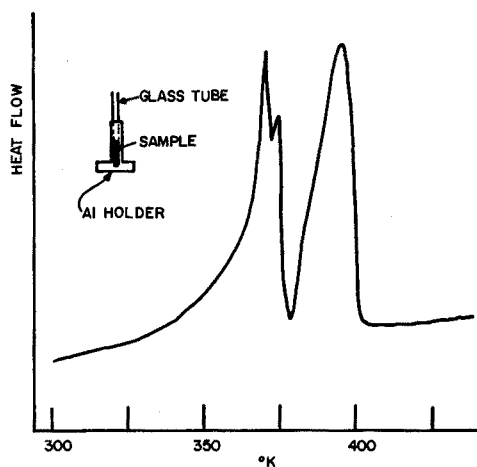
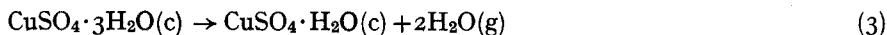
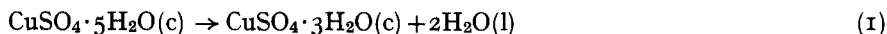


Fig. 1. DSC curve of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with the glass capillary tube sample holder. Sample size, 8 mg; heating rate,  $5^\circ/\text{min}$ ; static air atmosphere.

The DSC curve for copper(II) sulfate pentahydrate, with the capillary tube sample holder, is illustrated in Fig. 1. This compound dehydrates according to the reactions<sup>1</sup>:



Reactions (1) and (2) are present in the first endothermic peak in the curve while the second peak is due to reaction (3) giving  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  as the residue in the tube.

Not only are the capillary tubes useful for the DSC investigation of corrosive substances but they may also be used for pure liquids and solutions (if sealed at both ends) and for numerous other investigations.

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### The determination of cyanide ions in waters and effluents by an Auto-Analyzer procedure

The method currently used in these laboratories for the determination of less than 10 p.p.m. of cyanide ions in waters, *e.g.* in trade effluents or river waters, is based on distillation of hydrogen cyanide from an acid, and argentometric titration with rhodamine as indicator<sup>1</sup>. When large numbers of samples must be handled, this method is time-consuming and tedious; moreover, it is difficult to automate, and a colorimetric procedure would be more suitable.

Analytical methods for cyanide have been reviewed<sup>2-4</sup>, the conclusion being that the most satisfactory colorimetric procedure is the ALDRIDGE method<sup>5</sup> based on the KÖNIG synthesis<sup>6</sup>; this method is favoured by the S.A.C.<sup>1</sup> and the A.P.H.A.<sup>7</sup>. In this procedure, cyanide is brominated to cyanogen bromide, excess of bromine is removed by a reductant, and cyanogen bromide is coupled with pyridine and an aromatic amine (originally benzidine) to give a coloured complex. BARK AND HIGSON<sup>8</sup> indicated that *p*-phenylenediamine would provide better sensitivity, and would avoid the use of the carcinogenic benzidine. This method was therefore adapted for use with the Auto-Analyzer.

One feature of the procedure described below is a distillation stage, which not only improves the selectivity of the method, but also eliminates the necessity of filtering samples containing particulate matter. The distillation stage is designed to give a sample rate of 40/h. In the apparatus, bromine is generated *in situ* in an all-glass system, which simplifies reagent preparation and avoids the vigorous attack of bromine on the pumping tubes.

#### Apparatus

The apparatus, based on "Technicon" Auto-Analyzer modules, is shown schematically in Fig. 1. The sampling rate was chosen as 40 samples/h with a sample: wash ratio of 1:2; the wash used was distilled water.

There are several points of interest about the manifold. The distillation temperature is 98°; higher temperatures lead to splashing and carry-over at the B1 trap, whilst lower temperatures give reduced sensitivity. The B1 trap which separates the air containing gaseous hydrogen cyanide from the acidified sample should be as close



as possible to the exit from the heating coil, otherwise sensitivity will be lost. Bromine is liberated from an acidic bromide-bromate combination within the glass mixing coil, and excess is destroyed by sodium arsenite added at the centre of the coil. If wetting agents are used during a run, excessive frothing will occur in the B1 trap, and unreliable results will be obtained.

### Reagents

**Bromine reagent.** Dissolve 15 g of sodium bromide and 4.3 g of potassium bromate in water, and dilute to 1 l.

**Sodium arsenite.** Dissolve 25 g of sodium arsenite in *ca.* 800 ml of water, add 90 ml of concentrated hydrochloric acid and dilute to 1 l with water.

**Pyridine reagent.** Dilute 450 ml of pyridine and 125 ml of concentrated hydrochloric acid to 1 l with water.

***p*-Phenylenediamine reagent.** Dissolve 7.5 g of *p*-phenylenediamine dihydro-

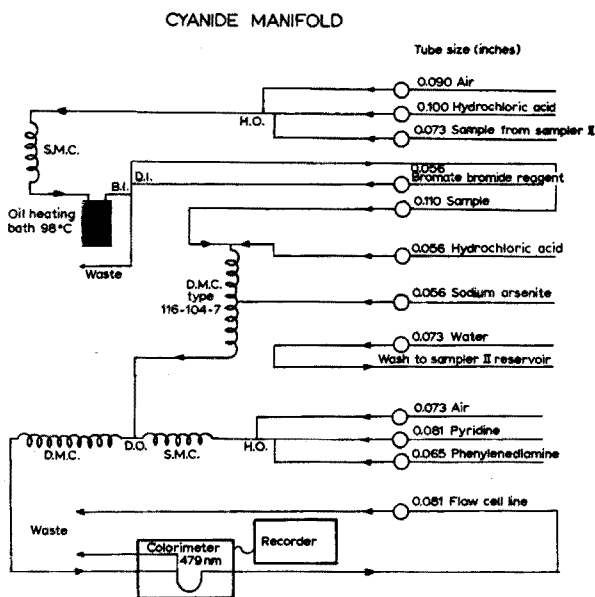


Fig. 1. Schematic representation of apparatus.

chloride in water, add 20 ml of concentrated hydrochloric acid and dilute to 1 l with distilled water.

Aqueous *ca.* 0.5 *M* hydrochloric acid and potassium cyanide (May & Baker, reagent grade) were also required.

All the reagent solutions were stable for a period of at least 4 weeks.

### Calibration and precision.

A stock solution of potassium cyanide was prepared containing 250 p.p.m. of cyanide; the solution also contained 0.1 *M* sodium hydroxide, to prevent volatilization of hydrogen cyanide. This solution remained stable for at least two months.

The concentration range of interest was 0.5–10.0 p.p.m. cyanide, hence the

stock solution was diluted to give 2.5, 5.0 and 10 p.p.m. cyanide solutions; these were stable for at least a day.

The calibration curve was prepared by submitting these standard solutions to the Auto-Analyzer procedure outlined above; a return to baseline between samples was achieved, and a straight line relationship between absorbance and cyanide concentration was obtained.

It was found separately that Beer's law was obeyed up to 40 p.p.m. of cyanide.

The precision obtained by the Auto-Analyzer method was shown to compare very favourably with that of the standard manual procedure<sup>1</sup> (see Table I).

#### *Analysis of water samples*

About 1000 water samples (mostly trade effluents) were examined by both the manual and automated methods. About 900 samples were found to contain less than 0.5 p.p.m. cyanide by both procedures; since this is the lower limit of detection for the manual method, they were not investigated further. However, 101 aqueous samples

TABLE I

MEAN VALUES AND STANDARD DEVIATIONS FOR THE MANUAL AND AUTOMATIC METHODS

| <i>Method</i> | <i>Mean cyanide content<br/>(p.p.m.)</i> | <i>No. of detns.</i> | <i>Standard deviation</i> |
|---------------|--|----------------------|---------------------------|
| Manual        | 2.1                                      | 6                    | 0.63                      |
| Auto-Analyzer | 2.5                                      | 16                   | 0.21                      |
| Manual        | 5.3                                      | 6                    | 0.53                      |
| Auto-Analyzer | 5.0                                      | 16                   | 0.20                      |
| Manual        | 9.8                                      | 7                    | 0.40                      |
| Auto-Analyzer | 10.0                                     | 16                   | 0.65                      |

contained more than 0.5 p.p.m. of cyanide and these data were evaluated statistically, with the following results, which show excellent correlation between the two methods.

|   |       |
|---|-------|
| Mean value for Auto-Analyzer procedure (p.p.m. cyanide) | 10.89 |
| Mean value for manual procedure (p.p.m. cyanide)        | 10.95 |
| Total number of samples analyzed by both procedures     | 101   |
| Mean difference (p.p.m. cyanide)                        | 0.06  |
| Student "t" test, value of t                            | 0.18  |
| Correlation coefficient                                 | 0.96  |

#### *Analysis of some complex cyanides*

Various complex metal cyanide solutions (containing 50 p.p.m. of cyanide) were prepared and aliquots were analyzed by both procedures. The results (Table II) were in very good agreement.

#### *Interferences*

Two types of interference are possible: compounds that can produce cyanogen bromide, e.g. thiocyanate, which can in fact be determined by the ALDRIDGE method; and oxidizable substances that react with the generated bromine, thus partly or wholly

TABLE II

ANALYSIS OF COMPLEX CYANIDES BY THE AUTO-ANALYZER AND MANUAL PROCEDURES

| Cyanide complex | Cyanide recovered (p.p.m.) |               |
|-----------------|----------------------------|---------------|
|                 | Auto-Analyzer method       | Manual method |
| $K_3Fe(CN)_6$   | 3.4                        | 1.2           |
| $K_4Fe(CN)_6$   | 2.8                        | 1.5           |
| $K_2Cd(CN)_4$   | 47.0                       | 48.8          |
| $K_2Zn(CN)_4$   | 50.3                       | 50.3          |
| $K_2Ni(CN)_4$   | 52.6                       | 50.6          |
| $Cd(CN)_2$      | 49.5                       | 49.0          |

preventing the formation of cyanogen bromide. The incorporation of a distillation stage in the automated method prevents various interferences (*cf.* Table III).

TABLE III

LEVELS OF TOLERANCE FOR VARIOUS SUBSTANCES WITH 10 p.p.m. OF CYANIDE

| Interfering substance | Level of interference (p.p.m.) | Interfering substance | Level of interference (p.p.m.) |
|-----------------------|--------------------------------|-----------------------|--------------------------------|
| Lead(II)              | 3,500                          | Thiosulphate          | 4,000                          |
| Nickel(II)            | 1,250                          | Bisulphite            | 500                            |
| Copper(II)            | 500                            | Nitrite               | 3,000                          |
| Mercury(II)           | 3,500                          | Hypochlorite*         | 5,000                          |
| Cyanate               | 5,000                          | Formaldehyde          | 25                             |
| Thiocyanate           | 1,250                          | Phenol                | 5,000                          |

\* Gives no blank but destroys cyanide ions.

TABLE IV

COMPARISON OF HYDROCHLORIC ACID AND ACIDIC LEAD ACETATE (pH 4.7) AS SUBSTRATES FOR DISTILLATION BY THE AUTO-ANALYZER PROCEDURE

| Sample no. | Cyanide content (p.p.m.) |                     | Sample no. | Cyanide content (p.p.m.) |                     |
|------------|--------------------------|---------------------|------------|--------------------------|---------------------|
|            | HCl distn.               | Lead acetate distn. |            | HCl distn.               | Lead acetate distn. |
| 1          | 1.7                      | 1.8                 | 9          | 4.6                      | 4.6                 |
| 2          | 2.4                      | 2.2                 | 10         | 0.8                      | 0.7                 |
| 3          | 5.9                      | 6.2                 | 11         | 12.3                     | 12.8                |
| 4          | 12.2                     | 10.8                | 12         | 6.3                      | 5.8                 |
| 5          | 0.6                      | 0.4                 | 13         | 14.2                     | 13.3                |
| 6          | 3.3                      | 3.0                 | 14         | 7.4                      | 7.1                 |
| 7          | 12.8                     | 10.4                | 15         | 15.8                     | 13.6                |
| 8          | 0.6                      | 0.8                 |            |                          |                     |

#### Comparison of distillation procedures

Although good agreement had been demonstrated between the manual procedure, which involved distillation of hydrogen cyanide from an acidic lead acetate solution, and the automated procedure involving a pseudo-distillation from a hydrochloric acid solution, a further comparison of the two distillation procedures was made

by the Auto-Analyzer technique. A statistical appraisal by the "t"-test, of the results obtained (Table IV) showed that there was no significant difference between the two techniques.

### Discussion

The Auto-Analyzer procedure for the determination of cyanide is sensitive, selective and precise. The range 0.5–10 p.p.m. of cyanide ions was the primary interest, but it was found that Beer's law was obeyed up to 40 p.p.m. of cyanide without any change within the system. For higher concentrations, the relevant solution may be diluted or the filter can be changed. If more sensitivity is desired, two approaches are possible: the distillation stage may be omitted entirely, giving a 10-fold sensitivity increase; or if distillation is essential, the pumping rate of the sample tube can be increased.

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- 1 *Recommended Methods for the Analysis of Trade Effluents*, The Society for Analytical Chemistry, London, 1967, pp. 88 *et seq.*
- 2 L. S. BARK, *Ind. Chemist*, (1962) 525.
- 3 L. S. BARK AND H. G. HIGSON, *Talanta*, 11 (1964) 471, 621.
- 4 L. S. BARK AND H. G. HIGSON, *Analyst*, 88 (1963) 751.
- 5 W. N. ALDRIDGE, *Analyst*, 69 (1944) 262; 70 (1945) 474.
- 6 W. KÖNIG, *J. Prakt. Chem.*, 69 (1904) 105; *Z. Angew. Chem.*, (1905) 115.
- 7 *Standard Methods for the Examination of Water and Waste-water*, American Public Health Association, Inc., New York, 1960, p. 356.

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*Anal. Chim. Acta*, 49 (1970) 188–192

## A simple gas chromatographic method for the determination of diethyl ether in ether-petroleum ether mixture

Liquid column chromatography of fat-soluble compounds usually employs an eluent gradient system that may be continuous, discontinuous, convex, linear, or concave. Such systems can give a discrete separation of sample components<sup>1-4</sup>, but a procedure that would determine precisely the changing ratio of liquids in an eluent mixture would be useful.

Gas-liquid chromatography (GLC) can be successfully applied to determine the percentage of ethyl ether and petroleum ether in an eluent mixture used to separate vitamin D from nonfat dry milk powder. As this technique may be applicable to other analytical situations of a similar nature, it is described in this communication.

*Anal. Chim. Acta*, 49 (1970) 192–194

### Instrumentation

A Victoreen 4000 gas chromatograph with flame ionization detector was used under the following conditions: glass column (5 mm × 6') packed with 3% OV-1 Gas Chrom Q (100–200 mesh), column temperature 60°, injection port temperature 80°, carrier gas (He) flow 45 ml/min, injection volume 2  $\mu$ l, electrometer setting  $5 \cdot 10^6$  (1.5  $\mu$ A input for driving recorder full scale).

### Results

It was observed that the GLC response to the injection of a sample of petroleum ether (boiling range, 30–60°) was in a form of double peaks, one minor and one major (Fig. 1). Increasing additions of diethyl ether caused the minor peak height to decrease, while the major peak height remained approximately unchanged. It was, therefore, concluded that the GLC peak caused by diethyl ether must be superimposed on the

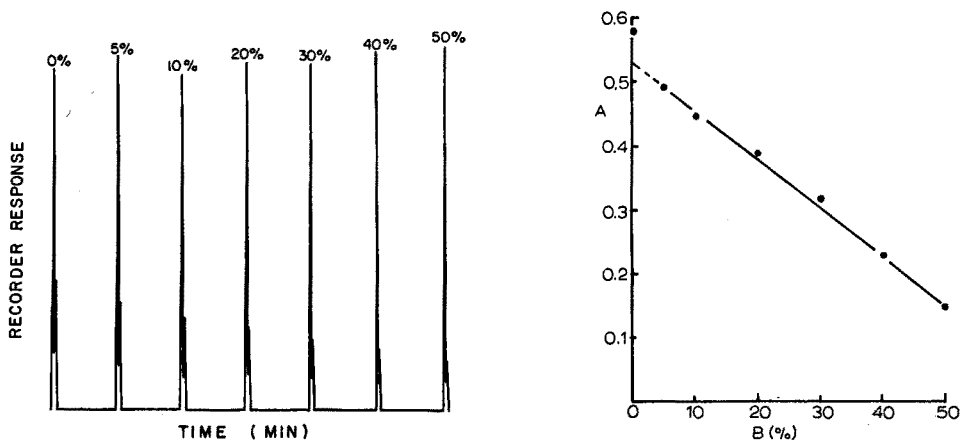


Fig. 1. Gas chromatogram obtained from a series of injections of mixtures, ranging from 0 to 50% of diethyl ether in petroleum ether.

Fig. 2. A plot illustrating the linear relationship between log of ratio of minor peak height  $\times 10$  to that of major peak (A) to the % concentration of diethyl ether in a mixture (B).

major petroleum ether peak. From the chromatogram obtained from injections of 0–50% (v/v) of diethyl ether in petroleum ether as shown in Fig. 1, the logarithm (to the base 10) of the ratio of the height of a minor peak ( $\times 10$ ) to that of a major peak was directly proportional to the percentage concentration of diethyl ether in the mixture. From the plot of this linear relationship (Fig. 2), the concentration of diethyl ether in the eluate could be estimated.

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- 1 J. J. WREN, *J. Chromatog.*, 4 (1960) 173.
- 2 S. KATZ, *Anal. Biochem.*, 5 (1963) 7.
- 3 W. R. MIDDLETON, *Anal. Chem.*, 39 (1967) 1839.
- 4 L. HAGDAHL, in E. HEFTMANN, *Chromatography*, Reinhold, New York, 1961, p. 56.

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*Anal. Chim. Acta*, 49 (1970) 192-194

## Chemical identification of Cannabis

The chemistry of the resin obtained from *Cannabis sativa L.* indicates that the major part of the resin consists of a group of closely related constituents, namely, cannabidiolic acid, cannabidiol, tetrahydrocannabinol and cannabinol, which may be called cannabinolic compounds or cannabinoids. It is believed that hemp resins contain a mixture of isomeric tetrahydrocannabinols, which are the active principle of the drug<sup>1</sup>.

As the cannabinoids are phenolic compounds that have a free *ortho*-position relative to the phenolic group, it is suggested that Feigl's test<sup>2</sup> based on conversion of *o*-nitrophenols to complex cobalt(III) compounds could be applied for the identification of cannabinoids. The reaction involves nitrosation to form *o*-nitrosophenols which can be identified by the production of brown cobalt(III) chelate compounds which can be extracted into chloroform. The reaction is carried out by heating the resin with a solution of sodium cobaltinitrite in acetic acid.

### Procedure

The constituents of the resin are extracted by heating a few cg of the *Cannabis* sample (in small pieces) with 2 ml of petroleum ether, for 2 min. If necessary, the extract is filtered through active carbon in order to remove colored impurities such as carotenoids, chlorophyll and xanthophylls.

The extract, or the dry crude resin obtained by evaporation of the solvent, is then treated in a micro test tube with a drop of the reagent and a drop of glacial acetic acid. The test tube is then placed in boiling water for 2 min and allowed to cool. Chloroform (2 drops) is then added. A positive response is shown by a brown color in the organic layer.

*Reagent.* A freshly prepared aqueous 5% solution of sodium cobaltinitrite.

The test requires very little time and can be done with amounts of resin down to 0.5 mg without any difficulty. The procedure should therefore be particularly suitable for forensic purposes.

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1 See, e.g., L. GRILIĆ, *Bull. Narcotics, U.N. Dept. Social Affairs*, 14 (1962) 37.

2 F. FEIGL, *Spot Tests in Organic Chemistry*, 7th Edn., Elsevier, Amsterdam, 1966, p. 183.

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*Meconic acid*

DTA and TGA studies of meconic acid were performed. TGA was carried out both on the trihydrate, and on material dried for 1 h at 100°. Only the dried material was submitted to DTA. After the DTA curve had been obtained, samples of material were heated to slightly past each thermal event, and then submitted for microanalysis. Microanalytical results are shown in Table I, and thermal analysis results in Figs. 1 and 2.

TABLE I  
MICROANALYTICAL RESULTS

| Sample identity          |     | Assumed formula | Carbon (%) |       | Hydrogen (%) |       |
|--------------------------|-----|-----------------|------------|-------|--------------|-------|
|                          |     |                 | Found      | Calc. | Found        | Calc. |
| Meconic (BDH)            | (a) | $C_7H_4O_7$     | 41.93      | 42.02 | 1.89         | 2.02  |
|                          | (b) | $C_7H_4O_7$     | 41.79      | 42.02 | 2.26         | 2.02  |
|                          | (c) | $C_6H_4O_5$     | 46.19      | 46.17 | 2.58         | 2.58  |
| Comenic (prep) (Pfizer)  |     | $C_6H_4O_5$     | 46.32      | 46.17 | 2.59         | 2.58  |
|                          | (d) | $C_6H_4O_5$     | 46.25      | 46.17 | 2.77         | 2.58  |
| Pyromeconic (resublimed) | (e) | $C_5H_4O_3$     | 54.01      | 54.45 | 3.52         | 3.57  |

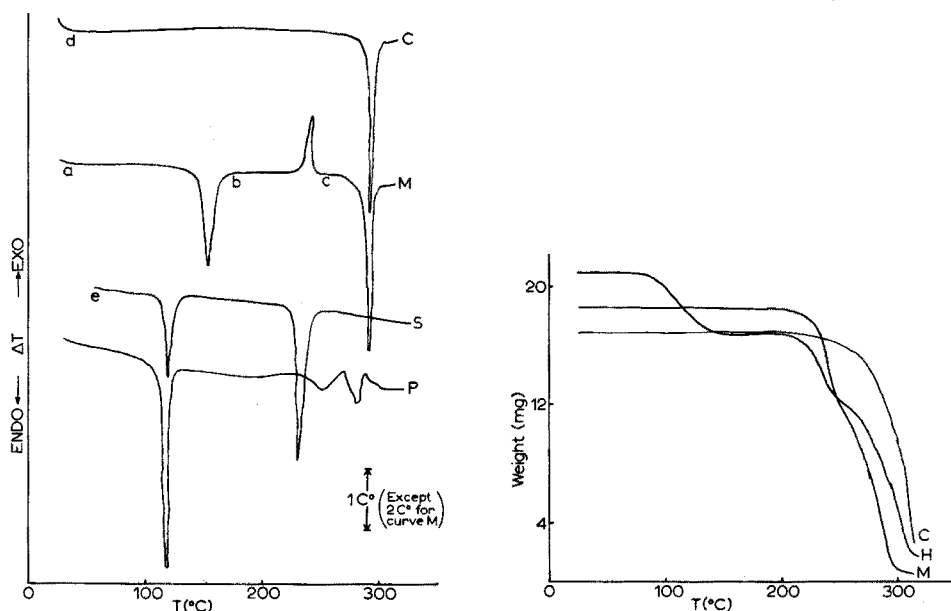


Fig. 1. DTA curves: (M) Meconic acid, (C) comenic acid, (P) pyromeconic acid (crude), (S) pyromeconic acid (resublimed). Lower-case letters refer to microanalytical samples (see Table I for results).

Fig. 2. TGA curves. (H) Meconic acid trihydrate, (M) meconic acid, (C) comenic acid.

When elemental analysis, and infrared and ultraviolet spectra, revealed no change at the 150° transition, X-ray powder patterns were obtained. These showed only a few lines in common before and after the thermal event. It is suggested that a



change in crystal structure occurs at this temperature. The decarboxylation of meconic acid to comenic acid appears to occur at the exothermic peak between 240 and 250°.

#### *Comenic acid*

Meconic acid was dried for 1 h at 100° and placed in a porcelain boat in a tube furnace maintained at  $250 \pm 10^\circ$ . The product was swept out into a long, water-cooled condenser by a gentle stream of dried air. Traces of sublimate first appeared when the furnace temperature passed 212°, and took the form of yellow needles. The product was titrated with standard potassium hydroxide solution, and its purity (calculated as comenic acid) was found to be  $98.9 \pm 0.2\%$ .

DTA and TGA studies were carried out as before on the material prepared, and on authentic comenic acid (DTA only) (Figs. 1 and 2). Infrared and ultraviolet spectra were recorded.

#### *Pyromeconic acid*

Equal weights of copper powder and dried comenic acid were sifted together into a flask and heated to 240° under a stream of carbon dioxide. A yellow sublimate was collected in a water-cooled condenser, and purified by resublimation at 100° to give white hexagonal crystals (m.p. 117°).

The tendency to sublime rapidly at low temperature made TGA experiments inappropriate, but DTA measurements were made as before on both the impure yellow sublimate, the white crystals, and an authentic sample. These results are also presented in Table I and in Figs. 1 and 2. The DTA curves suggest the possibility that comenic acid is the impurity in the initial product obtained.

#### *Conclusions*

Comenic acid is formed by decarboxylation of meconic acid in a reaction giving an exothermic DTA peak at 240°. At and above this temperature, the product sublimes. About 290°, comenic acid shows an endothermic DTA peak corresponding to its decomposition.

Pyromeconic acid is formed at a temperature well above its melting point. It displays a reversible DTA peak corresponding to its melting point at 117°. Even below this temperature, the acid sublimes rapidly.

Meconic acid displays an endothermic DTA peak about 150° which is not associated with a change of composition or spectra. X-Ray evidence suggests that it corresponds to a change in crystal structure.

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1 BEILSTEIN'S *Handbuch*, Vol. 18, p. 503.

2 M. I. GORYAEV AND U. S. BAZALITSKAYO, *Med. Prom. SSSR*, 16 (1962) 19.

3 L. L. WOODS, *J. Org. Chem.*, 22 (1957) 339.

- 4 G. A. GARKUSHA, *J. Gen. Chem. USSR*, 16 (1946) 2025.  
 5 G. A. GARKUSHA, *Zh. Obshch. Khim.*, 23 (1953) 1578.  
 6 D. B. DOTT, *Pharm. J.*, 106 (1921) 232.  
 7 S. KUHZOLZA AND V. HAHN, *Croat. Chem. Acta*, 33 (1961) 229.  
 8 I. S. BELONOSOV AND A. A. KONSTANTINOVA, *Zh. Prikl. Khim.*, 25 (1952) 1233.

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*Anal. Chim. Acta*, 49 (1970) 195-198

## Eine indirekte bromometrische Bestimmung von Harnsäure-Xanthin-gemischen

Zur analytischen Bearbeitung von Harnsäure-Xanthingemischen sind bisher chromatographische Trennungen und darauffolgende Einzelbestimmungen<sup>1-4</sup> oder enzymatische Abbaureaktionen mit Verfolgung der Veränderungen der u.v.-Absorption<sup>5</sup> beschrieben worden. Die Tatsache, dass die Umsetzung von Harnsäure mit Brom<sup>6</sup> nahezu unabhängig vom Redoxpotential der Lösung, welches durch das Verhältnis Brom zu Bromid gegeben ist, verläuft (siehe Abb. 1 obere Kurve), die des Xanthins unter denselben Bedingungen jedoch eine starke Abhängigkeit zeigt<sup>7</sup> (siehe Abb. 1 untere Kurve), macht indirekte Bestimmungen von Gemischen dieser Substanzen möglich. Da der Bromverbrauch für das Xanthin von der Temperatur abhängig ist (siehe Abb. 2), ist es zweckmässig bei 20° zu arbeiten. Gemische von Coffein, Theobromin und Theophyllin können nach einem analogen Verfahren analysiert werden<sup>8</sup>.

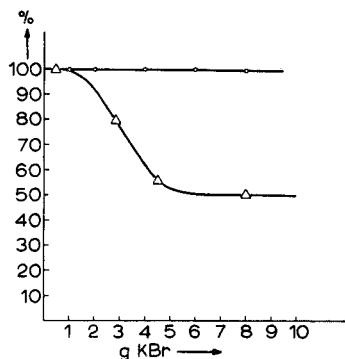


Abb. 1. Abhängigkeit der Umsetzungen mit Brom vom Redoxpotential. (○) Harnsäure, 100% bezogen auf MG/2; (△) Xanthin, 100% bezogen auf MG/4.

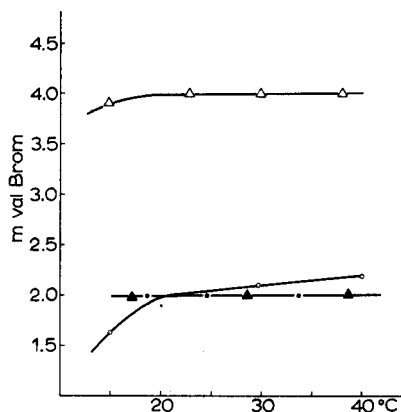


Abb. 2. Abhängigkeit des Bromverbrauches von der Reaktionstemperatur. (△△) Xanthin, 1 g KBr, 5 mval KBrO<sub>3</sub>; (○○) Xanthin, 8 g KBr, 5 mval KBrO<sub>3</sub>; (▲▲) Harnsäure, 1 g KBr, 5 mval KBrO<sub>3</sub>; (●●) Harnsäure, 8 g KBr, 5 mval KBrO<sub>3</sub>.

Von mehreren möglichen Wegen<sup>9,10</sup> zur Ermittlung des Puringehaltes eines Gemisches wurden von uns, die in folgenden Arbeitsvorschriften beschriebenen eingeschlagen.

*Arbeitsvorschriften*

*Methode a.* In einem 200-ml Schliffkolben werden etwa 100 mg des Puringemisches in 30 ml Wasser und einigen Tropfen 2 N Natronlauge gelöst, mit 50 ml 0.1 N KBrO<sub>3</sub> und 10 ml KBr (1.0 g) versetzt und auf 20° temperiert. Danach werden 10 ml 4 N H<sub>2</sub>SO<sub>4</sub> (20°) rasch zugefügt und das Reaktionsgefäß verschlossen. Nach 30 Minuten lässt man entlang des wenig gelüfteten Stopfens einige ml KJ-Lösung einfließen und titriert das ausgeschiedene Jod mit 0.1 N Thiosulfat gegen Stärke.

TABELLE I

BROMOMETRISCHE BESTIMMUNG VON HARNSÄURE-XANTHINGEMISCHEN

| Geg. (mg)        |                | Gef. (mg) |      | Fehler (%) |        |
|------------------|----------------|-----------|------|------------|--------|
| H <sup>a</sup>   | X <sup>b</sup> | H         | X    | H          | X      |
| <i>Methode a</i> |                |           |      |            |        |
| 55.2             | 52.7           | 55.6      | 52.3 | + 0.7      | - 0.7  |
| 71.6             | 30.0           | 72.2      | 29.8 | + 0.8      | - 0.8  |
| 79.0             | 26.7           | 78.8      | 27.6 | - 0.3      | + 0.3  |
| 117.5            | 25.5           | 114.1     | 24.8 | - 2.9      | + 2.9  |
| 34.3             | 69.5           | 34.8      | 68.5 | + 1.5      | - 1.5  |
| 23.8             | 79.9           | 24.4      | 66.5 | + 2.5      | - 2.5  |
| 47.8             | 72.0           | 48.8      | 70.6 | + 2.0      | - 2.0  |
| <i>Methode b</i> |                |           |      |            |        |
| 51.6             | 61.5           | 57.3      | 67.5 | + 11.0     | + 9.8  |
| 80.0             | 38.7           | 73.5      | 41.7 | - 8.1      | + 7.8  |
| 95.9             | 27.5           | 89.0      | 30.4 | - 7.2      | + 10.5 |
| 31.1             | 58.0           | 30.5      | 61.9 | - 1.9      | + 6.7  |
| 37.1             | 97.4           | 35.1      | 97.0 | - 5.4      | - 0.4  |
| 48.4             | 77.3           | 58.4      | 81.5 | + 20.6     | + 5.4  |

<sup>a</sup> Harnsäure.<sup>b</sup> Xanthin.

*Methode b.* Von einer Lösung des Substanzgemisches werden zwei gemessene Teile entnommen. Der eine nach Methode *a* umgesetzt, der zweite in gleicher Weise, nur mit dem Unterschied, dass statt 1 g KBr 8 g KBr (gelöst in 20 ml H<sub>2</sub>O) und 4 ml 10 N H<sub>2</sub>SO<sub>4</sub> zugesetzt werden.

Beleganalysen nach der Methode *a* für Gemische mit 24–118 mg Harnsäure und 26–80 mg Xanthin in Verhältnissen von 1:3 bis 5:1 und nach der Methode *b* für Gemische mit 31–96 mg Harnsäure und 39–97 mg Xanthin in Verhältnissen von 1:2.5 bis 3.5:1 ergaben relative Standardabweichungen von 1.9 bzw. 9.5%.

*Die Berechnung*

$$E_1 = \text{Einwaage in mg für die Umsetzung bei 1 g KBr.}$$

$$E_2 = \text{Einwaage in mg für die Umsetzung bei 8 g KBr.}$$

$$V_1, V_2 = \text{Verbrauch in ml 0.1 N KBrO}_3 \text{ für die Umsetzungen von } E_1 \text{ bzw. } E_2.$$

$$(a) \quad \% \text{ Xanthin} = 693.0 \frac{V_1}{E_1} - 82.5$$

$$\% \text{ Harnsäure} = 693.0 \frac{V_1}{E_1} + 182.5$$

$$(b) \quad \text{mg Xanthin} = 7.593 (V_1 - V_2)$$

$$\text{mg Harnsäure} = 16.81 V_2 - 8.405 V_1$$

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- 1 O. E. SCHULTZ UND D. STRAUSS, *Arzneimittel-Forsch.*, 50 (1955) 342.
- 2 G. LEHMANN UND P. MARTINOLD, *Z. Physiol. Chem.*, 341 (1965) 155.
- 3 H. MICHL UND F. HABERLER, *Monatsh. Chem.*, 85 (1954) 779.
- 4 R. OTT UND H. RABER, *Sci. Pharm.*, 28 (1960) 206.
- 5 M. B. BLAUCH UND F. C. KACH, *J. Biol. Chem.*, 130 (1939) 443.
- 6 H. RABER UND M. DIELACHER, *Sci. Pharm.*, 37 (1969) 129.
- 7 H. RABER, *Sci. Pharm.*, 36 (1968) 157.
- 8 H. RABER, *Sci. Pharm.*, 34 (1966) 202.
- 9 P. FUCHS, *Z. Anal. Chem.*, 79 (1930) 417.
- 10 P. FUCHS, *Z. Anal. Chem.*, 121 (1941) 305.

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*Anal. Chim. Acta*, 49 (1970) 198–200

## ANNOUNCEMENT

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### SYMPOSIUM ON NON-AQUEOUS ELECTROCHEMISTRY

*Paris*  
*July, 1970*

An international symposium on non-aqueous electrochemistry will be held in Paris on July 8–10, 1970, under the auspices of the International Union of Pure and Applied Chemistry. The Honorary President is Professor I. M. KOLTHOFF and the President, Professor G. CHARLOT.

The topics of the symposium will be: solvation, electroanalytical methods in non-aqueous solvents, electrochemical investigation of ionic equilibria (acid–base, redox, complexation, etc.), organic electrode reactions. Studies encompassing these subjects in fused salts will also be included in the coverage.

The number of participants will be restricted to 200; the registration fee will be \$ 30.

Further information can be obtained from the Executive Chairman, Dr. J. BADOZ-LAMBLING, Laboratoire de Chimie Analytique, E.S.P.C.I., 10 rue Vauquelin, Paris 5, France.

*Anal. Chim. Acta*, 49 (1970) 200

## BOOK REVIEWS

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ORION E. SCHUPP III, *Technique of Organic Chemistry. Vol. XIII. Gas Chromatography*, Edited by E. S. PERRY AND A. WEISSBERGER, Interscience Publishers—J. Wiley and Sons, Inc., New York, 1968, xxi+437 pp., price 155 s.

The number of standard texts relating to gas chromatography in general or to particular aspects of the technique is now quite large and the appearance of another, even in a well-established series such as the *Technique of Organic Chemistry*, must clearly show an advance in both content and presentation. Dr. SCHUPP aims to present a review of the subject for the practising organic chemist rather than for the analytical research worker to whom much of the content of this volume will be well known.

In this aim he is reasonably successful although it may be argued that the theoretical section is somewhat over-elaborate for the general reader. A similar criticism applies to the section on operation and design of equipment. The chapter on columns, however, is most useful, particularly in the number of practical details given which are not often collected in similar volumes.

The author treats analytical applications under the two major headings of qualitative and quantitative analysis and gives full treatment to mathematical methods for the extraction of maximum data from chromatograms. However, such topics as temperature and flow programming and preparative G. C. receive relatively scant treatment.

The book is well written, clearly laid out and up to date and should be well received.

*Anal. Chim. Acta*, 49 (1970) 201

ALFRED A. SCHILT, *Analytical Applications of 1,10-Phenanthroline and Related Compounds*, Pergamon Press, Oxford, 1969, viii+193 pp., price 70 s (\$ 9.00).

This monograph, one of the latest to appear in the Pergamon International Series dealing with selected topics in analytical chemistry, provides the first comprehensive account of that important series of analytical reagents containing the iron(II)-methine chromophore and exemplified by 2,2'-bipyridine and 1,10-phenanthroline.

The text has a short introductory chapter detailing history, nomenclature and properties of the compounds. This is followed by a general chapter describing the formation and properties of the many metal chelates of phenanthroline-type ligands. The next two chapters contain information on the most widely recognised analytical applications of these reagents, namely as colorimetric reagents and redox indicators. Three further chapters deal in turn with uses as metathesis indicators, as precipitants, and as reagents in a miscellany of analytical processes. The text concludes with a short but useful account of the determination of the ligands, 1,10-phenanthroline and 2,2'-bipyridine, and their recovery from aqueous solutions of their metal complexes. The

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importance of the ferriin- and cuproin-type reagents need not be emphasised for readers of this analytical journal. There are few other reagents, particularly for spectrophotometric purposes, which can compare with them for sensitivity and selectivity. But their versatility may not be so widely recognised and for this reason, the present volume is to be welcomed. In recent years, largely as a result of the synthetic work of F. H. CASE making new ligands available, and the analytical work of G. F. SMITH and his colleagues describing new and better reagents, the literature on these compounds has become quite extensive; however, the relative merits of individual reagents have become less well defined. The present monograph brings all this new information together in the concise and critical fashion one would expect from someone who is actively engaged in furthering the analytical chemistry of the ferriin-type reagents. This is a most worthwhile monograph which can be thoroughly recommended as the only up-to-date authoritative source of information on this most versatile range of organic reagents.

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*Encyclopedia of Industrial Chemical Analysis. Vol. 6. Antifreezes to Benzaldehyde*, Edited by F. D. SNELL AND C. L. HINTON, Interscience Publishers—J. Wiley & Sons, Inc., New York, 1968, xi+680 pp., price 425 s (subscription price 310 s).

The subjects covered in this volume are antifreezes, antihistamines, antimony, antioxidants and antiozonants, antipyretics and analgesics, arsenic, asbestos, asbestos-cement products, asphalts, tar and pitches, automotive chemical specialities, azines and related dyes, azo dyes, bakery chemicals, bakery products, barbiturates, barium and its compounds, bead and flame tests, and benzaldehyde and its derivatives. Probably the only topic that is not self-explanatory is automotive chemical specialities, which term, in fact, covers a miscellany of items such as antirusts, cooling system cleaners, waxes and polishes, engine tuners, etc.

One is rather relieved to see that this Encyclopedia has finally reached B after  $2\frac{2}{3}$  volumes of discussion of A subjects. The bulk to come becomes awesome in terms of effort, weight and cost; one wonders if an effort to improve the cost-effectiveness of each volume would not be worthwhile. For example, detailed descriptions of the purpose of each item in a cake or a loaf scarcely seem necessary in an industrial analysis book; similar objections could be made about the automotive chemical specialities, which is surely an improbable heading to look under if one means car or even automobile accessories. Why include two similar detailed diagrams of storage apparatus for titanium(III) solutions, particularly when alternative simpler methods, *e.g.* storage under heptane, are ignored?

These volumes contain a good deal more information, both mundane and physical, than is implied by the title. Each section is written by experts from American industrial laboratories from a properly practical viewpoint, and thoroughly tested analytical methods abound. The current volume maintains the standard of its predecessors and will doubtless prove as useful.

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GYÖRGY PATAKI, *Techniques of Thin-Layer Chromatography in Amino Acid and Peptide Chemistry*, Revised Edition, Ann Arbor Science Publishers, Ann Arbor, 1968, xviii + 218 pp.

This monograph, first published in German in 1966, and revised (with selected up-dated references) by the author for translation into English in 1967, presents a general survey of the use of TLC for the analysis of amino acids and peptides. The text is divided into four main parts: part 1 deals with the technique of TLC in sufficient detail for the reader to apply it without further recourse to the literature. Parts 2, 3 and 4 describe published and unpublished work on the TLC of amino acids, peptides and related compounds, the sequential analysis of proteins and peptides, and the examination of biological material. The bibliography of 485 references covers the literature to 1966. The text is well tabulated and illustrated. The importance of chromatographic methods to the study of amino acids is well recognised, particularly with respect to paper chromatography; the present volume establishes the advantages of the thin layer technique in this field, and provides a timely and useful source of practical information.

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T. R. CROMPTON, *Analysis of Organoaluminium and Organozinc Compounds*, International Series of Monographs in Analytical Chemistry, Vol. 31, Pergamon Press, Oxford, xiv + 354 pp., price £ 6-6s.

The analysis of organometallic compounds is one of the problems which has taxed the ingenuity of the analytical chemist in recent years. Very often classical methods fail because of interferences from metals or because of the instability of the compounds themselves. Thus extremely specialised techniques must be devised, and this monograph describes the wide range developed for this particularly important group of organometallics which are now of considerable commercial importance.

The problems of handling these frequently pyrophoric and unstable compounds are stressed throughout and much of the technique is of considerable general interest. Similarly, many of the analytical methods necessitate a good understanding of physical properties and reaction chemistry, these being well documented by the author.

Analytical methods are classified under the headings: functional group and elemental analysis of organoaluminium compounds, solution methods of analysis including electrometric methods, iodimetry, thermometric titration and spectroscopic methods. Chromatographic techniques are also stressed and modifications of methods for organozinc compounds indicated where appropriate.

The subject matter is very clearly presented and the monograph will be an essential reference for all involved in this field. It is unfortunate that the high price may limit its wider readership, for much of general interest to the organometallic chemist is included.

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## PUBLICATIONS RECEIVED

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*Radiochemical and Radioanalytical Letters*, Vol. 1, No. 1, edited by J. TÖLGYESSY AND T. BRAUN, Elsevier Sequoia, Lausanne; Akademiai Kiadó, Budapest, 1969.

This is the first issue of a new international journal for rapid communication in the relevant fields.

*Absorption Spectra in the Ultraviolet and Visible Region, Cumulative Index for Vols. VI-X*, edited by L. LANG, Akademiai Kiadó, Budapest, 1969, 113 pp., price 15 s.

*Fibrous Proteins*, edited by W. G. CREWHER, Butterworth (Australia) Ltd., Sydney, 1968, 432 pp., price 200 s.

This volume contains the Proceedings of the third Symposium on fibrous proteins which was held in Canberra in August 1967. There are 49 papers dealing with the relation between amino-acid composition and conformation of polypeptides and proteins, muscle and flagella, collagen and elastin, and keratin.

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