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

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 41, No. 1, 1–188, April 1968
Published monthly

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1. J. J. Lingane and A. M. Hartley, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. Feigl, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

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ห้องสมุด กรมวิทยาศาสตร์

aromatic amine oxides

by **E. OCHIAI**

Emeritus Professor of Pharmaceutical Chemistry,
University of Tokyo (Japan)

6 x 9", ix + 456 pages, 87 tables, 31 illus., 1150 lit. refs., 1967, Dfl.85.00, £10.5.0, $ 30.00.

A general review of developments in the chemistry of aromatic amine oxides has been necessitated by the marked progress of the last twenty years, and is presented here by the world's outstanding expert in the field.

The book opens with a general survey of tertiary amine oxides in which the characteristic nature of aromatic amine oxides is outlined. Three chapters, devoted to the chemical reactivity of these compounds, should be very useful to those carrying out synthetic work in the field or aromatic N-heterocyclic compounds. Other chapters are devoted to various synthetic methods which have been developed for aromatic amine oxides, and to the physico-chemical examination of the characteristics of these compounds. Numerous data are given for dipole moments, X-ray diffraction, polarography, dissociation constants, and nuclear magnetic resonance, infrared and ultraviolet spectra. An attempt has been made to correlate these physical data with the chemical reactivity of the compounds described by means of the molecular orbital theory.

The final chapter deals with the biological activities of some aromatic amine oxides, including their antimicrobial and antiprotozoal action, mutagenic, carcinogenic, and carcinostatic properties, use as tranquillizers, etc.

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1. Introduction.
2. General survey of amine oxides.
3. Preparation of aromatic amine oxides.
4. Physico-chemical properties of aromatic N-oxides.
5. Reactivity of the aromatic N-oxide group.
6. Electrophilic substitution.
7. Nucleophilic substitution.
8. Effect of the N-oxide group on substituents.
9. Biological properties of aromatic amine oxides.

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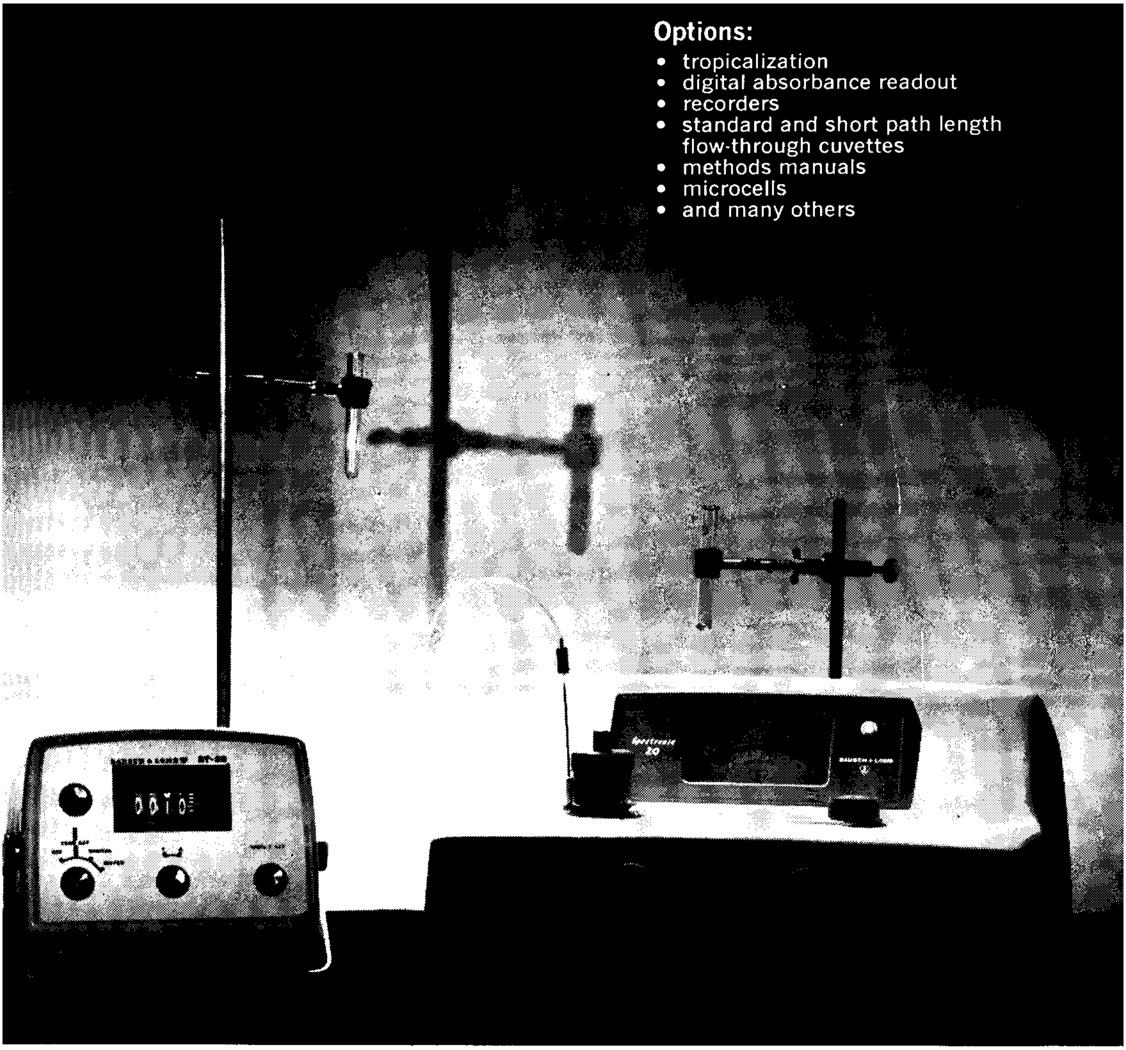

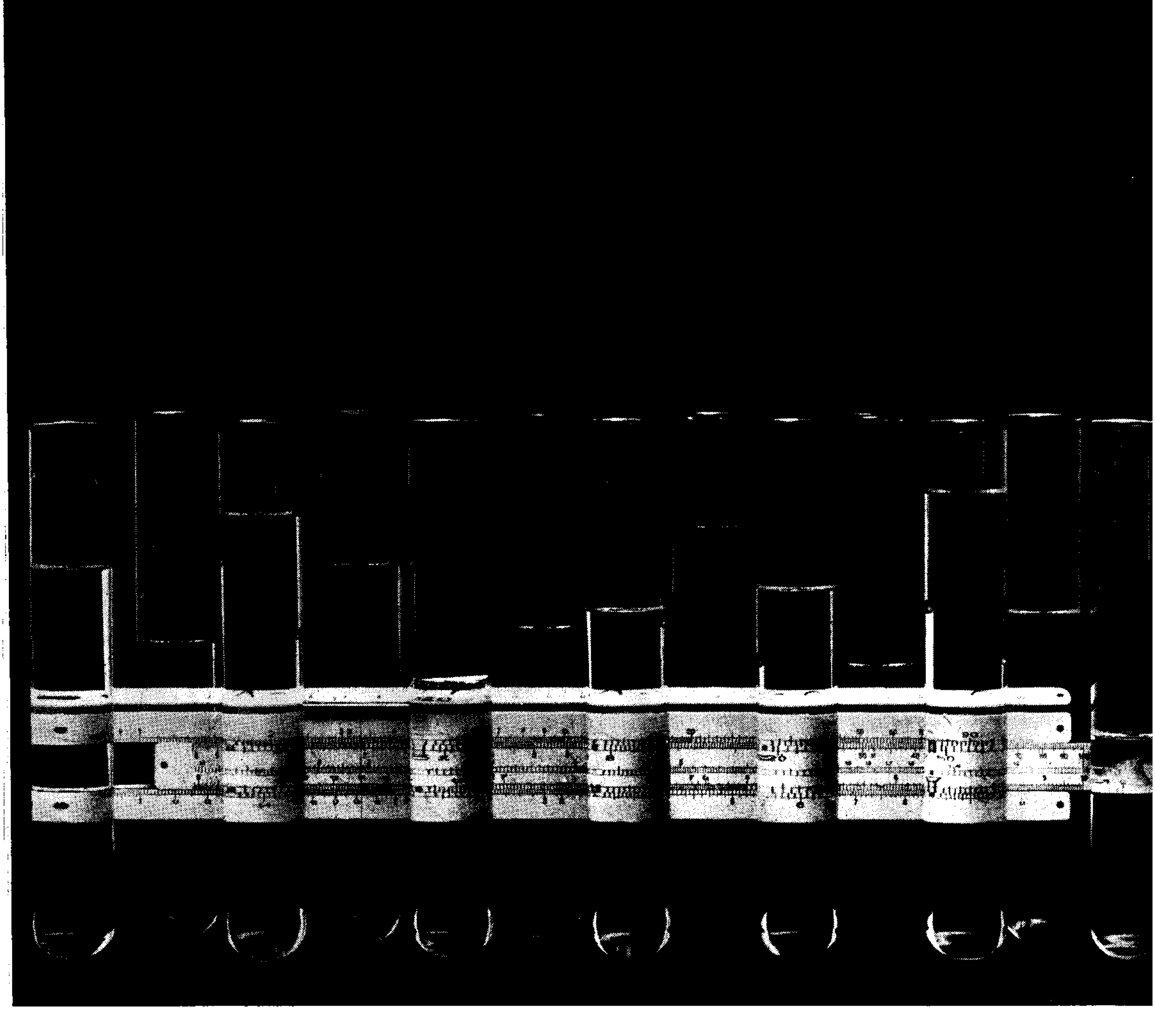

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA,

Volume 41, No. 1, April 1968

A POTENTIOMETRIC STUDY OF THE WATER-SOLUBLE SILVER(I) COMPLEXES OF N,N′-BIS(2-HYDROXYETHYL)-DITHIO-OXAMIDE

PART II. DETERMINATION OF THE MEAN COMPOSITION $\bar{p}$ AND $\bar{q}$

A method is described for determining the mean composition of the complex compounds of silver(I) and HEDTO. The values obtained do not agree with those calculated on the assumption that only $B(AB)_n$ complexes are formed. It is concluded that besides the complexes $B(AB)_n$, other complexes with formula $(AB)_n$ are present.

L. C. VAN POUCKE AND M. A. HERMAN,
Anal. Chim. Acta, 41 (1968) 1–7

THE APPLICATION OF SALICYLALDOXIME IN SOLVENT EXTRACTION

The extraction of divalent magnesium, manganese, cobalt, nickel, copper, zinc, cadmium, mercury, and lead with solutions of salicylaldoxime in benzene was investigated. The effect of the reagent concentration and particularly the pH of the aqueous phase on the extractability was studied. The application of salicylaldoxime extractions in the separation and determination of various elements is discussed.

I. DAHL,
Anal. Chim. Acta, 41 (1968) 9–14

EXTRACTION STUDIES OF ANTIMONY BROMIDE INTO BENZENE

Antimony(III) can be extracted rapidly and quantitatively into benzene from a 10 M H_2SO_4–0.03 M HBr system. The extracted antimony bromide has an antimony to bromine ratio of 1:3. Under the above optimum conditions for extraction of antimony, the behaviour of 35 other elements was studied; As^{3+}, Ge^{4+}, Se^{4+}, and Sn^{2+} were extracted almost quantitatively, and the percentage extraction of Hg^{2+}, Bi^{3+}, and Te^{4+} was 74.1%, 10% and 5.5% respectively. The extraction of the elements into benzene from a 5 M H_2SO_4–0.01 M KI system was also investigated. A comparison of the two systems is given.

A. P. GRIMANIS AND I. HADZISTELIOS,
Anal. Chim. Acta, 41 (1968) 15–21

THE SOLVENT EXTRACTION OF INDIUM(III) WITH CARBOXYLIC ACIDS

The extractions of 10^{-5}–10^{-7} M indium from aqueous 0.1 M sodium perchlorate solutions into various organic media containing different concentrations of monocarboxylic acids and into pure monocarboxylic acids have been studied. Both saturated and unsaturated acids have been employed; the number of carbons in the acids was 1–18. Detailed studies of one of the better systems, hexanoic acid in chloroform, have been carried out, the system has been described with a general overall equation, and identifications of the major species have been proposed.

G. K. SCHWEITZER AND M. M. ANDERSON,
Anal. Chim. Acta, 41 (1968) 23–28

APPLICATION OF MODIFIED COUNTER-CURRENT TECHNIQUE TO THE DETERMINATION OF TUNGSTEN IN MOLYBDENUM

More than trace amounts of molybdenum interfere in the determination of tungsten by the dithiol method. A simplified counter-current extraction method is described which allows the determination of 5 p.p.m. or more of tungsten in a molybdenum matrix. The optimum conditions for the separation were a 6 M HCl–2.4 M HF medium and methyl isobutyl ketone as extractant; the percentage extractions in a single pass were 85% and 15% for molybdenum and tungsten, respectively.

S. Kallmann, E. W. Hobart and H. K. Oberthin,
Anal. Chim. Acta, 41 (1968) 29–34

PREPARATION OF *o,o'*-DICHLORODITHIZONE AND A STUDY OF ITS METAL COMPLEXING PROPERTIES

o,o'-Dichlorodithizone was synthesised and its spectral characteristics were measured in carbon tetrachloride. The pH ranges for quantitative extraction of various metal complexes were determined. Values for wavelengths of maximum absorption and molar extinction coefficients are given; the former increase in the order $Ag^{+} < Hg^{2+} < Bi^{3+} < Pb^{2+} < Cd^{2+} < Zn^{2+} < Cu^{2+}$ and the latter in the order $Ag^{+} < Bi^{3+} < Cu^{2+} < Hg^{2+} < Pb^{2+} < Cd^{2+} < Zn^{2+}$. Substitution of chlorine produces a regular bathochromic shift in wavelength of maximum absorption for reagent and their metal complexes compared to the dithizonates. No evidence was found that a "steric effect" of the *o*-substituent interferes with chelate ring formation for Zn, Cd, Hg and Pb; the results confirm the view that complex formation takes place through the thio-H of the reagent. The extractability of lead as its *o*-dichlorodithizonate into carbon tetrachloride was investigated in the pH range 5–11 and the extraction constant was measured.

R. S. Ramakrishna and M. Fernandopulle,
Anal. Chim. Acta, 41 (1968) 35–41

THE FORMATION OF HYDROGEN PEROXIDE IN METALLIC REDUCTORS

The formation of hydrogen peroxide in various types of metallic reductors both in the presence and absence of oxygen has been studied. Only when oxygen is rigorously excluded is peroxide undetectable. The oxidimetric determination of iron is seriously affected by this peroxide when the test solution and reductor are open to atmospheric oxygen. Systems which are completely oxygen-free give satisfactory results.

M. A. Salam Khan and W. I. Stephen,
Anal. Chim. Acta, 41 (1968) 43–49

POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

PART XIII. ANODIC WAVES OF DIALKYLDITHIOCARBAMATES

Dialkyldithiocarbamates give only a one-electron anodic wave. The various adsorption phenomena are probably caused by varying orientation of the mercury compounds on the electrode surface; the irregular *i–t* curves recorded at -0.04 V and the anomalous behaviour of the anodic current between $+0.2$ V and -0.4 V can be interpreted as the behaviour of an adsorbed film at the electrode. Analytical measurements are best made in 60% ethanolic 0.1 M sodium hydroxide media at concentrations of about 10^{-5} M dialkyldithiocarbamate; a method is given for the analysis of the monoalkyl and dialkyl compounds in mixtures.

D. J. Halls, A. Townshend and P. Zuman,
Anal. Chim. Acta, 41 (1968) 51–62

POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

PART XIV. ANODIC WAVES OF ETHYLENE-1,2-BISDITHIOCARBAMATE AND REACTIONS WITH HEAVY METALS

The presence of two 2-electron anodic steps on polarographic curves of ethylene-1,2-bisdithiocarbamates together with the shifts of the half-wave potentials with pH and the adsorption phenomena, indicate a simultaneous reaction of both dithiocarbamate groupings at the electrode surface. In the homogeneous alkaline solutions, cadmium(II), copper(II) and lead(II) ions form an intermediate 1:1 compound with ethylene-1,2-bisdithiocarbamate in which only one dithiocarbamate group reacts. A 1 *M* sodium hydroxide solution is most suitable for the determination of the ethylene-1,2-bisdithiocarbamate anion liberated from zinc or manganese derivatives in the analysis of pesticides ZINEB and MANEB. Waves of disodium ethylene-bisdithiocarbamates (NABAM) allow $1 \cdot 10^{-5}$ *M* solutions to be analysed.

D. J. Halls, A. Townshend and P. Zuman,
Anal. Chim. Acta, 41 (1968) 63–74

SOME VANADIUM(V) COMPLEXES AS REAGENTS FOR THE PHOTOMETRIC DETERMINATION OF ALCOHOLS

Vanadium(V) complexes with an acidic hydroxy group attached to the metal form the corresponding esters with alcohols. These esters show a characteristic absorption at 445–480 nm, so that alcoholic hydroxy groups can be determined photometrically. The formation constants of the *n*-butanol esters of vanadium maltolate and 2-methyl-8-hydroxyquinolinate were determined in benzene or benzene–chloroform (1:1). Simple methods are described for the determination of alcohol in the concentration range 10^{-1}–10^{-4} *M*.

M. Tanaka and I. Kojima,
Anal. Chim. Acta, 41 (1968) 75–81

THE APPLICATION OF X-RAY DIFFRACTION ANALYSIS TO URANIUM CERAMICS

PART II. QUANTITATIVE ANALYSIS OF THE URANIUM CARBIDES

Different X-ray diffractometer methods are proposed for the determination of uranium carbides in binary and multicomponent mixtures (direct methods, internal standard and active dilution method). The relative standard deviation was found to be 2%. Limits of detection for UC_2 and UO_2 in UC were about 0.04%. Calculations showed that the UC_2 in the samples used contained 9.00 and 9.28 ± 0.04 wt % of combined carbon, corresponding to $UC_{1.96\pm0.01}$ and $UC_{2.03\pm0.01}$.

R. Conti, C. J. Toussaint and G. Vos,
Anal. Chim. Acta, 41 (1968) 83–91.

SOME INTERFERENCES IN THE ATOMIC ABSORPTION SPECTROPHOTOMETRY OF CALCIUM

The effects of anions, cations and complexing agents on the absorbance of calcium in the air–propane flame are investigated. Mechanisms for the various enhancing and depressive effects are suggested.

C. Rocchiccioli and A. Townshend,
Anal. Chim. Acta, 41 (1968) 93–98

THE DEVELOPMENT OF FLUORIDE-SENSITIVE MEMBRANE ELECTRODES

PART I. MEMBRANES CONTAINING THORIUM, LANTHANUM OR CALCIUM FLUORIDE

Fluoride-sensitive membrane electrodes of the PUNGOR type are described. In these electrodes, a fluoride precipitate is incorporated in a silicone rubber membrane; fluorides of thorium, lanthanum and other rare earths, and calcium have been examined. The method of preparing the precipitate is important; an excess of metal is vital for correct functioning of the final electrode. The most reliable results were obtained with calcium fluoride electrodes, though their sensitivity was less than that of the best lanthanum fluoride electrodes. With these electrodes, linear responses are obtained in the 10^{-2}–10^{-4} M fluoride range.

A. M. G. MACDONALD AND K. TOTH,
Anal. Chim. Acta, 41 (1968) 99–106

THE DETERMINATION OF METALLIC IRON, NICKEL AND COBALT IN REDUCED ORES AND OXIDES

A procedure is described for the determination of metallic iron, nickel and cobalt in reduced ores and oxides. The metallic phases are dissolved in bromine–methanol solution, excess of bromine is destroyed by reaction with hydroxylamine hydrochloride and the analysis is completed by atomic absorption spectrophotometry. Solution of oxide phases is not observed if free or combined water is removed from the samples. Results are presented for an ore and standard alloys.

K. KINSON, J. E. DICKESON AND C. B. BELCHER,
Anal. Chim. Acta, 41 (1968) 107–112

DETERMINATION OF BIURET IN UREA AND MIXED FERTILIZERS

A new method has been developed for the determination of biuret in urea, based on the separation of the copper–biuret complex with the aid of an anion-exchanger, followed by titration of the bound copper with EDTA. This method may be used directly for the determination of biuret in solutions and in end-products of a urea factory, even with biuret contents down to 0.001%. The well-known photometric method cannot be used for less than 0.1% biuret contents; corrections are needed for the interference of urea, and ammonia and insoluble products have to be removed. Both methods are suitable for the determination of biuret in mixed fertilizers down to 0.5%, provided that cations are first removed on a cation exchanger. However, the photometric determination calls for special precautions with regard to acidity when phosphates are present.

J. J. GEURTS, J. E. VAN STELLE AND E. G. BRINKMAN,
Anal. Chim. Acta, 41 (1968) 113–120

THE EFFECT OF CATALYSTS ON THE THERMAL DECOMPOSITION OF SODIUM SUPEROXIDE

Simultaneous differential thermal, thermogravimetric and differential thermogravimetric analysis have been made on samples of sodium superoxide and sodium superoxide containing 1% (w/w) copper(I) oxide. Decomposition of the superoxide involving oxygen production (weight loss) does not occur at a meaningful rate until temperatures approach 250°. The effects of 12 metallic oxide catalysts and one metallo-organic catalyst on the decomposition of sodium superoxide have been studied by differential thermal analysis. Six metallic oxides had no effect while 3 oxides (palladium oxide, titanium oxide and cadmium oxide) caused small but distinct changes in the DTA plots. A polymeric phthalocyanine, and the oxides of vanadium(III), vanadium(V) and manganese(IV) apparently reacted with the superoxide above 250°. Pretreatment of the superoxide by brief exposure to 100% humidity resulted in the formation of peroxyhydrates of sodium peroxide which upon dissociation produced water vapor in turn causing the release of oxygen from the superoxide and peroxide at lower temperatures than those experienced with untreated superoxide samples.

J. A. MARRIOTT, A. CAPOTOSTO, JR. AND A. W. PETROCELLI,
Anal. Chim. Acta, 41 (1968) 121–129

N-BENZOYL-N-PHENYLHYDROXYLAMINE AND THE DETERMINATION OF TITANIUM

Benzoylphenylhydroxylamine reacts with titanium in 10 *N* hydrochloric acid to give a ternary complex which, on extraction, permits the determination of 1–6 p.p.m. of titanium. Only niobium, in the presence of tin(II) chloride, is a serious interference. An enhanced sensitivity which is obtained if thioycanate is present is advantageous if iron is absent. Titanium is accurately determined in steels, other alloys and refractories.

B. K. AFGHAN, R. G. MARRYATT AND D. E. RYAN,
Anal. Chim. Acta, 41 (1968) 131–138

SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM IN ZIRCONIUM WITH 4-(2-PYRIDYLAZO)RESORCINOL

The direct spectrophotometric determination of niobium in zirconium alloys with 4-(2-pyridylazo)resorcinol is described. Samples are dissolved in hydrofluoric–sulphuric acid mixture and the colour developed without the removal of fluoride. In the presence of EDTA only Co^{2+}, Ta^{5+}, and V^{5+} cause serious interference. The molar absorptivity is $3.67 \cdot 10^4$ in the presence of 1 mg of zirconium, and Beer's law is obeyed up to 1.0 μg Nb/ml. The method can be applied to zirconium alloys containing as little as 0.005% niobium.

P. PAKALNS AND A. B. IVANFY,
Anal. Chim. Acta, 41 (1968) 139–145

NEUTRON ACTIVATION ANALYSIS OF HIGH-PURITY SELENIUM

PART II. DETERMINATION OF TELLURIUM

Neutron activation determination of 15–25 p.p.b. of tellurium in selenium can be done by irradiating 100-mg samples for 4 days at a neutron flux of $6 \cdot 10^{12}$ n.cm^{-2}.sec^{-1}. The daughter isotope of ^{131}Te, ^{131}I, is separated by distillation and extracted into carbon tetrachloride. Finally the silver iodide precipitate is measured by β,γ-coincidence counting. The standard deviation is 3–7%.

C. BALLAUX, R. DAMS AND J. HOSTE,
Anal. Chim. Acta, 41 (1968) 147–154

THE DETERMINATION OF PHOSPHORUS IN ROCKS BY NEUTRON ACTIVATION

(Short Communication)

A. O. Brunfelt and E. Steinnes,
Anal. Chim. Acta, 41 (1968) 155–158

A METHOD FOR THE DETERMINATION OF INTERFERENCES IN AUTOMATIC COLORIMETRIC ANALYSIS

(Short Communication)

J. E. Lindquist,
Anal. Chim. Acta, 41 (1968) 158–160

SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH 3,3′-DIMETHYLENE-4,4′-DIPHENYL-2,2′-DIQUINOLYL

(Short Communication; in German)

E. Uhlemann and K. Waiblinger,
Anal. Chim. Acta, 41 (1968) 161–164

A STUDY OF INTERFERENCES IN THE SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM WITH SULFOSALICYLIC ACID

(Short Communication)

M. Qureshi, J. P. Rawat and F. Khan,
Anal. Chim. Acta, 41 (1968) 164–166

THE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL IN SEA WATER WITH PYRIDINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE

(Short Communication)

B. K. Afghan and D. E. Ryan,
Anal. Chim. Acta, 41 (1968) 167–170

COMBINED THERMO-DILATOMETRIC AND DERIVATOGRAPHIC EXAMINATION OF HYDRARGILLITE AND BARIUM CHLORIDE DIHYDRATE

(Short Communication)

F. Paulik, J. Paulik and L. Erdey,
Anal. Chim. Acta, 41 (1968) 170–172

TITRIMETRIC DETERMINATION OF BERYLLIUM IN PRESENCE OF LARGE AMOUNTS OF URANIUM

(Short Communication; in French)

G. UNY, TRAN VAN DANH AND J. SPITZ,
Anal. Chim. Acta, 41 (1968) 173–175

THE USE OF CHELATING ION EXCHANGE IN THE DETERMINATION OF MOLYBDENUM AND VANADIUM IN SEA WATER

(Short Communication)

J. P. RILEY AND D. TAYLOR,
Anal. Chim. Acta, 41 (1968) 175–178

FLUORIMETRIC DETERMINATION OF GLYCINE AND OTHER AMINO ACIDS WITH 2,4-BUTANEDIONE

(Short Communication)

E. SAWICKI AND R. A. CARNES,
Anal. Chim. Acta, 41 (1968) 178–180

DETERMINATION OF LANTHANUM, HOLMIUM, AND URANIUM IN THEIR TUNGSTEN BRONZES BY THERMAL NEUTRON ACTIVATION

(Short Communication)

M. A. WECHTER AND A. F. VOIGT,
Anal. Chim. Acta, 41 (1968) 181–184

ountercurrent
eparation Processes

by H. R. C. Pratt

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

× 9″, xxii + 537 pages, 30 tables, 173 illus., 415 lit.refs., 1967, Dfl. 95.00, £11.0.0, US$34.00

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

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

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

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

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Pigments

An Introduction to their Physical Chemistry

edited by David Patterson

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

5½ × 8½″, ix + 210 pages, 93 illus., 1967, Dfl. 32.50, 65s., US $ 12.00

In this book the principles of physical chemistry are applied to the problems of making ar using the insoluble organic and inorganic pigments manufactured for use in paints, printir inks, plastics and synthetic fibres. Development over many years has resulted in a high degr of technical quality in many of these pigments, achieved by purely empirical methods, but tl use of such methods means that each case must be judged on its merits. On the other han the application of physico-chemical theories can bring unifying concepts to a wide range 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 compound and to emphasize this the purely preparative chemistry of pigments has been left outside tl scope of this book. Instead, pigments are regarded as substances produced to exert particul optical effects on certain media by colouring and opacifying them. The ways in which pi ments can be prepared to carry out these functions, together with the appropriate techniqu for appraising their performance of them are consequently the main content of the book. A the problems cannot be solved at present, but this book by showing what can be achiev and attempting to provide signposts to some of the unexplored areas, will undoubtedly stim late and encourage further work in a field that is of considerable industrial importance.

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AMSTERDAM LONDON NEW YORK

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ANALYTICA CHIMICA ACTA

Vol. 41 (1968)

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

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 41 (1968)

PRINTED IN THE NETHERLANDS

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A POTENTIOMETRIC STUDY OF THE WATER-SOLUBLE SILVER(I) COMPLEXES OF N,N'-BIS(2-HYDROXYETHYL)DITHIO-OXAMIDE

PART II. DETERMINATION OF THE MEAN COMPOSITION $\bar{p}$ AND $\bar{q}$

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(Received October 5th, 1967)

In a previous paper[1] it was found that the composition of the complexes formed between silver(I) and N,N'-bis(2-hydroxyethyl)dithio-oxamide (HEDTO) can be represented by the general formula $B(AB)_n$, in which B is the ligand and A the metal ion. However, in the region where $Z=(C_A-A)/C_B$ tends to 1, deviations from this formula are found. These deviations can be explained by the formation of complexes with the general formula $(AB)_n$, although the existence of these complexes was not proved.

In this paper the results of further examination and the experimental determination of the mean coefficients $\bar{p}$ and $\bar{q}$ are described.

$\bar{p}$ and $\bar{q}$ are defined as follows[2,3]:

$$\bar{p}=(C_A-A)/S \text{ and } \bar{q}=(C_B-B)/S$$

where

$$S = \sum_{p=1}^{p=P} \sum_{q=1}^{q=Q} C_{pq}$$

and C_{pq} is the concentration of the complex A_pB_q.

The values of C_A-A and C_B-B used here are obtained from experimental data mentioned in the previous paper[1].

S was determined by a method analogous to those used by BYE[4,5] and LEFEBVRE[6,7].

Description of the method

The change in free energy at constant pressure and temperature is given by the following expression:

$$dF=\mu_1 dn_1+\mu_2 dn_2+ \ldots +\mu_n dn_n \tag{1}$$

where μ_i is the chemical potential of species i, and n_i is the number of moles of this species present.

For each complex i we can write the following general reaction equation[1]:

$$p_iA+q_iH_2X \rightleftarrows A_{p_i}H_{2q_i-r_i}X_{q_i}+r_iH^+$$

For each of these equations the equilibrium relation holds:

$$p_i\mu_A+q_i\mu_B-r_i\mu_H=\mu_{C_{p_iq_ir_i}} \tag{2}$$

$C_{p_iq_ir_i}$ is the concentration of the complex $A_{p_i}H_{2q_i-r_i}X_{q_i}$. In the solution the following components are present: H_2O, A, B, H^+, ClO_4^-, Na^+ and n complexes $A_{p_i}H_{2q_i-r_i}X_{q_i}$. Thus eqn. (1) becomes:

$$\begin{aligned} dF=&\mu_A dn_A+\mu_B dn_B+\mu_H dn_H+\mu dn+\mu_{ClO_4^-}dn_{ClO_4^-}\\ &+\mu_{Na^+}dn_{Na^+}+\sum_i \mu_{c_{p_iq_ir_i}}dn_{c_{p_iq_ir_i}} \end{aligned} \tag{3}$$

μ and n are the chemical potential, respectively the number of moles of the solvent. Substitution of eqn. (2) in eqn. (3) gives:

$$\begin{aligned} dF=&\mu_A d(n_A+\sum_i p_i n_{c_{p_iq_ir_i}})+\mu_B d(n_B+\sum_i q_i n_{c_{p_iq_ir_i}})\\ &+\mu_H d(n_H-\sum_i r_i n_{c_{p_iq_ir_i}})+\mu dn+\mu_{ClO_4^-}dn_{ClO_4^-}\\ &+\mu_{Na^+}\cdot dn_{Na^+} \end{aligned} \tag{4}$$

In this:

$$n_A+\sum_i p_i n_{c_{p_iq_ir_i}}=a=\text{the total number of moles of A}$$

$$n_B+\sum_i q_i n_{c_{p_iq_ir_i}}=b=\text{the total number of moles of B}$$

$$n_H-\sum_i r_i n_{c_{p_iq_ir_i}}=h=\text{the total number of moles of mineral acid HClO}_4$$

Thus, eqn. (4) can be written:

$$dF=\mu_A da+\mu_B db+\mu_H dh+\mu_{ClO_4^-}dn_{ClO_4^-}+\mu_{Na^+}dn_{Na^+}+\mu dn \tag{5}$$

The method exists in the dilution of a solution containing a moles of metal ion, b moles of ligand, h moles of perchloric acid and a quantity of indifferent electrolyte (sodium perchlorate), with a solution of mineral acid and indifferent electrolyte (sodium perchlorate) in such a way that the concentration of the indifferent electrolyte (0.09 M) and the mineral acid (0.01 M) remains constant. Since the experiments are carried out in dilute solution, it can be assumed that the number of moles of the solvent is proportional to the volume of the solution:

$$dn=k\,dV$$

Moreover

$$h=C_H V=0.01\ V$$

$$n_{Na^+}=0.09\ V$$

$$n_{ClO_4^-}=n_{HClO_4}+n_{NaClO_4}+n_{AgClO_4}=0.1\ V+a$$

When allowance is made for this, eqn. (5) becomes:

$$dF=(\mu_A+\mu_{ClO_4^-})\,da+\mu_B db+(0.01\ \mu_H+k\mu+0.1\ \mu_{ClO_4^-}+0.09\mu_{Na^+})\,dV \tag{6}$$

Applying the "cross-differentiation" principle to the total differential dF, gives:

$$\left(\frac{\partial \mu_{\mathrm{A}}}{\partial V}\right)_{a,b}+\left(\frac{\partial \mu_{\mathrm{ClO}_4^-}}{\partial V}\right)_{a,b}=0.01\left(\frac{\partial \mu_{\mathrm{H}}}{\partial a}\right)_{V,b}+k\left(\frac{\partial \mu}{\partial a}\right)_{V,b}$$

$$+0.1\left(\frac{\partial \mu_{\mathrm{ClO}_4^-}}{\partial a}\right)_{V,b}+0.09\left(\frac{\partial \mu_{\mathrm{Na}^+}}{\partial a}\right)_{V,b} \qquad (7)$$

The experimental conditions are selected so that:

$$\left(\frac{\partial \mu_{\mathrm{ClO}_4^-}}{\partial V}\right)_{a,b}=0 \qquad \left(\frac{\partial \mu_{\mathrm{Na}^+}}{\partial a}\right)_{V,b}=0$$

In dilute solutions, the following equations are valid: for the solvent,

$$\mu=\mu_{\gamma=1}+RT\ln\gamma$$

where γ is the mole fraction of the solvent, and for the solutes,

$$\mu=\mu^0+RT\ln c+RT\ln f$$

At constant ionic strength eqn. (7) may be written as follows:

$$\left(\frac{\partial \ln \mathrm{A}}{\partial V}\right)_{a,b}=0.01\left(\frac{\partial \ln \mathrm{H}}{\partial a}\right)_{V,b}+\left(\frac{\partial \ln \gamma}{\partial a}\right)_{V,b}+0.1\left(\frac{\partial \ln (\mathrm{ClO}_4^-)}{\partial a}\right)_{V,b} \qquad (8)$$

Integration of eqn. (8) gives:

$$-\left[\int_0^a\left(\frac{\partial \ln \mathrm{A}}{\partial V}\right)_{a,b}\mathrm{d}a\right]_{V,b}=0.01\ln\frac{C_{\mathrm{H}}}{\mathrm{H}}+k\ln\frac{\gamma_0}{\gamma}+0.1\ln\frac{(\mathrm{ClO}_4^-)_0}{(\mathrm{ClO}_4^-)} \qquad (9)$$

By means of the development of the series $\ln(1+x)$ with omission of higher terms, eqn. (9) can be transformed with the following relations:

$$\ln(\mathrm{H}/C_{\mathrm{H}})=\ln\{(H_{\mathrm{u}}+C_{\mathrm{H}})/C_{\mathrm{H}}\}=H_{\mathrm{u}}/C_{\mathrm{H}} \qquad (10)$$

where H_{u} = the concentration of hydrogen ions released by the complex formation, and

$$\ln(\gamma/\gamma_0)=\ln[\{n/(n+N')\}/\{n_0/(n_0+N_0')\}] \qquad (11)$$

where: N_0' = the number of moles of solute for $a=0$, N' = the number of moles of solute for $a=a$, n_0 = the number of moles of the solvent for $a=0$, n = the number of moles of the solvent for $a=a$.

Since $n_0'+N_0'=kV$, eqn. (11) becomes after a few transformations:

$$\ln(\gamma/\gamma_0)=-(1/k)(N-N_0) \qquad (12)$$

where $N_0=N_0'/V$ = the concentration of all solutes for $a=0$, $N=N'/V$ = the concentration of all solutes for $a=a$.

$$\ln\frac{(\mathrm{ClO}_4^-)}{(\mathrm{ClO}_4^-)_0}=\ln\frac{(\mathrm{ClO}_4^-)_0+C_{\mathrm{A}}}{(\mathrm{ClO}_4^-)_0}=\frac{C_{\mathrm{A}}}{(\mathrm{ClO}_4^-)_0} \qquad (13)$$

Substitution of eqns. (10), (12) and (13) in eqn. (9) gives:

$$-\left[\int_0^a \left(\frac{\partial \ln \mathrm{A}}{\partial V}\right)_{a,b} \mathrm{d}a\right]_{V,b} = N - H_\mathrm{u} - C_\mathrm{A} - N_0 \tag{14}$$

Since

$$N = \mathrm{B} + \mathrm{A} + H + S + (\mathrm{ClO_4^-}) + (\mathrm{Na^+})_0$$

and

$$N_0 = B_0 + H_0 + (\mathrm{ClO_4^-})_0 + (\mathrm{Na^+})_0$$

the value of the integral (14) becomes:

$$N - H_\mathrm{u} - C_\mathrm{A} - N_0 = \mathrm{B} - \mathrm{B}_0 + \mathrm{A} - S$$

From this, S can be determined and from S, $\bar{p}$ and $\bar{q}$ can be calculated.

EXPERIMENTAL

Apparatus and reagents

Apparatus and reagents were the same as used previously[1]. All measurements were carried out at 25.0° ±0.1.

Titration procedure

All titrations were performed in the following manner. A solution with a definite value for a, b, $C_{\mathrm{NaClO_4}} = 0.09$ M and $C_\mathrm{H} = 0.01$ M is diluted with a solution containing two components: $C_{\mathrm{NaClO_4}} = 0.09$ M and $C_\mathrm{H} = 0.01$ M $\mathrm{HClO_4}$. The concentration of the free silver(I) ions is determined as described before[1].

For a definite value of V, $(\partial \ln \mathrm{A}/\partial V)_{a,b}$ is determined from the ln A *vs.* V curve.

The repetition of this procedure for different values of a, gives the possibility of calculating the integral (14).

RESULTS AND DISCUSSION

In Table I the values of $\bar{p}_\mathrm{exp}$ and $\bar{q}_\mathrm{exp}$, obtained in this way, are given together with the values calculated on the assumption that only $\mathrm{B(AB)}_n$ complexes are formed.

In these calculations S was obtained from:

$$S = \frac{C_\mathrm{A} - \mathrm{A} + \mathrm{ZA} - \mathrm{Z}C_\mathrm{A} - \mathrm{ZB}}{Z} \quad \text{with} \quad Z = \frac{C_\mathrm{A} - \mathrm{A}}{C_\mathrm{B}} \tag{15}$$

The experimental data mentioned in the previous paper[1] are used.

From Table I it can be seen that, for $C_\mathrm{B} = 2.00 \cdot 10^{-4}$ M, the experimental and calculated values for $\bar{p}$ and $\bar{q}$ are almost the same. For lower values of C_B the differences become much larger. We note that $\bar{q}_\mathrm{calc} - \bar{p}_\mathrm{calc}$ is always 1.0. The difference $\bar{q}_\mathrm{exp} - \bar{p}_\mathrm{exp}$ varies between 0.9 and 0.4. It can also be seen that the calculated values for

TABLE I

VALUES OF $\bar{p}$ AND $\bar{q}$ FOUND

C_A	$C_B = 2.00\cdot10^{-4}\ M$				$C_B = 1.40\cdot10^{-4}\ M$				$C_B = 1.20\cdot10^{-4}\ M$			
	$\bar{p}_{calc}$	$\bar{p}_{exp}$	$\bar{q}_{calc}$	$\bar{q}_{exp}$	$\bar{p}_{calc}$	$\bar{p}_{exp}$	$\bar{q}_{calc}$	$\bar{q}_{exp}$	$\bar{p}_{calc}$	$\bar{p}_{exp}$	$\bar{q}_{calc}$	$\bar{q}_{exp}$
$1.96\cdot10^{-5}M$	1.4	1.24	2.4	2.15	1.9	1.40	2.9	2.21	2.1	1.49	3.1	2.21
3.10	1.7	1.52	2.7	2.45	1.9	1.53	2.9	2.34	2.3	1.62	3.3	2.32
4.21	1.7	1.61	2.7	2.57	2.1	1.65	3.1	2.43	2.4	1.69	3.4	2.38
5.30	1.8	1.74	2.9	2.69	2.3	1.76	3.3	2.53	2.7	1.80	3.7	2.46
6.37	2.1	1.96	3.1	2.90	2.6	1.92	3.6	2.67	3.3	2.00	4.3	2.60
7.40	2.3	2.06	3.3	2.98	2.9	2.06	3.9	2.77	4.1	2.12	5.1	2.64
8.09	2.4	2.15	3.4	3.06	3.2	2.19	4.2	2.87	4.9	2.20	6.1	2.64
9.09	2.5	2.38	3.5	3.32	3.8		4.8		5.6		6.6	2.54

$\bar{p}$ and $\bar{q}$ become larger for small values of C_B and large values of C_A, while the changes of the experimentally determined values are comparatively small.

The experimental results communicated in the previous paper can be compared with the experimental results obtained here, using a calculation method of SILLÉN[8].

The following integral makes it possible to calculate R.

$$R = R_0 - \left[\int_{\log A_0}^{\log A} \left(\frac{\partial Z}{\partial \log C_B}\right)_{\log A} \mathrm{d} \log A\right]_{C_B}$$

with $R = (S + B)/C_B$.

From R, S can be calculated, and from S the values of $\bar{p}$ and $\bar{q}$. However the integration constant R_0 is not known. Therefore, R_0 was calculated once on the assumption that only $B(AB)_n$ complexes are formed, and once from the experimental data in this investigation.

When the data $-\log A_0 = 7.100$ and $C_B = 1.00\cdot10^{-4}\ M$ are used, it was found that $R_0 = 8.37$ in the case of the first assumption and $R_0 = 8.22$ from the experimental data.

In Table II the values of $\bar{p}$ and $\bar{q}$ calculated from eqn. (15) together with the experimentally determined values and those calculated by the method of SILLÉN for $R_0 = 8.37$ and for $R_0 = 8.22$ respectively are given.

It can also be seen that the experimentally determined values of $\bar{p}$ and $\bar{q}$ agree with those calculated by the method of SILLÉN with $R_0 = 8.22$, while the values calculated from eqn. (15) do not agree over the whole range with those calculated by the method of SILLÉN for $R_0 = 8.37$. Consequently, it can be concluded that the experimental values for $\bar{p}$ and $\bar{q}$ are correct. From Table I it can be seen that $\bar{q}_{exp} - \bar{p}_{exp}$ diminishes for decreasing values of C_B and tends to 1 for increasing values of C_B. From this it seems that complexes with the general formula $(AB)_n$ dominate in the former case, while complexes with the general formula $B(AB)_n$ dominate in the latter case.

TABLE II

COMPARISON OF FOUND AND CALCULATED VALUES FOR $\bar{p}$ AND $\bar{q}$

pA	$\bar{q}_{calc}$	$\bar{p}_{calc}$	*Sillén method* $R_0 = 8.37$		$\bar{q}_{exp}$	$\bar{p}_{exp}$	*Sillén method* $R_0 = 8.22$	
			$\bar{q}$	$\bar{p}$			$\bar{q}$	$\bar{p}$
7.00	3.5	2.6	3.7	2.7	2.1	1.6	2.1	1.6
6.90	3.4	2.4	3.7	2.6	2.4	1.7	2.3	1.7
6.80	3.4	2.4	3.6	2.5	2.5	1.7	2.4	1.7
6.70	3.5	2.5	3.5	2.5	2.6	1.8	2.6	1.8
6.60	3.8	2.8	3.6	2.6	2.6	1.9	2.7	2.0
6.50	4.0	3.0	3.6	2.7	2.7	2.0	2.7	2.0
6.40	3.8	2.8	3.6	2.7	2.7	2.0	2.8	2.1
6.30	4.4	3.4	3.6	2.4	2.8	1.9	2.9	1.9
6.20	4.7	3.8	3.6	2.6	2.7	2.0	2.9	2.1
6.10	5.1	4.3	3.4	2.5	2.7	2.1	2.9	2.2

The authors are very grateful to Prof. Dr. Z. EECKHAUT for his kind interest and helpful discussions.

SUMMARY

A method is described for determining the mean composition of the complex compounds of silver(I) and HEDTO. The values obtained do not agree with those calculated on the assumption that only $B(AB)_n$ complexes are formed. It is concluded that besides the complexes $B(AB)_n$ other complexes with formula $(AB)_n$ are present.

RÉSUMÉ

Une nouvelle méthode est décrite pour déterminer la composition moyenne $\bar{p}$ et $\bar{q}$ des complexes formés par l'ion argent et le ligand HEDTO. L'on trouve que les valeurs obtenues ne correspondent pas à celles calculées lorsque l'on admet que seuls les complexes de type $B(AB)_n$ sont formés. On peut conclure que d'autres complexes dont la composition est representée par la formule $(AB)_n$ sont présents.

ZUSAMMENFASSUNG

Es wird eine potentiometrische Methode beschrieben zur Bestimmung der mittleren Zusammensetzung der wasserlöslichen Komplexverbindungen von Silber mit N,N'-bis(2-hydroxyäthyl)dithio-oxamid. Die gemessenen Werte stimmen nicht mit denen überein, die unter der Voraussetzung, dass nur $B(AB)_n$-Komplexe gebildet werden, berechnet wurden. Es wird daraus geschlossen, dass neben den genannten Komplexen auch andere mit der Formel $(AB)_n$ vorliegen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE APPLICATION OF SALICYLALDOXIME IN SOLVENT EXTRACTION

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(Received September 11th, 1967)

Salicylaldoxime is recognized as a selective precipitant for copper, although it forms water-insoluble chelates with a number of elements[1]. The absorption spectra in chloroform of some metal chelates of salicylaldoxime have been discussed[2]. The solubility of the salicylaldoximates in organic solvents has been utilized in the solvent extraction of various elements[3-11]. Subsequent determinations of the extracted metals have been accomplished either by optical methods, *i.e.* emission spectrography[3], colorimetry[4], absorption[5,10] and emission[6,9] spectrophotometry, and atomic absorption spectroscopy[11], or by radiometric measurements[7,8].

The present paper describes a comparative investigation of the extractability of 9 selected metal ions with solutions of salicylaldoxime in benzene, special attention being given to the effect of pH.

EXPERIMENTAL

Apparatus

All analytical absorbance measurements were made with a Zeiss PMQ II spectrophotometer; absorption curves were obtained with a recording Beckman DB spectrophotometer. A matched set of 1.000-cm quartz cells with stoppers was used.

The pH was measured with a Beckman Research pH meter with glass (pH range 0–14) and saturated calomel electrodes. The instrument was calibrated against standard reference solutions[12].

Separating funnels (100 ml) with polyethylene stoppers and 50-ml ground-glass stoppered bottles were used in the extractions. A rapid separation of suspended water from the organic phase was obtained in an ordinary laboratory centrifuge (3000 rev./min).

Reagents

All chemicals were of reagent-grade quality.

Salicylaldoxime solutions. Exactly weighed amounts of salicylaldoxime (E. Merck A. G., Darmstadt) were dissolved in benzene to give 1.00, 0.10, and 0.01 M solutions, these being stored in brown bottles.

Stock solutions of metals (ca. $5 \cdot 10^{-3}$ M). These were prepared by dissolving appropriate amounts of the sulphate, nitrate, or chloride salt in distilled water, adding — where required — a minimum of acid to prevent precipitation, and diluting to a known volume with additional water. The stock solutions were stored in polyethylene bottles and standardized by titration with EDTA (disodium salt). Freshly made standard solutions of the metals of lower concentration were prepared by dilution.

Buffer solutions were made by mixing standard solutions of hydrochloric acid and/or sodium hydroxide with solutions of potassium chloride, potassium hydrogen phthalate, potassium dihydrogen phosphate, boric acid, and disodium hydrogen phosphate, at the concentrations and volumes given in the literature[13].

Distribution determinations

The concentrations of metal in the aqueous and organic phases after extraction were determined respectively by compleximetric titration and spectrophotometry. Knowing the total concentration of metal present, generally $1.0 \cdot 10^{-4}$ *M*, the percentage extracted was calculated. (Changes in volume were negligible and were ignored.)

All experiments were performed at room temperature (20–25°).

Procedure

To 5 ml each of standard metal and buffer solution 10 ml of salicylaldoxime solution were added. The two phases were manually shaken for 5 min and allowed to separate. In all experiments the final pH of the aqueous phase was measured. In most cases, the amount of unextracted metal was then determined by titration with EDTA, applying micro methods.

For the spectrophotometric measurements volumes of the organic phase were withdrawn, centrifuged, and transferred to a photometric cell. The absorbance was measured against a reagent blank prepared by extracting 5 ml of distilled water and 5 ml of buffer solution with 10 ml of the salicylaldoxime solution.

RESULTS

Choice of organic solvent

Various organic solvents, *viz.* chloroform[3,7,8,10], benzene[4], *n*-amyl acetate[5], and methyl isobutyl ketone[6,9,11] have been used in salicylaldoxime extractions.

Preliminary experiments confirmed that the four solvents listed above, as well as carbon tetrachloride, diisopropyl ether and ethyl acetate, could be employed. On the basis of earlier investigations[14], it was assumed that a hydrocarbon or its halogen-substituted derivative would be a more selective extracting agent than an oxygen-donor solvent. Accordingly, benzene was selected for the detailed studies of the extractions made at different pH and reagent concentrations.

Influence of pH

Solutions of the metal ions were extracted with a 0.01 *M* reagent solution. Plots of the percentage extraction *versus* pH for various metals are shown in Fig. 1. With increasing pH, copper(II), nickel(II), lead(II), cobalt(II) and manganese(II) are extracted in the same order as they are precipitated[1]; these systems all show extraction curves of the regular pattern. Mercury(II) is not extracted in the pH region investigated (2–10), probably because of hydrolysis.

Copper(II) is quantitatively extracted in the pH range 3–9.5; this result is in excellent agreement with that obtained by SIMONSEN AND BURNETT[5] who used a 0.02 *M* solution of salicylaldoxime in *n*-amyl acetate.

Complete extraction of nickel(II) takes place at pH 6.5–9. It has been found previously[6], that, when a 1% solution of the reagent in methyl isobutyl ketone is used, maximum extraction from mannitol–aqueous ammonia solutions occurs at somewhat higher pH values.

Lead(II) is completely extracted from boric acid–sodium hydroxide buffered solutions at pH 7.5–9. Maximum extraction of cobalt(II) is reached at pH 7.5–8. More than 70% of manganese(II) is extracted at a pH of about 10.5.

Magnesium(II) is not extracted in the presence of boric acid/sodium hydroxide buffers. From alkaline solutions, however, a maximum extraction of about 90% is achieved.

An irregular extraction curve is exhibited by cadmium(II), although more than 90% is extracted at higher pH values. Anomalous extraction behaviour of cadmium(II) with 0.1 *M* solutions of salicylaldoxime in chloroform has also been reported[7].

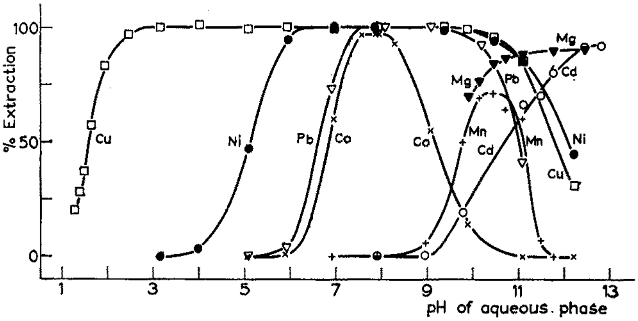
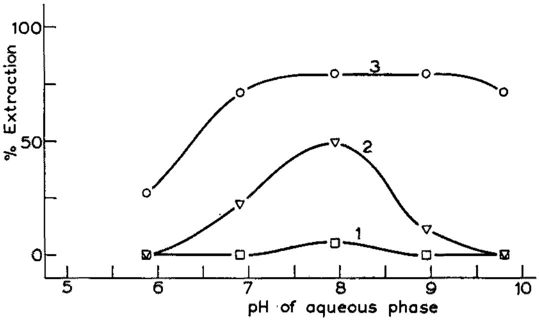


Fig. 1. Extraction of $1.0 \cdot 10^{-4}$ *M* solutions of Cu(II), Ni(II), Pb(II), Co(II), Mn(II), Mg(II) and Cd(II) with 0.01 *M* salicylaldoxime in benzene.



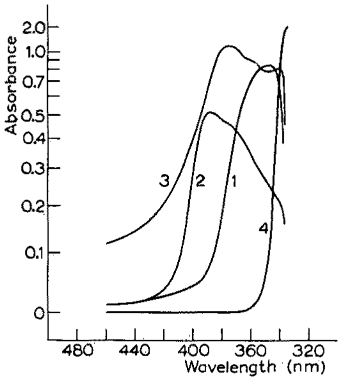


Fig. 2. Extraction of a $1.0 \cdot 10^{-4}$ *M* solution of Zn(II) with salicylaldoxime in benzene: 0.01 *M* (curve 1), 0.10 *M* (curve 2), 1.00 *M* (curve 3).

Fig. 3. Absorbance curves of $1.0 \cdot 10^{-4}$ *M* solutions of Cu(II) (curve 1), Ni(II) (curve 2), and Co(II) (curve 3) extracted into an equal volume of 0.01 *M* salicylaldoxime in benzene. Absorbance curve of a reagent blank recorded against benzene (curve 4).

Influence of reagent concentration

The importance of the reagent concentration in the organic phase was clearly demonstrated by extracting zinc(II) with various solutions of salicylaldoxime. The percentages extracted with 0.01, 0.10, and 1.00 *M* solutions as a function of pH are given in Fig. 2. With 0.01 *M* salicylaldoxime concentration, only about 5% of zinc(II) is extracted at pH 8. But when 0.10 and 1.00 *M* solutions are used, the percentage extracted is increased to about 50% and 80%, respectively.

Spectrophotometry

Of the salicylaldoxime chelates investigated, only those of copper(II), nickel(II), and cobalt(II) absorb strongly at wavelengths above 340 nm. Absorption spectra of the above chelates were recorded against reagent blanks at the pH of maximum extraction. The spectra are shown in Fig. 3. The absorbance maxima are in good agreement with those obtained in other solvents[2,5]. Absorbance spectra of the blanks were recorded against benzene. Since the curves were practically identical, only one of them is reproduced in Fig. 3.

At the wavelength of maximum absorption, calibration curves for the metals were plotted. In all cases, Beer's law was found to be obeyed over the entire range of concentration studied.

Data related to the spectrophotometric determination of copper(II), nickel(II), and cobalt(II) with salicylaldoxime are collected in Table I. This Table contains the percentages extracted in a single pass, as well as the sensitivities of the colour reactions — in terms of the molar absorptivity and Sandell's sensitivity index.

TABLE I

SPECTROPHOTOMETRIC DETERMINATION OF SOME METAL IONS WITH SALICYLALDOXIME

Ion determined	*Conditions of measurement*		*Linear range of calibration curve ($M \cdot 10^6$)*	*% Extracted*	*Sensitivity*	
	pH	*Wavelength (nm)*			*Molar absorptivity (l/g at · cm)*	*Sensitivity index (μg/cm², A = 0.001)*
Cu(II)	4.0	347	2.5–100	>99.5	8400	0.0076[a]
Ni(II)	7.0	387	5 –200	>99	5300	0.011
Co(II)	7.9	375	2.5–100	~97	10000	0.006

[a] The value given by SANDELL[15] (0.0008), which was calculated from the data of SIMONSEN AND BURNETT[5], is wrong by one power of 10.

ANALYTICAL APPLICATIONS

With a 0.01 *M* salicylaldoxime solution in benzene, and by selecting the proper pH, it is possible to make analytical separations of the metal ions investigated. For instance, at pH 3–3.5 copper may be quantitatively extracted and separated from all the other elements studied. Separation of nickel and cobalt is obtained at pH 6. Lead is completely separated from manganese at pH 8 and from zinc at pH 9. Separations of cadmium and magnesium from other metals may be performed in strongly alkaline media.

The influence of reagent concentration may also be utilized for separation purposes. Thus, by consecutive extractions with 0.01 and 1.00 M salicylaldoxime solutions, cadmium and zinc, respectively, are separated from mercury.

Copper(II) may be determined spectrophotometrically with a 0.01 M solution of salicylaldoxime in benzene after its selective extraction at pH 3–4. The sensitivity of this method is of the same magnitude as that of the well-known copper(I) reagent, neocuproine[15]. The determination is rapid and the stability of the colour system very good. Salicylaldoxime has already been applied for the determination of copper in aluminium and zinc-base alloys[5]. The method is probably also applicable to the determination of copper in a matrix of other metals, *e.g.* nickel and cobalt.

As apparent from Table I, nickel(II) and cobalt(II) may be determined spectrophotometrically with salicylaldoxime. It should be stressed, however, that these systems are less stable, hence absorbance measurements should be made as soon as possible after the extraction.

SUMMARY

The extraction of divalent magnesium, manganese, cobalt, nickel, copper, zinc, cadmium, mercury, and lead with solutions of salicylaldoxime in benzene was investigated. The effect of the reagent concentration and particularly the pH of the aqueous phase on the extractability was studied. The application of salicylaldoxime extractions in the separation and determination of various elements is discussed.

RÉSUMÉ

On a examiné l'extraction des cations divalents des éléments: Mg, Mn, Co, Ni, Cu, Zn, Cd, Hg et Pb à l'aide de solutions de salicylaldoxime dans le benzène. On a étudié l'influence de la concentration du réactif et particulièrement du pH de la phase aqueuse sur l'extractibilité. Une discussion est présentée sur l'application des extractions "salicylaldoxime" pour la séparation et le dosage de divers éléments.

ZUSAMMENFASSUNG

Die Extraktion von zweiwertigem Magnesium, Mangan, Kobalt, Nickel, Kupfer, Zink, Cadmium, Quecksilber und Blei mit Lösungen von Salicylaldoxim in Benzol wurde untersucht. Der Einfluss der Reagenzkonzentration und besonders des pH-Werts der wässrigen Phase auf die Extrahierbarkeit wurde geprüft. Die Anwendung dieser Extraktionen zur Trennung und Bestimmung zahlreicher Elemente wird diskutiert.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

EXTRACTION STUDIES OF ANTIMONY BROMIDE INTO BENZENE

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(Received August 17th, 1967)

The extractability of antimony into organic solvents from iodide[1-4] and bromide[5-8] systems has been investigated by several workers. However, these investigations have shown that many other elements follow antimony. RAMETTE[9], on the basis of a specific spot test[10,11] for the isolation of antimony, found that highest extraction coefficient for antimony into benzene is observed with a 5 M sulphuric acid–0.01 M potassium iodide solution. However, the extraction of other elements under these conditions has not been studied.

In this paper a study of the extractability of antimony(III) by the system benzene–sulphuric acid–hydrobromic acid is reported. The behaviour of 35 other elements at the optimum concentration of sulphuric and hydrobromic acids for antimony extraction (10.0 M H_2SO_4–0.03 M HBr) has been investigated. The extractability of these elements by the system benzene–5 M sulphuric acid–0.01 M potassium iodide is also described.

EXPERIMENTAL

Apparatus and counting

A Cahn electrobalance model M-10 was used for accurate weighings.

A NaI (Tl) well-type scintillation crystal (2 × 1.75″) connected with a single-channel analyzer was used to measure γ-activities of liquid samples contained in glass test tubes (10 × 75 mm). The radiochemical purity of the prepared radiotracers was examined with a NaI (Tl) crystal (3 × 3″) coupled with a 400-channel analyzer.

An end-window G-M tube (1.4 mg/cm^2) was employed to assay the β-activities of liquid samples contained in plastic planchets (6 × 20 mm). β-Counting was done only in the extraction experiments of Y^{3+}, Bi^{3+}, and Ni^{3+}, where the tracers ^{90}Y, ^{210m}Bi, and ^{65}Ni, respectively, were used.

Reagents

Analytical reagent grade materials were used.

Radioactive stock solutions of antimony. Solution A. Antimony trioxide (60 mg) in aluminum foil was irradiated for 20 min at a neutron flux of $2.2 \cdot 10^{12}$n.cm^{-2}.sec^{-1}. After cooling for 16 h, the antimony trioxide was dissolved by heating in 25 ml of 10 M sulphuric acid (2 mg Sb^{3+}/ml) giving a total γ-activity of ^{122}Sb of *ca.* $8 \cdot 10^6$ counts. min^{-1}.ml^{-1}.

Solution B. Solution B contained 10 μg of Sb^{3+} per ml of 10 M sulphuric acid.

Antimony trioxide (1.2 mg) in a quartz tube was irradiated for 20 h in the swimming pool of the reactor. After 24 h the sample was dissolved in 100 ml of 10 M sulphuric acid; other solutions containing 1.0, 0.1 and 0.01 μg of Sb^{3+} per ml were prepared by dilution.

Radiotracers

Radiotracers of the elements investigated were prepared and used.

Procedures

In order to establish the optimum concentrations of sulphuric acid and hydrobromic acid for the extraction of the antimony into benzene, experiments were performed in which antimony was extracted into benzene from aqueous phases of various molarities of the two acids. All experiments were carried out at least in duplicate. The concentration of antimony at the final volume of the aqueous phase for each experiment was $8.2 \cdot 10^{-4} M$.

Effect of sulphuric acid concentration on the extractability of antimony into benzene from 0.03 M hydrobromic acid solution. In these experiments the concentration of hydrobromic acid remained constant (0.03 M), whilst the concentration of sulphuric acid ranged from 0.5–16.0 M.

An aliquot (0.5 ml) of radioactive antimony solution A in a 50-ml centrifuge tube was placed in an ice-bath. Appropriate volumes of distilled water and concentrated sulphuric acid were added to give the desired concentration of acid at the final volume of the solution. The solution was mixed and cooled to room temperature, and 0.3 ml of 1 M hydrobromic acid was added to adjust the solution to 0.03 M HBr at the final volume (10 ml). The solution was transferred to a 100-ml separatory funnel and shaken with an equal volume of benzene for 2 min. After the separation of the two phases (less than 1 min), aliquots of each phase were taken for γ-radioactivity measurements (Fig. 1).

Effect of hydrobromic acid concentration on the extractability of antimony into benzene from 10 M sulphuric acid solution. In these experiments, the sulphuric acid concentration remained constant (10 M) while the hydrobromic acid concentration was varied from 0–2.0 M.

The solutions were prepared exactly as described immediately above, except that 5.3 ml of concentrated sulphuric acid was added to adjust the solution to 10 M H_2SO_4 at the final volume, and the appropriate volume of 0.01 M, 1 M or 4 M hydrobromic acid solution was added to give the desired final concentration of hydrobromic acid. The tests were completed as described above (Fig. 2).

Effect of the antimony concentration. Further experiments were made at the optimum molarities of acids (10 M H_2SO_4–0.03 M HBr) to establish the extractability of antimony as a function of its concentration. Antimony solutions A and B were used.

Extraction of other elements into benzene from 10.0 M H_2SO_4–0.03 M HBr and 5.0 M H_2SO_4–0.01 M KI systems. The optimum conditions for the extraction of antimony into benzene (10.0 M H_2SO_4 and 0.03 M HBr) were used in a study of the behaviour of 35 other elements. One, two or three elements of each subgroup of the periodic table were studied.

The extractability of the same elements was also examined for the system benzene–5 M H_2SO_4–0.01 M KI.

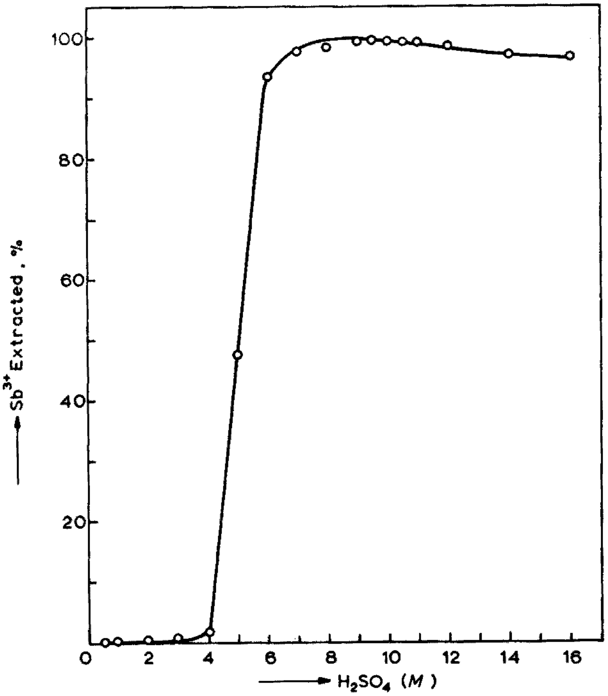

Fig. 1. Effect of sulphuric acid concentration on the extractability of antimony into benzene from 0.03 *M* HBr.

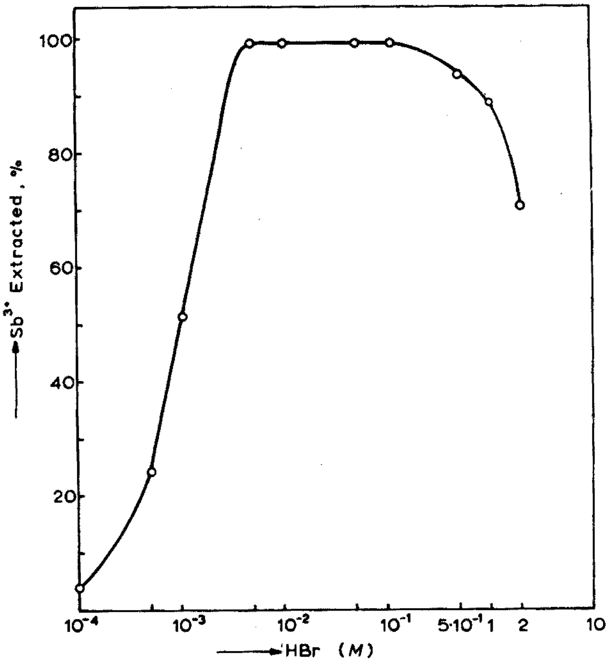

Fig. 2. Effect of hydrobromic acid concentration on the extractability of antimony into benzene from 10 *M* H_2SO_4.

RESULTS AND DISCUSSION

The extractability of antimony with benzene from 0.03 *M* hydrobromic acid as a function of sulphuric acid concentration is shown in Fig. 1. Extraction of antimony starts at 4 *M* sulphuric acid and increases rapidly with increase in concentration, reaching the value of 99% at 9 *M* and remaining practically constant up to 12 *M* sulphuric acid, with a maximum of 99.4% at 10 *M* sulphuric acid. At higher molarities of sulphuric acid, there appears a slight drop in extraction possibly because of the evolution of bromine.

Figure 2 is a semi-log plot showing the extraction behaviour of antimony into benzene from 10 *M* sulphuric acid as a function of hydrobromic acid concentration. At very low hydrobromic acid concentrations, antimony is only slightly extracted as would be expected; as the concentration increases, the extraction of antimony increases until it becomes quantitative (>99%) at 0.005 *M* hydrobromic acid. Extraction remains quantitative up to 0.1 *M* hydrobromic acid and decreases with further increase in this acidity.

Extraction into benzene from 10 *M* H_2SO_4–0.03 *M* HBr media is quantitative even at tracer levels of antimony and remains quantitative up to a concentration which corresponds to the stoichiometric proportion of antimony and bromide ions present in the aqueous phase of 1:3 (Table I). It was found that the equilibrium for the quantitative extraction of antimony under the recommended conditions was attained in 1 min; a 2-min extraction time was allowed for safety. The antimony could be stripped from the organic phase by thoroughly shaking it for 1 min with an equal volume of water; the amount of antimony stripped with water was more than 99.9%. The extraction of antimony(III) into benzene from hydrobromic acid solutions (0–8 *M*) in absence of sulphuric acid was less than 1%. The presence of oxidizing agents in the sulphuric acid and hydrobromic acid mixture containing antimony interfered with the recommended extraction.

TABLE I

EXTRACTABILITY OF ANTIMONY AS A FUNCTION OF ITS CONCENTRATION IN BENZENE FROM 10 *M* H_2SO_4–0.03 *M* HBr

Concentration of Sb (µg/ml)	*Corresponding molarity of Sb*	*Sb^{3+} extracted (%)*	*Concentration of Sb (µg/ml)*	*Corresponding molarity of Sb*	*Sb^{3+} extracted (%)*
0.001	$8.21 \cdot 10^{-9}$	98.1	200	$1.64 \cdot 10^{-3}$	99.4
0.01	$8.21 \cdot 10^{-8}$	98.3	600	$4.93 \cdot 10^{-3}$	99.4
0.1	$8.21 \cdot 10^{-7}$	98.5	1000	$8.21 \cdot 10^{-3}$	99.4
1 0	$8.21 \cdot 10^{-6}$	99.1	1200	$9.85 \cdot 10^{-3}$	99.3
10	$8.21 \cdot 10^{-5}$	99.2	1500	$1.23 \cdot 10^{-2}$	83.3 (99.0)[a]
50	$4.11 \cdot 10^{-4}$	99.4	2000	$1.64 \cdot 10^{-2}$	63.0 (99.2)[a]
150	$1.23 \cdot 10^{-3}$	99.4			

[a] Figures in brackets express the percent extraction of antimony from 10.0 *M* H_2SO_4–0.06 *M* HBr.

Table II shows the extractability into benzene of 35 other elements from 10 *M* H_2SO_4–0.03 *M* HBr and 5.0 *M* H_2SO_4–0.01 *M* KI media. It was found that As^{3+}, Se^{4+}, Sn^{2+}, and Hg^{2+} followed antimony in both systems. However, the percentage of

TABLE II

EXTRACTION OF ELEMENTS INTO BENZENE FROM 10.0 M H_2SO_4–0.03 M HBr AND FROM 5.0 M H_2SO_4–0.01 M KI SYSTEMS

(Element concentration in aqueous phase: 0.1 mg/ml. Volume of each phase: 10 ml. Extraction time: 2 min)

Element	*% Extn. from 10 M H_2SO_4–0.03 M HBr*	*% Extn. from 5 M H_2SO_4–0.01 M KI*	*Element*	*% Extn. from 10 M H_2SO_4–0.03 M HBr*	*% Extn. from 5.0 M H_2SO_4–0.01 M KI*
Sb^{3+}	99.4	99.8	Np^{6+}	0.2	0.2
As^{3+}	99.4	44.4	Al^{3+}	0.2	0.05
Ge^{4+}	98.2	0.08	Ba^{2+}	0.2	0.2
Sn^{2+}	95.7	99.0	Ni^{2+}	0.2	0.2
Se^{4+}	95.6	85.1	Zn^{2+}	0.1	0.5
Hg^{2+}	74.1	51.2	Fe^{3+}	0.1	0.1
Bi^{3+}	10.0	—[a]	Y^{3+}	0.08	0.03
Te^{4+}	5.5	—[a]	Ga^{3+}	0.08	0.09
Nb^{5+}	0.9	0.9	Ta^{5+}	0.04	0.04
Pa^{5+}	0.9	0.9	Cr^{3+}	0.03	0.01
Mg^{2+}	0.6	0.6	Cu^{2+}	0.03	—[a]
Au^{3+}	0.5	0.2	La^{3+}	0.03	0.004
Ti^{4+}	0.5	0.05	Mo^{6+}	0.03	0.01
In^{3+}	0.4	0.08	Sc^{3+}	0.02	0.02
Rb^{+}	0.4	0.05	Hf^{3+}	0.01	0.01
Re^{7+}	0.3	0.01	Na^{+}	0.01	0.01
Br^{-}	0.3	0.3	Cd^{2+}	—	0.01
Mn^{2+}	0.2	0.06	Co^{2+}	0.007	0.003

[a] A thin precipitate is formed between the two phases.

extraction into benzene of these elements differed in each extraction system. Germanium was extracted almost quantitatively into benzene from the bromide system but only 0.08% of the germanium was extracted from the iodide system. Bismuth(III), tellurium(IV) and copper(II) were only slightly extracted from the bromide solution and they formed insoluble compounds in the iodide system, the iodide compounds being also insoluble in benzene. On extraction with benzene, thin layers of precipitate were formed between the two phases and on the walls of the separatory funnel; the remaining amounts of tellurium, bismuth and copper in the aqueous phase were 4.5%, 1.9% and 1.4% respectively. The extractability of all the other elements investigated by both systems was less than 1%. It appears that the separation of antimony is equally selective for both systems. However, extraction of antimony bromide is made from clear sulphuric–hydrobromic acid solutions, while the antimony iodide gives a precipitate in the sulphuric–hydriodic acid solution.

Nature of extracted antimony species

It was found by radiotracer and activation analysis methods that the antimony bromide species extracted into benzene from a 10 M sulphuric acid–0.03 M hydrobromic acid solution has an antimony to bromine ratio of 1:3; the extracted species is most probably the tribromide of antimony. A non-polar solvent such as benzene would be expected to dissolve covalent molecules such as $SbBr_3$. It has been postulated that in excess of hydrobromic acid, antimony tribromide exists as complex ions:

$$SbBr_3 + n\ HBr \rightleftarrows n\ H^+ + [SbBr_{(3+n)}]^{n-}$$

and it was observed that no antimony is extracted into benzene even in the presence of 8 M hydrobromic acid. Thus the role of the concentrated sulphuric acid would seem to be in the suppression of the right hand side of the above equilibrium, possibly by removing water needed for proton solvation.

Comparison with other methods

A comparison of the extraction behaviour of elements into benzene from the recommended 10 M sulphuric acid–0.03 M hydrobromic acid media with the results of BOCK *et al.*[6] on the extractability of elements into diethyl ether from 5 M hydrobromic acid solutions, shows that fewer elements follow antimony into benzene than into ether; for example, iron, gallium, indium and gold are extracted almost quantitatively into ether but not into benzene. Molybdenum and copper are extracted partially into ether but not at all into benzene. Tin and arsenic are extracted well into both solvents, while selenium is extracted partially into ether and almost quantitatively into benzene. Tellurium is extracted only slightly into both solvents. Germanium and mercury are readily extracted into benzene but their extraction behaviour into ether has not been studied.

There is some similarity between the present results and those reported by KITAHARA[1] for extraction into diethyl ether from 6.9 M hydriodic acid solutions, but again, fewer elements are extracted with antimony into benzene than into ether. Antimony, mercury, tin and arsenic are easily extracted, while tellurium and bismuth are only partially extracted into both solvents. On the other hand, gold is extracted completely into ether while molybdenum, zinc and indium are partially extracted; there is no extraction of these four elements into benzene. Germanium and selenium are almost quantitatively extracted by benzene, but their extraction behaviour into ether has not been investigated.

GOTO AND KAKITA[4] found almost complete extraction with methyl isobutyl ketone of the iodide compounds of antimony, cadmium, bismuth, copper, tellurium and lead, but did not report the behaviour of other elements. Other reported methods for the extraction of elements into benzene[7] from strong bromide media, or into ether[2] and methyl isopropyl ketone[3] from iodide media, only yield partial extraction of antimony.

The authors wish to express their appreciation to D. S. URCH for helpful discussions during the performance of this study and to N. A. KATSANOS for useful suggestions in the preparation of the manuscript. Thanks are also due to A. M. MALLEROS for his valuable assistance in performing the irradiations.

SUMMARY

Antimony(III) can be extracted rapidly and quantitatively into benzene from a 10 M H_2SO_4–0.03 M HBr system. The extracted antimony bromide has an antimony to bromine ratio of 1:3. Under the above optimum conditions for extraction of antimony, the behaviour of 35 other elements was studied; As^{3+}, Ge^{4+}, Se^{4+}, and Sn^{2+} were extracted almost quantitatively, and the percentage extraction of Hg^{2+}, Bi^{3+}, and Te^{4+} was 74.1%, 10% and 5.5% respectively. The extraction of the elements into benzene from a 5 M H_2SO_4–0.01 M KI system was also investigated. A comparison of the two systems is given.

RÉSUMÉ

L'antimoine(III) peut être extrait rapidement et quantitativement dans le benzène, en milieu H_2SO_4 10 M–HBr 0.03 M. Dans le bromure d'antimoine extrait le rapport antimoine/brome est de $\frac{1}{3}$. Le comportement de 35 autres éléments a été examiné: As^{3+}, Ge^{4+}, Se^{4+} et Sn^{2+} sont extraits presque quantitativement; le pourcentage d'extraction de Hg^{2+}, Bi^{3+} et Te^{4+} est respectivement de 74.1, 10 et 5.5. On a également examiné le comportement de ces éléments dans le benzène, en milieu H_2SO_4 5 M–KI 0.01 M. Une comparaison des deux systèmes est faite.

ZUSAMMENFASSUNG

Antimon(III) kann schnell und quantitativ mit Benzol aus einer Mischung von 10 M Schwefelsäure und 0.03 M Bromwasserstoffsäure extrahiert werden. Im extrahierten Antimonbromid ist das Verhältnis von Antimon zu Brom 1:3. Unter den genannten optimalen Extraktionsbedingungen für Antimon wird das Verhalten von 35 anderen Elementen untersucht. As^{3+}, Ge^{4+}, Se^{4+} und Sn^{2+} werden nahezu quantitativ extrahiert, die Extraktion von Hg^{2+}, Bi^{3+} und Te^{4+} beträgt 74.1%, 10% bzw. 5.5%. Ebenso wurde die Extraktion aus einer Mischung von 5 M H_2SO_4 und 0.01 M KI mit Benzol untersucht. Die beiden Systeme werden miteinander verglichen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE SOLVENT EXTRACTION OF INDIUM(III) WITH CARBOXYLIC ACIDS

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(Received September 22nd, 1967)

Numerous systems for the extraction of indium(III) from an aqueous medium into an organic phase have been reported in the literature[1]. These systems include some ion-association situations and numerous chelate situations. In a few instances, the extracting agent has been a monocarboxylic acid. EFENDIEV AND ALEKPEROV[2] employed naphthenic acids in kerosine to extract indium from aqueous solutions, studies being made of the pH dependence. JOHNSON[3] has extracted indium from neutral or slightly acid solutions as the benzoate into butyl alcohol, amyl alcohol, and ethyl acetate. CORNEA AND SEGARCEANU[4] reported on the distribution equilibria of indium between aqueous sulfate solutions and carboxylic acid mixtures (12–16 carbons) in kerosine. In addition to these researches on indium, several articles[5] dealing with the extraction of aluminum and gallium with carboxylic acids have been published. These lead to the expectation that carboxylic acid extractions of indium might be of interest. This paper consists of an extension of work along these lines.

EXPERIMENTAL

Indium-114m as the chloride (Oak Ridge National Laboratory) was converted to the perchlorate by 3 successive evaporations with perchloric acid. All water was triply distilled from a permanganate solution and all reagents were purified by either crystallization or distillation procedures.

In each determination, 7 ml of water, 0.1 M in sodium perchlorate and $10^{-7.0}$ M in labelled indium perchlorate, was equilibrated with 7 ml of either a pure liquid organic acid or with an organic solvent containing a known concentration of organic acid. The pH values were adjusted with sodium hydroxide and perchloric acid and all samples were stirred at $27 \pm 0.5°$ for at least 24 h. This time was shown to be adequate for equilibrium in all cases. Each sample was then centrifuged, its pH was measured, the two phases were sampled, radioactivity determinations were made by scintillation counting, and the distribution coefficient D was calculated by dividing the organic-phase activity by the aqueous-phase activity.

The values for P, the organic/aqueous partition coefficients of hexanoic and octanoic acids, and the values for C, the dimerization constants of the same acids, were estimated by two-phase titrations of the substances in organic media in contact with 0.1 M sodium perchlorate solution. The data have been treated in the manner of HÖK[6].

RESULTS

Figure 1 presents data showing the extraction of indium with 6 different pure organic acids. The saturated acids (filled figures) extract at pH values slightly lower than the unsaturated acids (open figures). The partition of indium is greater as the molecular weight of the saturated acids increases, heptanoic and octanoic acids being only slightly higher than hexanoic acid.

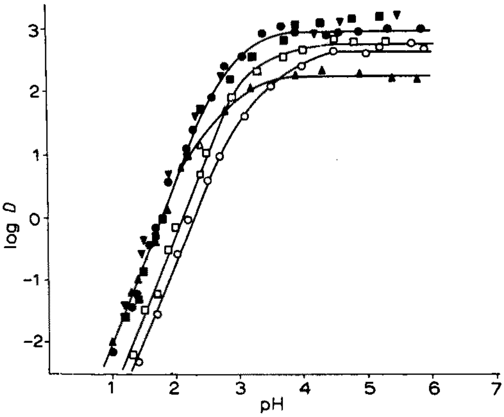

Fig. 1. Indium extraction with pure organic acids. ▲ pentanoic acid, ● hexanoic acid, ■ heptanoic acid, ▼ octanoic acid, □ 10-undecanoic acid, ○ 9-octadecanoic acid.

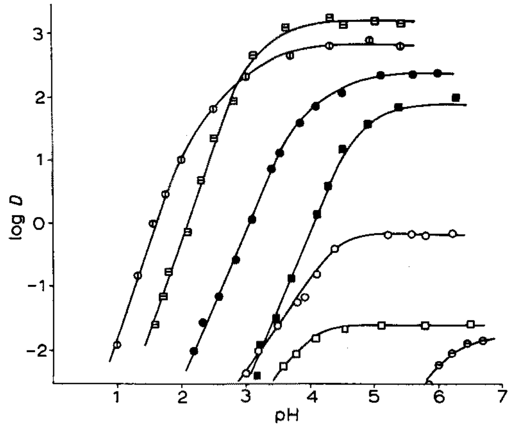

Fig. 2. Extractions of indium with chloroform solutions 0.1 *M* in various extractants. ⦶ N-benzoyl-N-phenylhydroxylamine, ⊟ thenoyltrifluoroacetone, ● octanoic acid, ■ hexanoic acid, ○ pentanoic acid, □ butanoic acid, and ⊖ propionic acid.

Figure 2 shows results obtained by using 0.1 *M* acids in chloroform for the extractions. In addition to those shown, systems involving formic and acetic acid were also run. In these as well as in the propionic acid systems, the initial aqueous phases rather than the organic phases contained the 0.1 *M* acid. Neither the formic nor the acetic acid system showed any extraction giving a log *D* value greater than

−2.50 over the range of pH from 1.5 to 7.0 Included in Fig. 2 are curves for extractions involving 0.1 *M* thenoyltrifluoroacetone in chloroform and 0.1 *M* N-benzoyl-N-phenylhydroxylamine in chloroform. These two reagents are excellent extractants for indium and are presented here for comparison.

Figure 3 sets forth a series of extractions into chloroform containing concentrations of hexanoic acid ranging from $10^{-1.5}$ to $10^{0.5}$ *M*. In addition, a curve for the pure acid is presented for comparison purposes. In experiments using hexanoic acid in chloroform, the concentration of indium was varied from 10^{-7} to 10^{-5} *M*. No shift in the curves of Fig. 3 was noted.

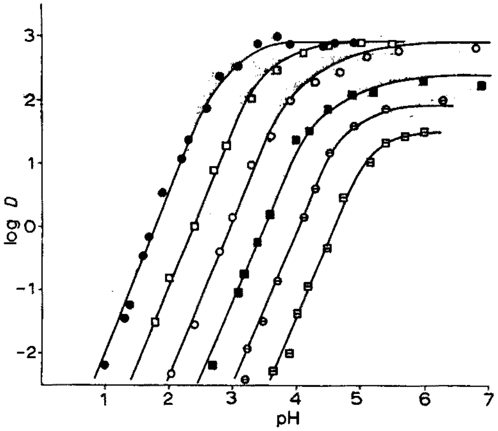

Fig. 3. Extraction of indium with chloroform containing various concentrations of hexanoic acid. ● pure hexanoic acid, □ $10^{0.5}$ *M*, ○ $10^{0.0}$ *M*, ■ $10^{-0.5}$ *M*, ⊖ $10^{-1.0}$ *M*, and ⊟ $10^{-1.5}$ *M*.

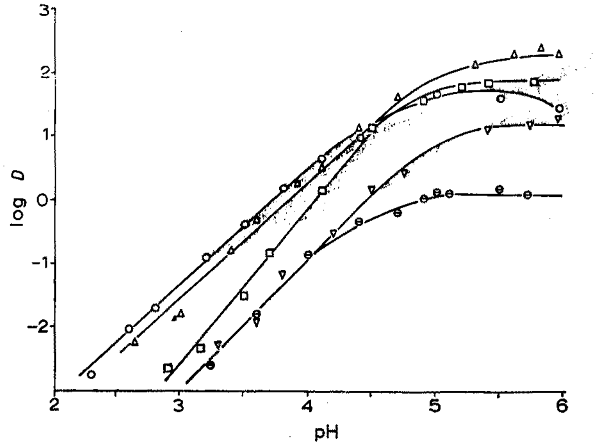

Fig. 4. Extraction of indium into various solvents containing 0.1 *M* hexanoic acid. ○ **hexanol**, △ hexanal, □ chloroform, ⊖ hexane, and ▽ methyl hexanoate.

Figure 4 is a presentation of data derived by employing 0.1 *M* hexanoic acid in 5 different organic solvents to extract indium. It should be noted that an alcohol, an aldehyde, an ester, plus chloroform and hexane have been used in order to ascertain the effects of various types of solvents.

When two-phase titrations and the graphical method of HÖK[6] were used, a log P value of 0.7 and a log C value of 2.1 were found for hexanoic acid in the chloroform/0.1 M $NaClO_4$ system, and a log P value of 1.4 and a log C value of 2.4 for octanoic acid in the chloroform/0.1 M sodium perchlorate system. These values compare favorably with the results of TANAKA, NAKASUKA AND GOTO[7] who give a log P of 2.8 and a log C of 2.4 for decanoic acid in the benzene/water system.

DISCUSSION

Quite a wide variety of monocarboxylic acids is available as possible extractants for metal ions. Metal ion extractions often can be facilitated by combined chelating agents and solvents which are generally referred to as chelating solvents[8]. The carboxylic acids are likely candidates for effective chelating solvents. The use of several such acids is shown in Fig. 1. It should be noted that the saturated acids with 5–8 carbons show about the same behavior on the rising portion of the extraction curves, but tend to plateau at different values. As the number of carbons increases, the plateau rises as would be expected from the increasing organophilicity of the extracting species. The 7- and 8-carbon acids seem to be only slightly more effective than the 6-carbon acid which is considerably more effective than the 5-carbon acid. Butanoic acid, which is miscible with water, could not be used. The unsaturated acids, even though they have a greater number of carbons, are less effective than hexanoic acid both from a pH standpoint and from the plateau positions.

The extraction behavior of the saturated monocarboxylic acids with 1–8 carbons in a concentration of 0.1 M in chloroform is shown in Fig. 2. As is to be expected, an increase in the number of carbons increases the hydrophobicity and results in more effective extractions. The two curves on the left are for benzoyl-N-phenylhydroxylamine and for thenoyltrifluoroacetone which are two very good extracting agents for indium. Neither formic nor acetic acid gave extraction values which would appear on the plot, all being below log D of -2.50.

A detailed study of the extraction using hexanoic acid in chloroform is presented in Fig. 3. Curve fitting techniques indicated that the following empirical equation fits the data quite well:

$$D^{-1} = 10^{1.6}[H]^3[HR]_0^{-6} + 10^{-0.3}[H][HR]_0^{-2} + 10^{-6.0}[HR]_0^{-2} + 10^{-4.0}[HR]_0^{-1}$$

Herein D represents the organic/aqueous distribution coefficient, [H] the hydrogen ion activity in the aqueous phase, and $[HR]_0$ the equilibrium concentration of the monomeric hexanoic acid in the organic phase. The $[HR]_0$ concentrations were calculated using the values of P and C determined in this work. A theoretical equation which fits this empirical expression can be derived by assuming that the predominant species in the organic phase is $InR_3(HR)_3$ and the predominant species in the aqueous phase are In^{3+}, $InR_2(HR)_2$, $InR_3(HR)$, and $InR_3(HR)_2$. Such considerations lead to the expectation that

$$D^{-1} = [In]/[InR_3(HR)_3]_0 + [InR_2(HR)_2]/[InR_3(HR)_3]_0 + [InR_3(HR)]/[InR_3(HR)_3]_0 + [InR_3(HR)_2]/[InR_3(HR)_3]$$

wherein the brackets with a subscripted "o" indicate organic phase concentrations and the unsubscripted brackets symbolize aqueous phase concentrations. By substituting appropriate constants after the generally employed manner[9], this equation becomes

$$D^{-1} = K_{33}^{-1}P_{33}^{-1}K^3P^6[\mathrm{H}]^3[\mathrm{HR}]_0^{-6} + K_{33}^{-1}P_{33}^{-1}C_{22}KP^2[\mathrm{H}][\mathrm{HR}]_0^{-2} + K_{33}^{-1}P_{33}^{-1}C_{31}\mathrm{P}^2[\mathrm{HR}]_0^{-2} + K_{33}^{-1}P_{33}^{-1}C_{32}P[\mathrm{HR}]_0^{-1}$$

where K_{33} indicates the aqueous association constant of $\mathrm{InR_3(HR)_3}$, P_{33} the organic/aqueous distribution coefficient of $\mathrm{InR_3(HR)_3}$, K the aqueous association constant of HR, P the organic/aqueous distribution coefficient of HR, C_{22} the aqueous association constant of $\mathrm{InR_2(HR)_2}$, C_{31} the aqueous association constant of $\mathrm{InR_3(HR)_1}$, and C_{32} the aqueous association constant of $\mathrm{InR_3(HR)_2}$. Employing the empirical equation which describes the curves and introducing known values of K and P allows the determination of the other constants: $\log K_{33} = 14.0$, $\log P_{33} = 3.0$, $\log C_{22} = 10.5$, $\log C_{31} = 9.6$, and $\log C_{32} = 12.3$. It is interesting to note that the indium extractions are not affected by concentration changes in the region 10^{-5}–10^{-7} M. This gives a good indication that the extracting species is monomeric. This is in accord with other studies which show that certain carboxylate monomers may be extracted at low concentrations even though polymers are formed at higher concentrations[7,10].

The influence of the supporting organic solvent on the extraction of indium is illustrated in Fig. 4. It is interesting to note that the rising slope in all cases except chloroform is approximately 2, the slope being 3 in the latter case. These phenomena are probably reflections of differing values of P and C for the various solvents which would give varied concentrations of the carboxylate ion in the aqueous phases. The plateau value in the hexane case is the lowest one, this behavior giving the impression that a polar solvent which could adduct to the metal carboxylate would enhance extraction. Any other generalizations would probably require a knowledge of the stoichiometries of the extracting species, which would take considerably more experimental work.

SUMMARY

The extractions of 10^{-5}–10^{-7} M indium from aqueous 0.1 M sodium perchlorate solutions into various organic media containing different concentrations of monocarboxylic acids and into pure monocarboxylic acids have been studied. Both saturated and unsaturated acids have been employed; the number of carbons in the acids was 1–18. Detailed studies of one of the better systems, hexanoic acid in chloroform, have been carried out, the system has been described with a general overall equation, and identifications of the major species have been proposed.

RÉSUMÉ

Une étude est faite sur les extractions d'indium (10^{-5}–$10^{-7}M$) en solutions aqueuses de perchlorate de sodium 0.1 M, dans divers milieux organiques contenant différentes concentrations d'acides monocarboxyliques purs. On a utilisé des acides saturés et non saturés avec des nombres de carbones de 1 à 18. On donne une étude détaillée de l'un des meilleurs systèmes: acide hexanoïque dans le chloroforme.

ZUSAMMENFASSUNG

Die Extraktionen von 10^{-5}–10^{-7} M Indium aus wässriger 0.1 M Natriumperchlorat-Lösung mit verschiedenen organischen Lösungsmitteln, die unterschiedliche Konzentrationen von Monocarboxylsäuren enthielten, und mit reinen Monocarboxylsäuren wurden untersucht. Sowohl gesättigte als auch ungesättigte Säuren wurden verwendet; die Zahl der Kohlenstoffatome in diesen Säuren variierte von 1–18. Genauer wurde das System Hexanonsäure in Chloroform untersucht und das System durch eine allgemeingültige Gleichung beschrieben. Die Identifizierung der wesentlichen Spezies wird vorgenommen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

APPLICATION OF MODIFIED COUNTER-CURRENT TECHNIQUE TO THE DETERMINATION OF TUNGSTEN IN MOLYBDENUM

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(Received August 28th, 1967)

Counter-current extraction techniques have been frequently used in biochemistry and organic chemistry to perform separations that would be difficult, if not impossible, by other means. However, little if any use has been made of this technique in inorganic analysis. The mathematics of the double withdrawal counter-current extraction technique have been presented by HIBBITS[1]. Because of the potential of the counter-current technique to the field of analytical chemistry, the application of the method to a rather difficult inorganic analytical problem was examined as described below. The determination of tungsten in molybdenum appears to be such a problem. Its direct determination (no separation) is not feasible by the dithiol procedure[2] because of the large concentration of molybdenum. Separations, such as removal of molybdenum as the sulfide in a tartaric–sulfuric acid medium[3], are tedious and cumbersome. Adsorption of molybdenum (elution of tungsten) on an anion-exchange column is feasible[4], but it is time-consuming and is restricted to a sample of about 1 g.

After this manuscript was written, a method by NEEF AND DOGE[5] was published which is based on the different behavior of molybdenum and tungsten toward reducing agents prior to the extraction of the respective thiocyanate complex.

The anion-exchange elution data of HAGUE *et al.*[4] indicate a difference in the stabilities of the chloride–fluoride complexes of tungsten and molybdenum. It was hoped that this difference could be utilized by replacing the anion-exchange resin by a suitable organic extractant, and that a solvent extraction procedure would allow the handling of larger quantities of molybdenum than is possible by the anion-exchange procedure.

EXPERIMENTAL

The following procedure indicates the application of a modified counter-current extraction technique to the determination of 5 p.p.m. or more of tungsten in 0.5–2.0 g of molybdenum.

Procedure

Transfer a sample, weighed to the nearest mg, containing at least 5 μg of tungsten, to a polyethylene beaker. Add 2 ml of water, 15 ml of 40% hydrofluoric acid and, dropwise, concentrated nitric acid until complete dissolution of the sample is obtained. Evaporate to dryness on a water bath. Add 3 ml of the hydrofluoric acid and again evaporate to dryness. Dissolve the salts by gentle heating for 1 min with 90 ml of 6 M hydrochloric acid–2.4 M hydrofluoric acid.

In a polyethylene separatory funnel shake 200 ml of methyl isobutyl ketone (MIBK) with 90 ml of the mixed 6 *M*–2.4 *M* acid solution. A few drops of methyl orange added to the acid aids in readily recognizing the liquid interface in the translucent plastic separatory funnel. Discard the acid layer.

In order to follow the procedure, it will be necessary to refer to Figs. 1 and 2.

Transfer the sample to the separatory funnel with a total of 90 ml of the mixed acid solution. Shake vigorously for 1 min. Call this funnel (a).

Pre-equilibrate 200 ml of MIBK with 90 ml of the mixed acid in another separatory funnel (b), discarding the acid layer. Transfer the acid layer from funnel (a) to funnel (b), shake for 1 min and allow the layers to separate. Add 90 ml of new mixed acid solution to funnel (a) and now label this funnel (c). Shake vigorously for

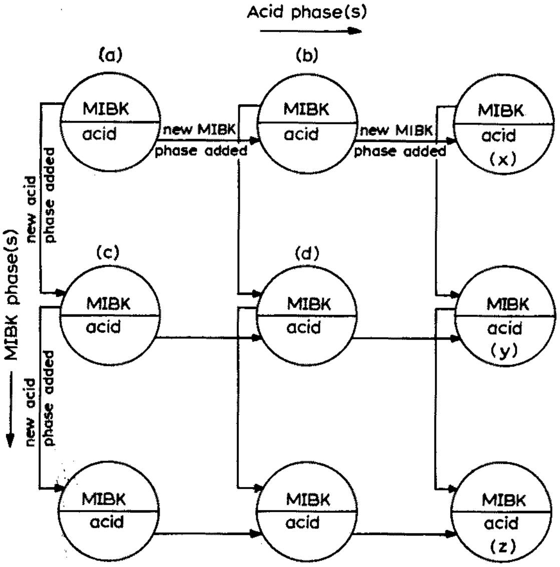
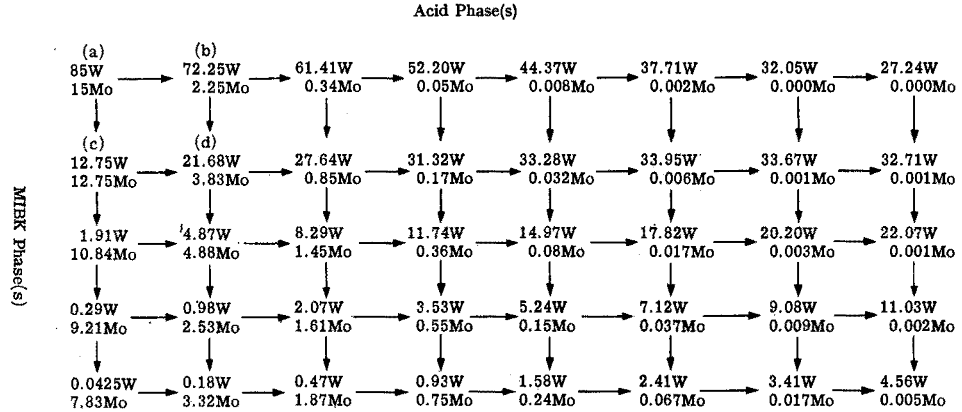


Fig. 1. Typical flow pattern for modified counter-current extraction.



(a) 85W 15Mo	(b) 72.25W 2.25Mo	61.41W 0.34Mo	52.20W 0.05Mo	44.37W 0.008Mo	37.71W 0.002Mo	32.05W 0.000Mo	27.24W 0.000Mo
(c) 12.75W 12.75Mo	(d) 21.68W 3.83Mo	27.64W 0.85Mo	31.32W 0.17Mo	33.28W 0.032Mo	33.95W 0.006Mo	33.67W 0.001Mo	32.71W 0.001Mo
1.91W 10.84Mo	4.87W 4.88Mo	8.29W 1.45Mo	11.74W 0.36Mo	14.97W 0.08Mo	17.82W 0.017Mo	20.20W 0.003Mo	22.07W 0.001Mo
0.29W 9.21Mo	0.98W 2.53Mo	2.07W 1.61Mo	3.53W 0.55Mo	5.24W 0.15Mo	7.12W 0.037Mo	9.08W 0.009Mo	11.03W 0.002Mo
0.0425W 7.83Mo	0.18W 3.32Mo	0.47W 1.87Mo	0.93W 0.75Mo	1.58W 0.24Mo	2.41W 0.067Mo	3.41W 0.017Mo	4.56W 0.005Mo

Fig. 2. Flow pattern for percentages (of the original amount present) of tungsten and molybdenum in the acid phase following the flow diagram of Fig. 1. See text for explanation of a, b, c, and d.

1 min and allow the layers to separate. Transfer the acid layer from (c) and the MIBK layer from (b) to a new funnel (d), shake for 1 min and allow the layers to separate.

The essential features of the procedure have now been given. By following the flow diagrams of Figs. 1 and 2, the analyst can either use the scheme presented in this paper, or devise one of his own. All new MIBK portions should be pre-equilibrated with the mixed acid mixture, before use in the procedure.

Combine all the acid layers in the far right-hand column of the flow pattern (labeled x, y, z in Fig. 1). Add 14 ml of 1:1 sulfuric acid and evaporate the solution to fumes of sulfur trioxide. Add 1 ml of nitric acid and fume again. Repeat, if necessary, the addition of nitric acid and fuming, until all organic matter is destroyed. Wash down the sides of the beaker with water, add 1 g of ammonium hydrogen sulfate and evaporate to strong fumes of sulfur trioxide. Continue with the removal of residual molybdenum and the development of the tungsten color as described in the literature[6].

RESULTS AND DISCUSSION

The optimum medium for the separation of tungsten and molybdenum was evaluated by individually determining the distribution of the two elements between solutions of varying acid concentration and MIBK. Data for this evaluation are presented in Table I.

TABLE I

DISTRIBUTION OF TUNGSTEN AND MOLYBDENUM BETWEEN AQUEOUS CHLORIDE–FLUORIDE SOLUTIONS AND MIBK

HCl (M)	*HF (M)*	*% Extracted*[a]	
		Mo	*W*
1.2	0.2	55	45
1.2	2.4	50	40
3.6	0.2	75	25
3.6	1	70	20
3.6	4	60	15
6.0	0.2	94	25
6.0	1.5	90	20
6.0	2.4	85	15
8.0	0.2	80	27
8.0	2.4	75	18

[a] Percent extracted by 200 ml of MIBK from 90 ml of the acid mixture.

Because of the significant difference in the percentage extractions of tungsten and molybdenum in a 6 *M* hydrochloric acid – 2.4 *M* hydrofluoric acid (15 and 85%, respectively), the separation of the two metals by counter-current extraction is feasible. Theoretical values of the amount present in the combined aqueous phases using the double-withdrawal counter-current extraction technique[1], are shown in Table II. These data indicate that quantitative separations can be obtained using the double-withdrawal technique. However, it was hoped that a modified counter-current technique could be used which would require significantly fewer extractions and yet permit a quantitative determination of small amounts of tungsten in molybdenum. The extraction scheme evaluated is shown in Fig. 1.

In this procedure, MIBK is added to the acidic solution of the sample (funnel (a)), and the phases are shaken and permitted to separate. The MIBK phase is transferred to another separatory funnel, (c), and a fresh acid phase added. The acid phase is also transferred to another separatory funnel, (b) and a fresh MIBK portion added. After these two funnels are shaken, the acid phase from (c) and the MIBK phase from (b) are combined in another separatory funnel (d), shaken and separated, etc.

TABLE II

TOTAL AMOUNT[a] OF TUNGSTEN AND MOLYBDENUM IN THE COMBINED AQUEOUS PHASES BY THE DOUBLE-WITHDRAWAL COUNTER-CURRENT EXTRACTION TECHNIQUE USING 6 *M* HCl–2.4 *M* HF MEDIUM

No. of stages	*No. of extractions*	*% W*	*% Mo*
9	13	97.2	0.02
11	16	98.08	$2.96 \cdot 10^{-3}$
13	17	97.29	$5.19 \cdot 10^{-4}$
15	20	98.15	$9.23 \cdot 10^{-5}$
23	26	97.13	$8.86 \cdot 10^{-8}$

[a] Theoretical results.

Figure 2 shows the percentage of tungsten and molybdenum present in the acid phases (*after each extraction*) following the flow diagram of Fig. 1. For example, when equilibrium is reached, the acid phase from the first extraction will contain 85% of the tungsten and 15% of the molybdenum originally present (marked (a) on Fig. 2). If the acid phase is treated with a new MIBK phase [(b) in Fig. 2], after extraction and equilibrium, the acid phase will contain 72.25% (85% of 85%) of the tungsten and 2.25% of the molybdenum originally present. If the MIBK phase from (a) is treated with new acid [(c) in Fig. 2], then, after extraction and equilibrium, this acid phase will contain 12.75% of the tungsten (85% of the 15% which remained in the MIBK phase after extraction at (a)) and 12.75% of the molybdenum. If the MIBK phase from (b) is combined with the acid phase from (c) and these phases shaken and equilibrated [(d) in Fig. 2], the acid phase will contain 21.68% of the tungsten, and 3.83% of the molybdenum originally present. The following information can be obtained from Fig. 2.

(*1*) After the first extraction of the acid phase with MIBK, if the acid phase is treated 7 times with new MIBK phases, the final acid phase will then contain 27.24% of the original tungsten present and a negligible amount of the original molybdenum.

(*2*) Treating the original MIBK phase 5 times with fresh acid will result in 0.0425% of the original tungsten and 7.83% of the original molybdenum being present in the final acid phase.

It is apparent that in order to obtain quantitative recovery of the tungsten, the acid portions must be combined. Thus, in the example shown in Fig. 2, the acid phases containing 27.24% W, 0.000% Mo; 32.71% W, 0.001% Mo; 22.07% W, 0.001% Mo; 11.03% W, 0.002% Mo; and 4.56% W, 0.005% Mo, would be combined. The total amount of tungsten in the combined acid portions equals 97.61% of the amount originally present, together with 0.009% of the amount of molybdenum originally present. These data can be represented more readily, if the flow scheme in Fig. 2 is called 8 "across" and 5 "down".

Table III summarizes the *total* percentage of the original tungsten and molybdenum obtained in the combined acid portions (combined as in the preceding example) after other combinations are calculated by computer[7].

Thus, when the procedure labeled 6 across, 3 down is used, 89.48% of the tungsten originally present should be obtained in the final acid portions, contaminated by only 0.024% of the amount of molybdenum originally present. This small amount of molybdenum does not interfere in the dithiol procedure of HOBART AND HURLEY[2].

TABLE III

RECOVERY OF TUNGSTEN AND MOLYBDENUM BY MODIFIED COUNTER-CURRENT EXTRACTION AS A FUNCTION OF VARYING THE FLOW PATTERN (FIG. 1)

Flow procedure		*Total (%)*[a]	
		W	*Mo*
6 across	3 down	89.48	0.024
6	4	96.60	0.061
6	5	99.01	0.128
7	3	85.92	0.004
7	4	95.00	0.013
7	5	98.41	0.030
8	3	82.02	0.002
8	4	93.05	0.004
8	5	97.61	0.009

[a] Theoretical amount present in combined acid portions using flow pattern indicated.

TABLE IV

DETERMINATION OF TUNGSTEN IN MOLYBDENUM

Amount of sample (g)	*W added (μg)*	*W found (μg)*[a]	*p.p.m. W*
0.5	—	13	26
1.0	—	20	20
2.0	—	44	22
2.0	50	99	25
2.0	100	150	25
1.0	10	34	24
1.0	30	52	22
1.0	50	74	24
1.0	100	125	25
1.0	200	225	25

[a] Results corrected for solubility of tungsten in MIBK.

The method described here (6 across, 3 down) was applied to the determination of tungsten in a molybdenum sample containing 20 ± 3 p.p.m. of tungsten (as established by cooperative work in several laboratories with the ion-exchange method) to which varying amounts of tungsten were added. The results are shown in Table IV.

The successful application of this modified counter-current extraction technique to the determination of tungsten in molybdenum, will, it is hoped, stimulate others to apply this technique to other difficult separation problems in inorganic analytical chemistry.

SUMMARY

More than trace amounts of molybdenum interfere in the determination of tungsten by the dithiol method. A simplified counter-current extraction method is described which allows the determination of 5 p.p.m. or more of tungsten in a molybdenum matrix. The optimum conditions for the separation were a 6 *M* HCl–2.4 *M* HF medium and methyl isobutyl ketone as extractant; the percentage extractions in a single pass were 85% and 15% for molybdenum and tungsten, respectively.

RÉSUMÉ

Le molybdène gêne dans le dosage du tungstène par la méthode au dithiol. Un procédé simplifié par extraction à contre courant est décrit; il permet le dosage de 5 p.p.m. ou plus de tungstène dans une matrice de molybdène. Les conditions optima sont: milieu HCl 6 *M*–HF 2.4 *M* et méthyl isobutylcétone comme extractant. Les % d'extraction dans un simple passage sont 85% pour le molybdène et 15% pour le tungstène.

ZUSAMMENFASSUNG

Sind mehr als Spuren Molybdän vorhanden, so stören sie die Bestimmung von Wolfram mit der Dithiol-Methode. Es wird ein vereinfachtes Gegenstromextraktionsverfahren beschrieben, das die Bestimmung von 5 p.p.m. oder mehr Wolfram in einer Molybdänmatrix gestattet. Die optimalen Bedingungen zur Trennung sind ein Gemisch aus 6 *M* HCl und 2.4 *M* HF und Methyl-isobutylketon als Extraktionsmittel. Die prozentuale Extraktion bei einem Schritt beträgt 85% für Molybdän und 15% für Wolfram.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

PREPARATION OF *o,o'*-DICHLORODITHIZONE AND A STUDY OF ITS METAL COMPLEXING PROPERTIES

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(Received September 28th, 1967)

TAKEI AND KATO[1] have studied the syntheses and applications in analytical chemistry of *p*- and *o*-disubstituted dithizones. They determined the spectral properties of these reagents and their complexes, and reported that the introduction of substituents in the phenyl radicals shifts the absorption peaks of the reagents to lower frequencies in both cases, whereas the absorption peaks of the metal complexes of the *o*-substituted dithizone shift to higher frequencies. According to TAKEI AND KATO, in comparison with dithizone itself, there is a decrease in the reactivity of the *o*-substituted dithizone with metals, and a decrease in sensitivity and hence an increase in selectivity of the *o*-derivatives towards mercury, copper or silver. These observations have been attributed to the "steric effect" of the methyl group and the consequent inhibition of complex formation. These conclusions seem to have been drawn on the basis that "imino" hydrogens are involved in the complex formation.

This paper describes the synthesis of *o,o'*-dichlorodithizone and a quantitative study of the complexes formed with several metals. The spectral characteristics were determined for purer samples by means of the "reversion technique"[2]. Quantitative studies of the extractability[3] of the lead complex were made, the results being at variance with those of TAKEI AND KATO. However, the present results confirm those of previous workers[4] that the "thio-hydrogens" and not the "imino-hydrogens" are involved in complex formation and hence no "steric effect" is possible if *o*-substituents are introduced in the phenyl radicals of the reagent. It would appear, on the assumption that metal–nitrogen bonds are involved in complex formation, that steric hindrance to coordination due to the proximity of four bulky phenyl groups would be so large as to inhibit complex formation completely with metals such as copper and nickel which adopt square planar configurations in their inner chelate complexes. In fact, the present results indicate that there appears to be no great difference between the ease of complex formation with the *o*-substituted dithizones and with dithizone itself. The absorption spectra of the corresponding complexes also present no distinguishing features.

Synthesis

o,o'-Dichlorodithizone (1,5-di-*o*-chlorophenyl-3-mercaptoformazan) was prepared by reducing the nitroformazan obtained by coupling nitromethane with *o*-chlorobenzene diazonium chloride following the general method of BAMBERGER *et al.*[5].

Samples of di-*o*-chlorodithizone were purified by COWLING AND MILLER'S[6] method and the molecular extinction coefficient of the reagent determined by the mercury titration procedure[7,8] after a preliminary study of the pH range over which the quantitative extraction of the mercury complex could be realised. The mercury complex was found to have the high extinction coefficient of 33,100 at 670 nm, the wavelength of maximum absorbance. Similar studies were then made of the pH range for complete extraction of complexes with ions Ag^+, Bi^{3+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+}. The molecular extinction coefficients of these complexes were determined by a reversion procedure[9]. The results are shown in Fig. 1.

The extraction constant K, of lead was determined by VOUK AND WEBER's method[3] for aqueous phases containing citrates over the pH range 6–11; the hydrolysis

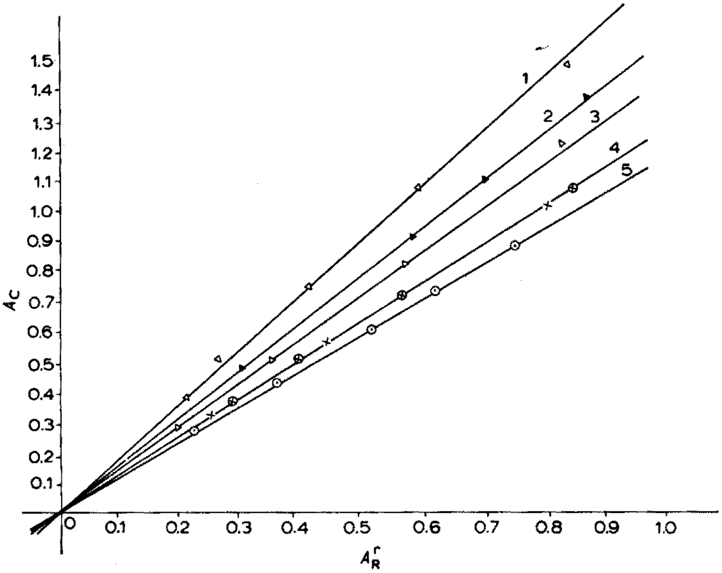

Fig. 1. Reversion method for the determination of molecular extinction coefficients of metal dichlorodithizonate complexes. (1) Zinc, (2) cadmium, (3) lead, (4) copper and silver, (5) bismuth.

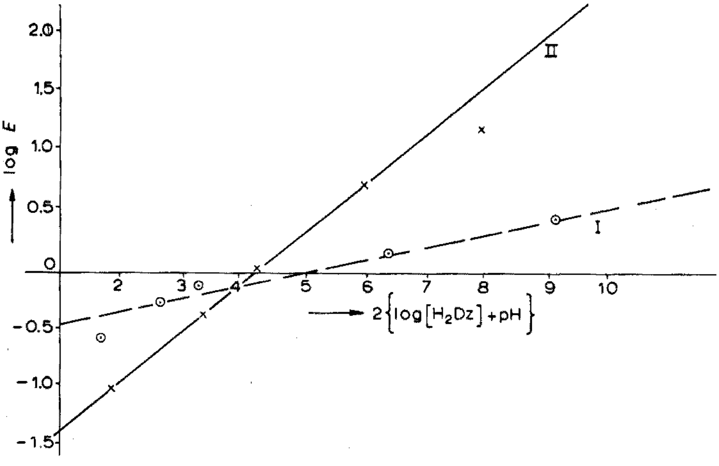

Fig. 2. Extraction constant of the lead complexes. (I) Dichlorodithizonate, (II) dithizonate.

of lead was neglected. It follows that a plot of log E *vs.* $2\{\log[H_2Dz]+pH\}$ should give a straight line of intercept log K as shown in Fig. 2. Here $E=[Pb(HDz)_2]_{org.}/[Pb]_{aq.}$ and H_2Dz represents unionized dithizone.

EXPERIMENTAL

Preparation of 1,5-di-o-chlorophenyl-3-mercaptoformazan

Preparation of the nitroformazan. *o*-Chloroaniline (0.2 moles) in concentrated hydrochloric acid (60 ml) and water (275 ml) was diazotised with sodium nitrite solution (14.5 g). The solution was quickly neutralized with sodium hydroxide (0°). This solution was poured into sodium acetate (700 g) and acetic acid (360 ml) and stirred vigorously. Nitromethane (0.1 mole) was added and the mixture was stirred for 3 h. The precipitate was washed thoroughly with water and recrystallised from ethanol (m.p. 157°; found: C 46.50, H 3.08, N 20.40; required: C 46.16, H 2.68, N 20.70).

Preparation of the thiocarbazide. Dry ammonia was passed through a solution of nitroformazan (6 g) in ethanol (250 ml) until it was saturated at 0°. Hydrogen sulphide was then passed through the cooled red solution until an orange colour developed. This was diluted with water and the precipitated thiocarbazide was washed with water and dried.

Oxidation of thiocarbazide. The crude thiocarbazide was treated with potassium hydroxide (3 g) in boiling methanol for 3–5 min. The deep red solution was poured into 2 N sulphuric acid (500 ml), stirred and cooled at 0°. 1,5-Di-*o*-chloro-3-mercapto-

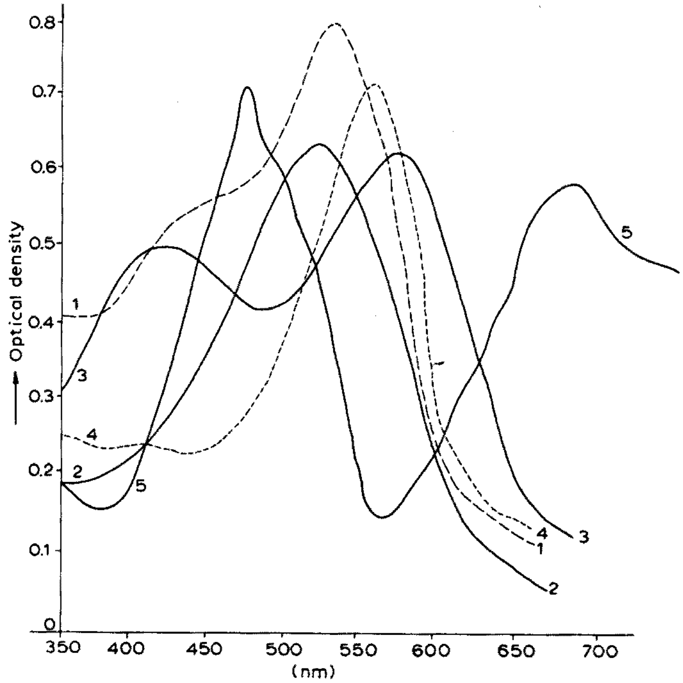

Fig. 3. Absorption spectra. (1) $8.63\cdot10^{-6}$ M lead complex, (2) $8.42\cdot10^{-6}$ M bismuth complex, (3) $7.05\cdot10^{-6}$ M zinc complex, (5) reagent alone.

phenylformazan was finally obtained as a black powder which was washed free from acid and dried *in vacuo* (m.p. 138° decomp.). A sample was dissolved in chloroform and filtered. The filtrate was evaporated almost to dryness and absolute ethanol added. This was dried *in vacuo* and the solid dichlorodithizone obtained. (Analysis: found C 48.30, H 3.26, N 17.64; required C 48.0, H 3.10, N 17.23.)

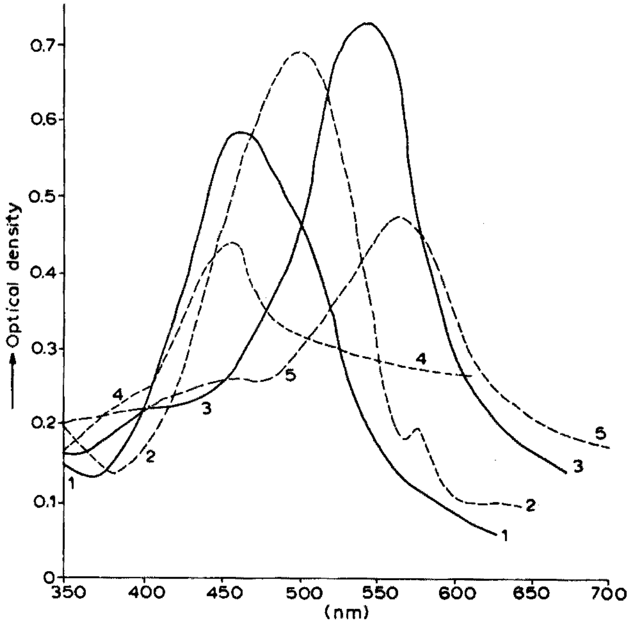

Fig. 4. Absorption spectra. (1) $15.50 \cdot 10^{-6}$ *M* silver complex, (2) $8.40 \cdot 10^{-6}$ *M* mercury complex, (3) $7.76 \cdot 10^{-6}$ *M* cadmium complex, (4) nickel complex, (5) cobalt complex.

TABLE I

PH RANGES OF MAXIMUM EXTRACTION OF METAL COMPLEXES OF DICHLORODITHIZONE IN COMPARISON WITH THOSE OF DITHIZONE[10] AND DIBROMODITHIZONE[2]

Metal	*Dichlorodithizone*	*Dithizone*	*Dibromodithizone*
Hg^{2+}	4–5	2–3	1
Ag^{+}	2–3	2–3	2–2.5
Cu^{2+}	3.5–5	2–3	1.8–2.8
Zn^{2+}	8	8.3	6.5–8.0
Pb^{2+}	10–12	8.5–11	8.6
Bi^{3+}	8–11	8	9
Cd^{2+}	8–9	12	—
Co^{2+}	9	8–9	—
Ni^{2+}	10	10	—

Absorption spectra

Dichlorodithizone was purified by COWLING AND MILLER'S[6] method. AnalaR quality salts were used in making up all solutions as previously described[2,9]. The absorption spectra of the reagent and its metal complexes (Figs. 3 and 4) were measured with a Unicam Spectrophotometer with matched silica cells. Preliminary studies were made, as described previously[2,9], to establish the pH range over which the maximum amount of metal was extracted (Table I). The extraction of cobalt and nickel decreased very sharply outside the range 9–10.

RESULTS AND DISCUSSION

The positions of the two absorption bands in the visible spectra of di-*o*-chlorodithizone in comparison with those of dithizone, the mono and dibromo substitution products and the di-*o*-methyl and di-*p*-methyl products are given in Table II together with values for the respective molecular extinction coefficients.

It is clear from Table II that the introduction of *o*-chloro atoms into diphenylthiocarbazone produces a bathochromic shift in the position of each of the prominent absorption bands in the visible region. A similar shift is also caused by the introduction of bromine to the *p*-position in diphenylthiocarbazone or a methyl group to the *o*-position. PELKIS *et al.*[11] stated "that with the introduction of electron acceptor substituents in the phenyl groups of dithizone, the molar coefficient of extinction is decreased, the latter having a value several times less than that of dithizone". The present data provide no support for such a generalisation. However, the present data lend support to their statement that "when halogens are introduced into the phenyl groups of 1,5-diphenylthiocarbazones, the intensity of the long wave maximum is decreased with a simultaneous increase in the short wave maximum".

TABLE II

ABSORPTION DATA IN CARBON TETRACHLORIDE

Reagent	$\lambda_{\max_1}$	$\lambda_{\max_2}$	$\varepsilon_{\max_2} \cdot 10^{-3}$	*Peak ratio*
Dithizone	450	620	32[a]	1.70[b]
Di-*o*-chlorodithizone	470	670	33.1	0.82
Di-*p*-bromodithizone	464	635	31.4[b]	1.64[b]
Mono bromodithizone	456	626	34.5[b]	1.60[b]
Di-*o*-methyldithizone	460	628	38.0[c]	2.30[c]
Di-*p*-methyldithizone	450	620	46.4[c]	2.50[c]

[a] Data from ref. 10. [b] Data from ref. 2. [c] Data from ref. 1.

From the gradients of the straight lines obtained in Fig. 1 and the molar extinction coefficient of di-*o*-chlorodithizone, it was possible to calculate values for the molecular extinction coefficients of various metal–dichlorodithizone complexes. Table III summarizes these values together with the wavelength of maximum absorption of the different complexes in comparison with those of dithizone and its dibromo and dimethyl substitution products. It is clear that for each reagent the wavelength of maximum absorption increased in the order $Ag^+ < Hg^{2+} < Bi^{3+} < Pb^{2+} < Cd^{2+} < Zn^{2+} < Cu^{2+}$. There is again a bathochromic shift for each metal caused by chlorine substitution which is similar to the effect of bromine substitution. The values for molar extinction coefficients of the dichlorodithizone complexes increase in the order $Ag^+ < Bi^{3+} < Cu^{2+} < Hg^{2+} < Pb^{2+} < Cd^{2+} < Zn^{2+}$ which varies slightly from that of dithizone itself where the order is $Ag^+ < Cu^{2+} < Pb^{2+} < Hg^{2+} < Bi^{3+} < Cd^{2+} < Zn^{2+}$. There is no systematic trend in individual values as a result of chlorine substitution.

TABLE III

ABSORPTION DATA OF THE METAL COMPLEXES

Reagent		Hg^{2+}	Ag^{+}	Bi^{3+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}
Dithizone[a]	λ_{max}	490	460	490	520	536	548	520	—	—
	$\varepsilon_{max} \cdot 10^{-3}$	72.2	29.1	84.6	66.5	92.0	45.0	84.2	—	—
Di-*o*-chloro-dithizone	λ_{max}	500	470	520	530	560	570	550	560	460
	$\varepsilon_{max} \cdot 10^{-3}$	80.9	38.7	76.1	90.3	105	77.4	94.6	—	—
Di-*p*-bromo-dithizone[a]	λ_{max}	502	472	500	—	552	566	—	—	—
	$\varepsilon_{max} \cdot 10^{-3}$	71.5	24.0	80.3	—	89.7	49.7	—	—	—
Di-*o*-methyl-dithizone[b]	λ_{max}	486	456	476	~500	525	538	515	—	—
	$\varepsilon_{max} \cdot 10^{-3}$	50.7	—	—	—	—	—	—	—	—
Di-*p*-methyl-dithizone[b]	λ_{max}	502	474	—	530	546	554	530	—	—
	$\varepsilon_{max} \cdot 10^{-3}$	80.2	—	—	69.7	98.8	—	99.3	—	—

[a] Data from ref. 2.
[b] Data from ref. 1.

The extraction constant for lead di-*o*-chlorodithizonate was calculated to be $49 \cdot 10^{-2}$ while that of lead dithizonate was found to be $45.5 \cdot 10^{-3}$ in the presence of citrates under identical conditions.

The unimpaired reactivity of zinc, cadmium and lead with di-*o*-chlorodithizone to form complexes does not support the earlier suggestion[1] that the "steric effect" of the substituents interferes with chelate ring formation in these metal complexes. However, this confirms the view that the imino-hydrogen atoms are not involved in coordination and that complex formation takes place through the thio-hydrogen of the reagent.

We are indebted to the Medical Research Institute, Colombo for the use of the SP 500 spectrophotometer.

SUMMARY

o,o'-Dichlorodithizone was synthesised and its spectral characteristics were measured in carbon tetrachloride. The pH ranges for quantitative extraction of various metal complexes were determined. Values for wavelengths of maximum absorption and molar extinction coefficients are given; the former increase in the order $Ag^{+} < Hg^{2+} < Bi^{3+} < Pb^{2+} < Cd^{2+} < Zn^{2+} < Cu^{2+}$ and the latter in the order $Ag^{+} < Bi^{3+} < Cu^{2+} < Hg^{2+} < Pb^{2+} < Cd^{2+} < Zn^{2+}$. Substitution of chlorine produces a regular bathochromic shift in wavelength of maximum absorption for reagent and their metal complexes compared to the dithizonates. No evidence was found that a "steric effect" of the *o*-substituent interferes with chelate ring formation for Zn, Cd, Hg and Pb; the results confirm the view that complex formation takes place through the thio-H of the reagent. The extractability of lead as its *o*-dichlorodithizonate into carbon tetrachloride was investigated in the pH range 5–11 and the extraction constant was measured.

RÉSUMÉ

On a préparé la *o,o'*-dichlorodithizone et examiné ses propriétés spectrales dans le tétrachlorure de carbone. On a déterminé également les zones de pH pour une extraction quantitative de divers complexes métalliques. On indique les valeurs de longueurs d'ondes d'absorption maximum et de coefficients d'extinction molaire; ces premières augmentent dans l'ordre $Ag^+ < Hg^{2+} < Bi^{3+} < Pb^{2+} < Cd^{2+} < Zn^{2+} < Cu^{2+}$. Quant aux coefficients d'extinction molaire, ils augmentent dans l'ordre $Ag^+ < Bi^{3+} < Cu^{2+} < Hg^{2+} < Pb^{2+} < Cd^{2+} < Zn^2$. Une étude a été effectuée sur les propriétés complexantes de ce composé. On a examiné l'extractibilité du plomb comme *o*-dichlorodithizonate dans le tétrachlorure de carbone, entre les pH 5 et 11; la constante d'extraction est mesurée.

ZUSAMMENFASSUNG

o,o'-Dichlorodithizon wurde synthetisiert und sein Spektrum in Tetrachlorkohlenstoff gemessen. Die pH-Bereiche zur quantitativen Extraktion zahlreicher Metallkomplexe wurden bestimmt. Es werden die Wellenlängen der maximalen Absorption und die molaren Extinktionskoeffizienten angegeben; die ersteren steigen in folgender Reihenfolge $Ag^+ < Hg^{2+} < Bi^{3+} < Pb^{2+} < Cd^{2+} < Zn^{2+} < Cu^{2+}$ und die letzteren in der Reihenfolge $Ag^+ < Bi^{3+} < Cu^{2+} < Hg^{2+} < Pb^{2+} < Cd^{2+} < Zn^{2+}$. Die Substitution von Chlor bewirkt eine regelmässige Verschiebung der Wellenlänge maximaler Absorption beim Reagenz und seinen Metallkomplexen im Vergleich zu den Dithizonaten. Es wurde kein Anzeichen gefunden, dass ein sterischer Effekt der *o*-Substitution zu Störungen einer Chelatringbildung für Zn, Cd, Hg und Pb führt. Die Ergebnisse bestätigen die Ansicht, dass die Komplexbildung über den Thio-Wasserstoff des Reagenzes geschieht. Die Extrahierbarkeit des Blei-*o*-Dichlorodithizonats mit Tetrachlorkohlenstoff im pH-Bereich 5–11 wurde untersucht und die Extraktionskonstanten gemessen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE FORMATION OF HYDROGEN PEROXIDE IN METALLIC REDUCTORS

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(Received September 15th, 1967)

The most widely used methods for the conversion of metal ions of high valency states to lower ones for subsequent titration with an oxidimetric titrant are those using metallic reductor columns; probably the amalgamated zinc or Jones reductor is the one which is still generally preferred, but in more recent years the silver or Walden reductor and to a lesser extent, the lead reductor of Treadwell, have found considerable application. An extensive account of the development and uses of reductors of all kinds was published in 1952–53[1], and standard text-books of titrimetric analysis give detailed information on the uses of both solid and liquid metal reductors, and the precautions which must be observed for their satisfactory operation.

One of the least recognised aspects of reductor performance is the production of hydrogen peroxide during the process of reduction and its effect on the subsequent analytical procedures. As long ago as 1893, TRAUBE[2] recognised that hydrogen peroxide was formed in the Jones reductor; since that time, this possibility has been examined by several investigators and considerable disagreement is to be found in their respective views. For example, some state that if peroxide is formed, it is reduced within the column and has no effect on the final titration. Others claim that if other (than Jones) metal reductors are used, hydrogen peroxide is not formed; these views have also been contradicted. This lack of agreement has been commented upon by KOLTHOFF AND BELCHER[3].

It is not proposed to outline all the opposing views in the present paper; these have been discussed in detail elsewhere[4] and do little to help a better appreciation of the practical applications of these metallic reductors. An exception is the work of MILLER AND CHALMERS[5] which deals with the micro-determination of iron using the silver reductor; this is one of the few papers in which the problem of peroxide formation is dealt with objectively. These workers recognised the adverse effect of hydrogen peroxide produced in the reductor column (*cf.* FRYLING AND TOOLEY[6]) and recommended the use of solutions saturated with carbon dioxide to minimise the formation of hydrogen peroxide. A suitable blank determination accounted for the small amount of iron reoxidised by the peroxide.

The present paper describes an extensive examination which has been made of the formation of hydrogen peroxide, both in solid metal reductor columns and with liquid metal amalgams, with the object of establishing the optimal conditions for stoicheiometric reduction.

The Jones (zinc) reductor, the silver reductor, the lead reductor and the bismuth reductor together with the liquid amalgams of zinc, cadmium, bismuth and lead were examined. All of these reductors gave appreciable amounts of hydrogen

TABLE I

FORMATION OF H_2O_2 IN SOLID AND LIQUID METAL REDUCTORS (IRON ABSENT)
(100-ml quantities of solution treated)

H_2SO_4[a] concn. (N)	*Peroxide formed (mg/l)*											
	Jones reductor			*Silver reductor*[a]			*Lead reductor*			*Bismuth reductor*		
	O_2	*Air*	*N_2*	*O_2*	*Air*	*N_2*	*O_2*	*Air*	*N_2*	*O_2*	*Air*	*N_2*
—	18.5	5.0	—	Not measurable			Not measurable			5.1	5.1	—
0.5	60.1	7.9	—	0.68	0.34	—	14.8	4.3	—	12.5	7.3	—
1.0	52.5	9.3	3.6	0.51	0.17	0.10	7.4	2.6	—	11.7	2.1	—
1.5	45.2	8.1	—	0.42	0.09	—	4.6	2.2	—	11.5	1.6	—
2.0	40.1	7.1	0.85	0.59	0.25	0.10	3.3	1.7	—	10.0	1.5	—
2.5	34.9	5.8	—	0.76	0.34	—	2.8	0.70	—	9.2	1.5	—
3.0	28.6	4.9	—	1.20	0.42	—	2.3	0.60	—	8.9	1.3	—
3.5	25.7	4.5	—	1.20	0.51	—	1.9	0.50	—	6.5	1.0	—
4.0	25.4	3.4	0.41	1.70	0.68	0.12	1.5	0.50	—	5.8	1.0	—
	Liquid zinc reductor			*Liquid cadmium*[b]			*Liquid lead reductor*			*Liquid bismuth reductor*		
—	16.8	1.9	1.7	Not measurable					PbO_2	Oxy-salts formed		
0.5	17.7	3.9	—	14.4	19.9	5.7			6.2	16.5	5.0	4.3
1.0	13.3	3.3	1.5	76.6	20.3	2.4		PbO_2 formation in solution prevented detn. of H_2O_2	2.1	16.5	4.9	2.7
1.5	10.0	2.0	—	84.5	19.9	2.2			1.9	13.2	2.5	2.4
2.0	9.0	1.6	1.0	148.7	20.3	2.7			1.7	14.0	2.2	2.0
2.5	8.1	1.4	—	80.3	13.9	3.2			1.6	13.0	2.2	1.7
3.0	6.3	1.4	—	68.8	23.3	2.1			1.5	14.7	2.1	1.7
3.5	5.7	1.3	—	60.7	23.3	3.4			1.4	11.4	2.7	1.0
4.0	5.1	1.0	—	62.8	33.1	2.2			1.3	11.3	1.9	1.5

[a] With the silver reductor, hydrochloric acid was used.
[b] Results very variable. Those quoted are maximal figures.

peroxide under conventional conditions, i.e. in the presence of atmospheric oxygen. The amount of peroxide formed was related to the amount of oxygen present, the acid concentration and the particular metal used in the reductor (see Table I). When pure oxygen was present in excess during passage of an aqueous solution containing only acid through the reductor, the amount of peroxide was at a maximum; lesser amounts were formed in the presence of air and still less when the solutions were de-aerated. When nitrogen gas only was present, the peroxide was still detectable, but the use of nitrogen gas scavenged by passage over hot reduced copper decreased the amount of peroxide to a negligible proportion. It is of interest to note that the small amount of oxygen present as an impurity in commercial nitrogen is sufficient to cause the formation of peroxide; it is only when these last traces are removed that the formation of peroxide is essentially prevented.

The immediate implication of these findings is that the reduction of metal ions by the reductor will be incomplete because of reoxidation by the peroxide simultaneously formed. In the case of iron(III), it is to be expected that the amount of iron(II) formed during the passage of the solution through the reductor column will be affected by the small amount of peroxide initially present in the column, either in the acid solution used to activate the reducing agent, or actually adsorbed on the metal surface. The amount of peroxide formed during the reduction of iron(III) in the reductor column may have little influence on the quantitative reduction to iron(II), because of the reduction of the peroxide by the newly formed iron(II). In the dynamic system involved in the reductor column, the iron(III) so produced might still be reduced before it leaves the reductor. The difficulty arises during the washing of the column with acid to remove the final traces of iron remaining in the reductor. Conditions are then most favourable for peroxide formation, and this, collected in the reduced iron solution, leads to re-oxidation of iron(II). MILLER AND CHALMERS[5] consider the washing process to be the sole source of error when the silver reductor is used, and their positive correction to the observed value for the oxidimetric titration is based on a blank run with an iron-free acid solution. Although these workers were able by careful control of conditions to obtain satisfactory results, nevertheless there is a strong possibility of a non-stoicheiometric conversion of iron(III) to iron(II) and results for the oxidimetric determination of iron by any form of reductor process will be low.

As the production of hydrogen peroxide was shown to be a phenomenon common to all metal reductors, only the Jones, silver and liquid zinc amalgam reductors, the more commonly used forms of reductor, were studied in greater detail. When a solution of iron(III) was allowed to pass through a previously washed Jones reductor in the presence of air and the eluate was collected separately in a clean flask, addition of thiocyanate to the eluate showed the presence of some iron(III). A similar test with the silver reductor was negative for iron(III), but positive with the liquid zinc amalgam. When the reductors were washed to remove all the iron solution, and the wash liquid was added to the previously collected eluates, all three solutions gave positive tests for iron(III).

When these processes were repeated with standard amounts of iron(III) and the eluates were titrated with cerium(IV) solution, the recoveries of iron were significantly low. That these low results are due to the re-oxidation of some of the iron(II) can be shown by a simple experiment. The iron(III) in the effluent can be determined by spectrophotometric means, and the amount found corresponds almost completely to the missing amount of iron. The Jones reductor shows a constant negative error of about 0.4%, the silver reductor of 0.35%, and the liquid zinc amalgam a variable but negative error of 0.1–0.4%, for 70-mg amounts of iron. For example, determinations of iron(III) by the Jones reductor under ordinary conditions, gave results of 70.32–70.37 mg, corrected for indicator and acid blanks, instead of the actual 70.77 mg originally taken. Measurement of the iron(III) present in the eluates by the thiocyanate procedure gave amounts in the range 0.45–0.50 mg which correspond within experimental error to the difference between the observed and actual iron content of the test solutions.

When the reductor systems were flushed continuously with oxygen-free nitrogen, blank determinations on pure acid solutions were very considerably reduced (by as much as 80%). It was found advantageous to pre-treat reductor columns which had been standing idle for some time by filling them with iron(II) solution and leaving them for 1–2 h. This removed accumulated peroxide adsorbed on the metal surface more readily than simple washing with dilute acid. The reductors were then washed in the normal way before use. This use of oxygen-free nitrogen led to recoveries of iron [as iron(II)] which were essentially complete. For example, with the Jones reductor under these conditions, the average result, corrected for acid and indicator blanks, was 70.78±0.03 mg for an actual amount of 70.77 mg present. However, the liquid zinc amalgam reductor tended to give a small but variable error. This may be due to the different conditions of the reduction, in which the solution and reductant are vigorously shaken together and the amalgam removed before the titration is effected.

During the course of the present work CHALMERS, EDMOND AND MOSER[7] described their findings on the oxidimetry of iron(II) and the peroxide effect. They compared three methods: reduction of iron(III) with tin(II) chloride, reduction with the silver reductor following the precaution recommended by MILLER AND CHALMERS[5], and reduction with liquid zinc amalgam. The first two methods gave essentially similar results, with a small (*ca.* 0.15%) positive error, whereas the third method gave variable but always negative errors of about 1%.

EXPERIMENTAL

Apparatus

The reductor columns were of conventional pattern[3], 2 cm in internal diameter and 65 cm in length. Glass tubes of 0.4 cm external diameter connected to the appropriate supply of gas through a simple pressure regulator extended internally to the base plugs of the reductor columns. The liquid amalgam reductors were of the Nakazono pattern, modified to allow the appropriate gas to be passed through the amalgam and the solution above it.

Spectrophotometric measurements were made on a Unicam S.P. 600 spectrophotometer.

Reagents

Zinc containing 2% mercury (for Jones reductor) was prepared in the usual way by treatment with mercury(II) chloride[3]. Suitable granular forms of A.R.-grade lead, bismuth, tin and cadmium were available. These metals were rinsed with dilute sulphuric acid, washed well with water and filled into the reductor columns.

Silver metal precipitated from silver nitrate solution by the action of copper was unsuitable for the present study. It formed a compact mass in the reductor which prevented the counter-current of gas from bubbling through the solution. The low-density crystalline silver prepared by SMITH AND CAGLE's electrolytic method[8] was found to be satisfactory. Liquid amalgams of zinc, cadmium, lead and bismuth were prepared by reacting 3 g of the pure metal with 97 g of redistilled mercury in the presence of dilute sulphuric acid for 0.5 h. The liquid metal was separated from any solid residue, washed well with water and stored under dilute sulphuric acid.

The determination of the amount of peroxide formed in the reductors under various conditions in the absence of iron

The reductor columns and liquid amalgam reductors were washed thoroughly with dilute acid and distilled water before use. Portions (100 ml) of distilled water or dilute acid of known concentration were placed in the reductors and a constant stream of pure oxygen, air, commercial nitrogen, or oxygen-free nitrogen was passed into the solutions in contact with the metal for 12 min. The solutions were drained out and the eluates were titrated with 0.05 *N* ceric sulphate and ferroin sulphate as indicator. When the amount of peroxide formed fell below about 1 mg/l, the titrimetric method proved unsuitable, and determinations were made spectrophotometrically on the peroxy-titanic acid complex.

The determination of iron by reduction and oxidimetric titration

A stock solution of iron(III) sulphate, containing approximately 7 mg of iron per ml, was standardised by the conventional gravimetric method[9]. Portions (10 ml) of this solution were treated with 20 ml of 10 *N* sulphuric acid in a 100-ml volumetric flask and distilled water was added to make up the volume. These solutions were transferred to the Jones, silver or liquid zinc amalgam reductor, and the solutions were allowed to drain into the receiving vessel at a rate of 10–15 ml/min whilst the counter-flow of oxygen, air or nitrogen was passing. (The liquid amalgam reductor involved shaking the test solution for about 10 min before draining off the amalgam.) The reductors were washed with a total of 125 ml of dilute acid in portions, and the wash liquid was added to the previously collected solution. After the addition of a standard amount of ferroin indicator, the solutions were titrated with 0.1 *N* ceric sulphate solution.

For the determination of iron(III) in the eluates, the same procedure for the reduction was followed. The whole of the eluate was then transferred to a 500-ml volumetric flask, 50 ml of 30% potassium thiocyanate were added and the volume was made up to 500 ml with distilled water. The optical density of the solution was determined and the amount of iron was calculated from a previously prepared calibration curve.

In all the oxidimetric titrations, the theoretical indicator blank was deducted from the titration values obtained.

DISCUSSION

The formation of peroxide in solutions in contact with metals and oxygen has long been recognised, but the significance of this in analytical procedures involving the use of metallic reductors has been little appreciated. The amount of peroxide formed varies considerably with the conditions and is dependent on the acid concentration, the metal or amalgam being used, and the amount of oxygen present in the solution. Under any given set of conditions, the amount of hydrogen peroxide formed is reasonably constant and the equilibrium between its formation and decomposition favours the former. Evidence of this is found in the constant presence of peroxide in an idle reductor column filled with dilute acid and open to atmospheric oxygen.

On purely thermodynamic grounds, the reduction potentials for the reduction of peroxide to water, and oxygen to water, would indicate a strong preference for the latter reaction to occur. LIEBHAFSKY's suggestion[10] for the formation and decomposition of peroxide in the presence of solid zinc amalgam

$$Zn + O_2 + 2\ H^+ \rightleftharpoons Zn^{2+} + H_2O_2 \qquad (1)$$

$$Zn + H_2O_2 + 2\ H^+ \rightleftharpoons Zn^{2+} + 2\ H_2O \qquad (2)$$

would indicate that reaction (1) is faster than reaction (2), and a simple mechanistic explanation has been advanced[7] to support the build-up of peroxide in the system.

That results for the determination of iron can be seriously affected when any one of the three common reductors is used (*i.e.* the Jones, Walden and liquid zinc amalgam reductors) is no longer open to question. Although the results outlined above give some measure of the magnitude of the errors involved when air is not excluded, these are bound to vary somewhat and the actual error on any particular determination may be affected as much by the peroxide formed during the washing of the reductor column *after* the reduction as by that formed during the actual reduction of iron. Whenever a heterogeneous reduction system is used in the presence of oxygen, this formation of peroxide is to be expected. For satisfactory results to be obtained in the determination of iron by any form of metallic reductor, it is necessary to exclude oxygen completely from the solutions in contact with the reducing agent. The present study has been confined to the determination of iron which is the most widely used application of metallic reductors. When other ions are to be determined by similar reductor processes, due attention should be given to the possible interference of hydrogen peroxide.

We are grateful to Professor R. BELCHER for his interest and encouragement and to the University of Sind (Pakistan) for a Scholarship for M.A.S.K.

SUMMARY

The formation of hydrogen peroxide in various types of metallic reductors both in the presence and absence of oxygen has been studied. Only when oxygen is rigorously excluded is peroxide undetectable. The oxidimetric determination of iron is seriously affected by this peroxide when the test solution and reductor are open to atmospheric oxygen. Systems which are completely oxygen-free give satisfactory results.

RÉSUMÉ

On a examiné la formation de peroxyde d'hydrogène dans divers types de réducteurs métalliques en présence et en l'absence d'oxygène. Le peroxyde ne peut être décelé en l'absence rigoureuse d'oxygène. Le dosage oxydimétrique du fer est sérieusement affecté par ce peroxyde lorsque la solution testée et le réducteur sont exposés à l'oxygène atmosphérique. Les systèmes tout à fait exempts d'oxygène donnent des résultats satisfaisants.

ZUSAMMENFASSUNG

Die Bildung von Wasserstoffperoxid mit verschiedenen Typen metallischer Reduktionsmittel wurde sowohl in Gegenwart als auch in Abwesenheit von Sauerstoff untersucht. Nur wenn Sauerstoff vollkommen ausgeschlossen ist, ist Peroxid nicht nachweisbar. Die oxydimetrische Bestimmung von Eisen wird durch dieses Peroxid ernsthaft beeinflusst, wenn die Probelösung und das Reduktionsmittel mit dem Sauerstoff der Luft in Berührung kommen. Völlig sauerstofffreie Systeme ergeben befriedigende Ergebnisse.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

PART XIII*. ANODIC WAVES OF DIALKYLDITHIOCARBAMATES

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(Received September 18th, 1967)

Of the dialkyldithiocarbamates that have been examined polarographically most attention has been paid to sodium diethyldithiocarbamate. The anodic waves obtained were first ascribed[1] to a reversible oxidation process, but it has been shown[2] that these waves correspond to mercury compound formation as was proved for other thiols[3]. The anodic waves have been used for the determination of diethyldithiocarbamate[4], for the titrimetric determination of some heavy metals[5-7] and for the determination of carbon disulphide[8]; those of various dialkyldithiocarbamates have been used for a study of their cleavage in acidic media[9]. Relatively little attention has been paid to the interpretation of the changes of these waves with concentration. Only recently[7,10] it has been observed that the anodic wave increases with increasing concentration to a greater extent than would correspond to a linear concentration dependence. This behaviour[7] was not found in the presence of high concentrations of a surface-active compound (gelatin) and was attributed to adsorption phenomena.

Mercury(II) diethyldithiocarbamate in organic solvent mixtures has been found[11,12] to give two cathodic waves which are very similar to the anodic waves of sodium diethyldithiocarbamate. Furthermore, a mixture of sodium and mercury(II) diethyldithiocarbamates gave[7] a composite anodic–cathodic wave.

Because the earlier work mentioned was restricted to certain specific problems, and because many of the results are contradictory, the polarographic behaviour of dialkyldithiocarbamates has been restudied in detail and compared with results obtained by some other electrochemical techniques.

The dialkyldithiocarbamates studied were sodium diethyldithiocarbamate (I) and potassium dibenzyldithiocarbamate (II) (R_2NCSSM; I, $R = C_2H_5$, $M = Na$; II, $R = CH_2C_6H_5$, $M = K$).

EXPERIMENTAL

Apparatus

The polarograph, Kalousek vessel, capillary, pH-meter, spectrophotometer

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[*] Part XII: *Anal. Chim. Acta*, 40 (1968) 459.
[**] On leave from J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague.

and the controlled-potential electrolysis apparatus were the same as those described previously[13]. A.C. polarographic curves were recorded using the Univector unit in connection with the Cambridge pen-recording polarograph. A Kalousek commutator, enabling a rectangular voltage polarization to be attained[14], was constructed and used. The *i–t* curves were recorded by means of a string galvanometer (Kipp and Zonen) and an arrangement which enabled the first drop to be recorded after polarization had started.

Chemicals

Sodium diethyldithiocarbamate (I) and potassium dibenzyldithiocarbamate (II) were recrystallized commercial products (B.D.H. AnalaR reagent, m.p. 90°, and Hopkin and Williams Organic reagent, m.p. 81° respectively). Both were trihydrates. Mercury(II) diethyldithiocarbamate was prepared by reacting together equal volumes of equimolar solutions of mercury(II) nitrate and compound I.

Stock solutions (0.01 *M*) of I and II in water, borate buffer (pH 9.2) and 0.01 *M* sodium hydroxide showed no deterioration after more than a week. Stock solutions in distilled water were therefore prepared freshly every 3–4 days.

Techniques

Polarographic studies, investigations of reactions with heavy metals and millicoulometric measurements were carried out as described previously[13].

The identification of the product in the controlled-potential electrolysis was attempted after the electrolysis had been carried out in a cell containing 2 ml of chloroform below the solution; the product was extracted from the falling mercury drops into the chloroform layer and after prolonged electrolysis, this layer was investigated spectroscopically.

RESULTS

Polarographic behaviour

The polarographic behaviour of both the dithiocarbamates studied was in some respects analogous.

The wave of dithiocarbamates I and II can conveniently be studied only at pH greater than about 6; at lower pH values acid cleavage* takes place[9] and the waves change with time.

More complex results were obtained for the diethyl derivative I and are reported first.

Diethyldithiocarbamates (I). At concentrations of sodium diethyldithiocarbamate (I) below $1.2 \cdot 10^{-4}M$, one wave (i_a) at -0.62 V is observed. At higher concentrations of I the height of this wave does not change with increasing concentration of I. Moreover, its height is linearly dependent on the height of the mercury column and hence is limited by adsorption.

At concentrations between $1.2 \cdot 10^{-4}$ and $2 \cdot 10^{-4}M$ in aqueous solutions another wave (i_1) at -0.3 to -0.4 V appears (Fig. 1). The sum ($i_a + i_1$) in this concentration range is a linear function of concentration of I (Fig. 2). The half-wave

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* The wave of carbon disulphide formed in the acid cleavage can be used for kinetic studies in addition to the decrease in the anodic wave[9].

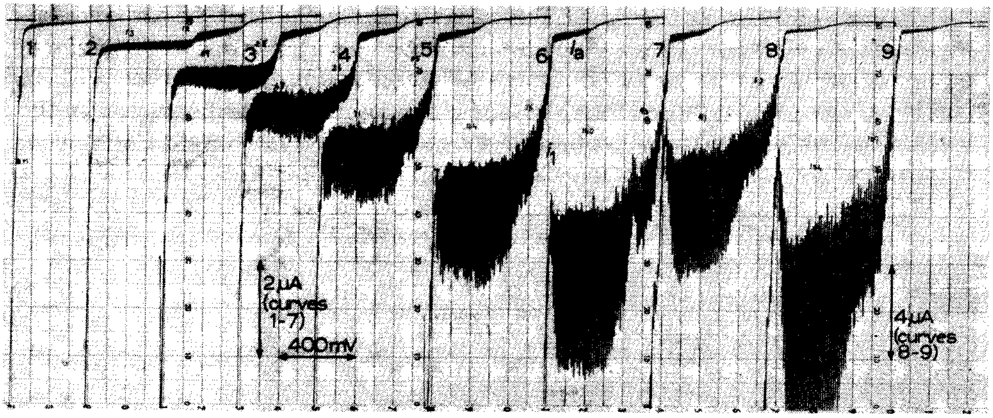


Fig. 1. The effect of concentration on the waves of sodium diethyldithiocarbamate. Borate buffer pH 9.2; concentration of diethyldithiocarbamate: (1) 0; (2) 2.0; (3) 3.9; (4) 5.7; (5) 7.4; (6) 9.1; (7) 10.7; (8) 12.0; (9) 16.7 ($\cdot 10^{-4}$ *M*). Curves recorded from − 1.0 V towards more positive potentials *vs.* S.C.E., 100 mV/absc., *h* = 68 cm.

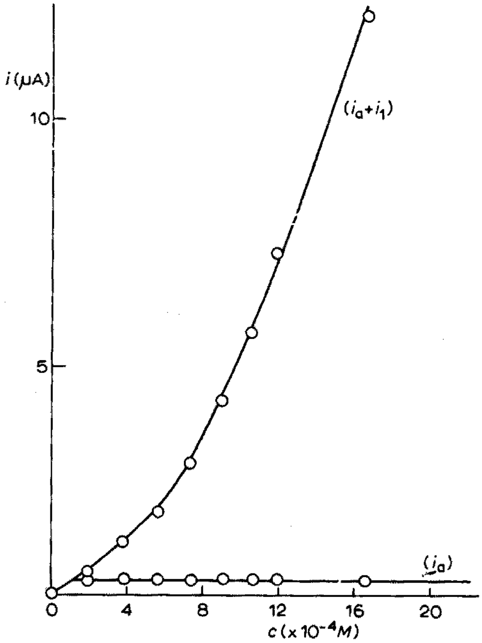


Fig. 2. The dependence of the height of the waves of sodium diethyldithiocarbamate on its concentration in a borate buffer, pH 9.2. (Sensitivity 10 μA. i_a measured at −0.5 V; i_a+i_1 measured at 0.0 V.)

potentials of waves i_a and i_1 are practically pH-independent between pH 5.5 and 11.9 which is in agreement with the findings of STRICKS AND CHAKRAVARTI[7] but in disagreement with the statement by SARTORI AND CALZOLARI[4].

At concentrations of I above $2 \cdot 10^{-4} M$, the anodic current tends to increase at about 0.0 V, but then shows a decrease at about +0.2 V (Fig. 1). The observed curves have a shape analogous in principle to that reported by STRICKS AND CHAKRAVARTI[7], but show (which these authors[7] did not mention) an irregularity of the current oscillations in the potential region between −0.4 V and +0.2 V. When the potential was kept constant inside this region, the current changed erratically with time (Fig. 3). This behaviour was not caused by a blockage of the capillary or contamination of the orifice. This was demonstrated by the fact that after the potential was reset to more negative values, the capillary immediately functioned properly and the oscillations were regular. Moreover, the *i–t* curves recorded at −0.04 V (Fig. 4) show an almost periodic, but irregular decrease and increase in current. All these observations indicate the presence of a heterogeneous process. The irregular increases in current can be explained, for example, by the formation of a rigid layer of the electrolysis product at the electrode surface, which bursts when the film reaches a certain thickness and when the mercury drop expands. The particles of the burst layer are carried off the surface and cause stirring of the solution: this brings more dithiocarbamate I than that brought by diffusion to the electrode surface, where a new layer is built up.

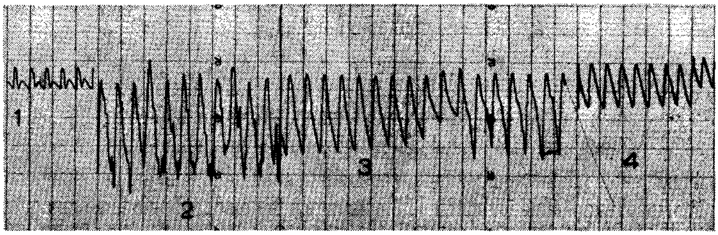


Fig. 3. The irregular oscillations of the current at various applied potentials corresponding to the limiting current. Chart speed 8 cm/min; sodium diethyldithiocarbamate $1.2 \cdot 10^{-3} M$, $0.1 M$ NaOH. (1) +0.2 V; (2) +0.1 V; (3) 0.0 V; (4) −0.1 V.

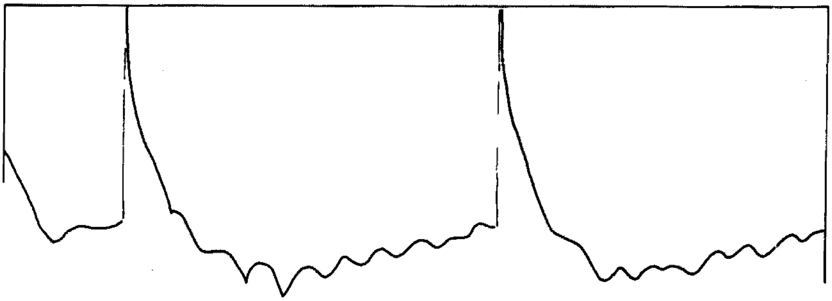


Fig. 4. The anodic *i–t* curve recorded at −0.34 V. $1.3 \cdot 10^{-3} M$ sodium diethyldithiocarbamate; borate buffer, pH 9.2.

This interpretation could explain the irregular dependence of current measured in the region between −0.4 and +0.2 V, showing at concentrations higher than $2 \cdot 10^{-4} M$ a greater increase with increasing concentration of I than corresponds to a linear relationship (Fig. 2). A non-linear dependence of the wave-heights on concentration of dimethyldithiocarbamate was reported by PASCIAK[10], but no explanation was offered.

When the wave height was measured at −0.3 V, at the foot of the wave, the current was proportional to the height of the mercury column and hence was adsorption limited. The anodic current in the region where irregularities occur (*i.e.* between

-0.2 and $+0.2$ V) showed only a slight dependence on the mercury pressure (Fig. 5). It was impossible to verify the statement[10] that the sum of the waves of a dialkyldithiocarbamate is proportional to h^3 (where h is the height of the mercury column).

The participation of adsorption in the irregularities observed was further proved by the effect of competitive adsorption of surface-active substances, such as ethanol or gelatin. In the presence of 60% ethanol, the shape of the curves was regular up to $1 \cdot 10^{-3}M$ (Fig. 6). No irregular oscillations were observed in the region of the limiting current (i_l), which was well developed, and (i_a+i_l) was strictly linearly proportional

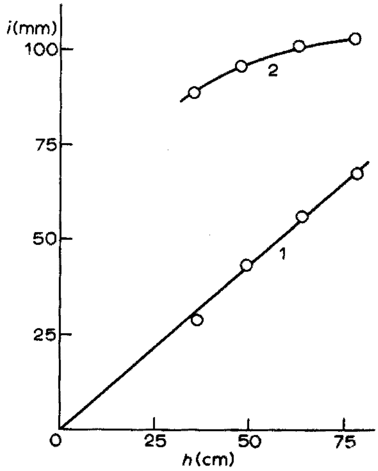


Fig. 5. The dependence of the height of the waves of sodium diethyldithiocarbamate on the height of mercury head. $1.2 \cdot 10^{-3}M$ sodium diethyldithiocarbamate; borate buffer, pH 9.2; sensitivity 20 μA. Wave height measured at (1) +0.1 V; (2) −0.3 V.

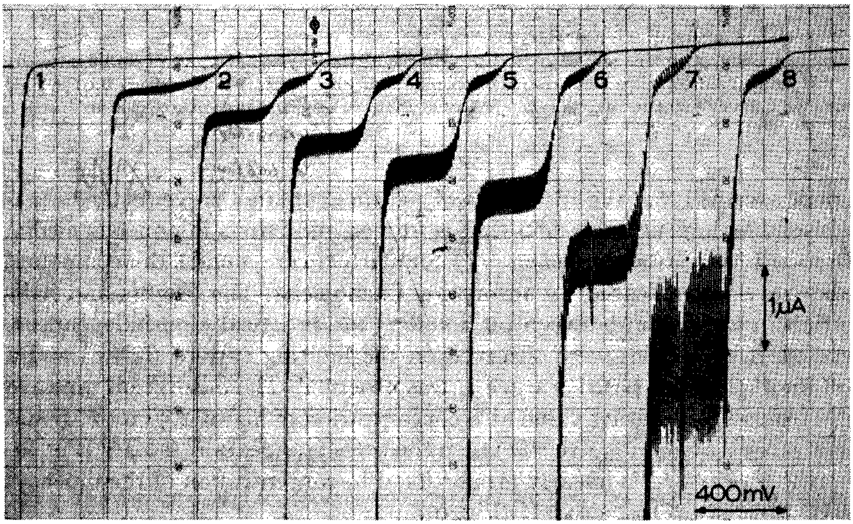


Fig. 6. The effect of concentration on the waves of sodium diethyldithiocarbamate in an ethanolic medium. 0.1 M sodium hydroxide, 60% ethanol; sodium diethyldithiocarbamate concentration: (1) 0; (2) 2.0; (3) 3.9; (4) 5.7; (5) 7.4; (6) 9.1; (7) 13.0; (8) 16.7 ($\cdot 10^{-4}M$). Curves recorded from −1.0 V towards more positive potentials, 100 mV/absc., h = 68 cm.

to the concentration of I. In 60% ethanolic solutions above $1 \cdot 10^{-3}M$, similar disturbances were observed as in aqueous solutions containing more than $2 \cdot 10^{-4}M$ dithiocarbamate I.

Addition of gelatin caused the excessive anodic current in the region between −0.35 V and +0.0 V (in 0.1 *M* sodium hydroxide) to decrease. The limiting current after addition of gelatin kept the value attained at −0.35 V, to which the current at 0.0 V practically returned in the absence of gelatin (curve 1, Fig. 7). Parallel with this observation was the fact that in the presence of 0.02% gelatin the total limiting current ($i_a + i_1$) was linearly proportional to concentration of I for up to $1 \cdot 10^{-3}$ *M* solutions.

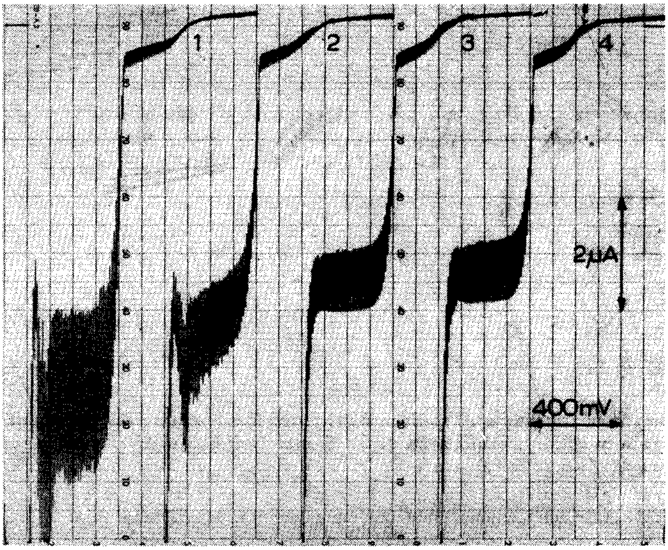


Fig. 7. The effect of gelatin on the waves of sodium diethyldithiocarbamate. 0.1 *M* sodium hydroxide, $1 \cdot 10^{-3}M$ sodium diethyldithiocarbamate, concentration of gelatin: (1) 0; (2) 0.01%; (3) 0.02%; (4) 0.04%. Curves recorded from −1.0 V towards more positive potentials, 100 mV/absc., h = 40 cm.

It can be assumed that the adsorption of gelatin or ethanol prevents the formation of the insoluble, impenetrable film that is formed and bursts in aqueous media.

Potassium dibenzyldithiocarbamate (II). Similarly to compound I, this compound shows anodic waves complicated by adsorption phenomena. The heights and half-wave potentials in the region between pH 6 and 13 are practically pH-independent. Nevertheless, no irregularities were observed on the limiting current ($i_a + i_1$) and a formation of another, more positive wave i_2 was observed. The adsorption prewave i_a at −0.7 V reaches its limiting value at a concentration of about $1.5 \cdot 10^{-4}$ *M*, and the wave i_1 at −0.5 V at about $5 \cdot 10^{-4}M$; then the wave i_2 appears at +0.1 V (Fig. 8). The total height ($i_a + i_1 + i_2$) is linearly proportional to concentration of the dibenzyl derivative (II) at least up to $1 \cdot 10^{-3}M$ (Fig. 9).

Number of electrons transferred and controlled-potential electrolysis

Comparison of waves of $2 \cdot 10^{-4}M$ solutions of compound I in a borate buffer

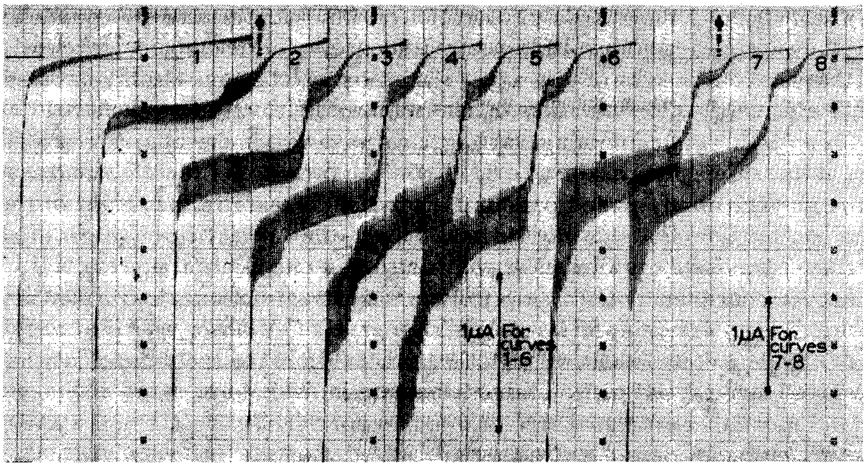
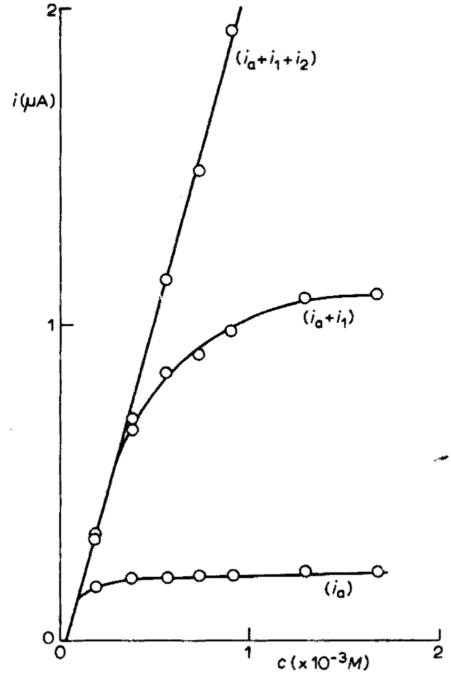


Fig. 8. The effect of concentration on the waves of potassium dibenzyldithiocarbamate. Borate buffer, pH 9.2, potassium dibenzyldithiocarbamate concentration: (1) 0; (2) 2.0; (3) 3.9; (4) 5.8; (5) 7.4; (6) 9.1; (7) 13.0; (8) 16.7 ($\cdot 10^{-4}$ *M*). Curves recorded from −1.0 V towards more positive potentials, 100 mV/absc., *h* = 68 cm.



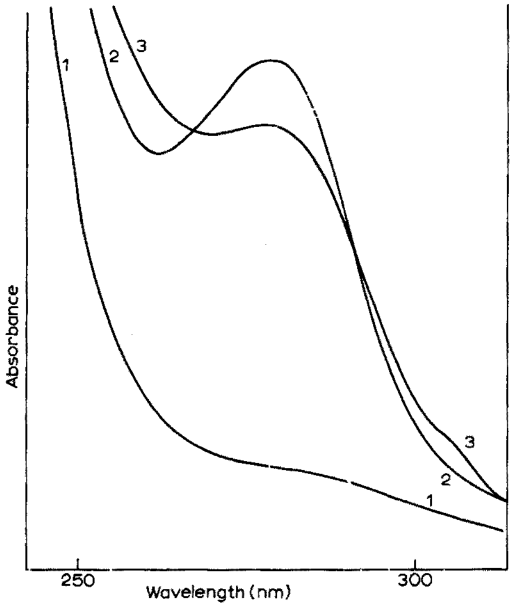


Fig. 9. The dependence of the wave-heights on concentration of potassium dibenzyldithiocarbamate in borate buffer, pH 9.2.

Fig. 10. The identification of the product of controlled-potential electrolysis of sodium diethyldithiocarbamate. U.V. spectra (1) $CHCl_3$, (2) mercury(II) diethyldithiocarbamate in $CHCl_3$, (3) $CHCl_3$ extract of electrolysed solution.

(pH 9.2) (which are not complicated by adsorption effects) with the waves of equimolar solutions of benzophenone, nitrobenzene and monoalkyldithiocarbamates clearly indicates that the total height of waves ($i_a + i_1$) corresponds to a one-electron process.

Millicoulometric determination of the number of electrons transferred (n) in $5 \cdot 10^{-4} M$ solutions of I containing 0.01% gelatin gave varying results, represented by a series of measurements: $n = 0.87$; 0.87; 0.86. The presence of metallic mercury, even in the absence of an applied potential, caused a decrease in the height of the anodic waves with time that was not corrected for in the calculation of values of n. The experimental evidence nevertheless points also to a one-electron process.

When the controlled-potential electrolysis was carried out for 12 h with mercury drops falling through a chloroform layer, this layer gave a U.V. absorption peak at 275 nm (Fig. 10). This peak was identical with the peak shown in the spectrum of synthetically prepared mercury(II) diethyldithiocarbamate in chloroform.

A.C. polarography and Kalousek commutator

The diethyldithiocarbamate gave 3 peaks on a.c. curves (Fig. 11). Peak 1 is observed in the potential region in which wave i_a is observed, peak 3 in the region of wave i_1 and peak 2 has no corresponding wave on the d.c. curve. The comparison of the a.c. curve in the presence and absence of the dithiocarbamate in the supporting electrolyte indicates that compound I is adsorbed from the threshold of wave i_a at -0.64 V to $+0.24$ V (where the decrease in current in d.c. at higher concentrations of I is observed, Fig. 1).

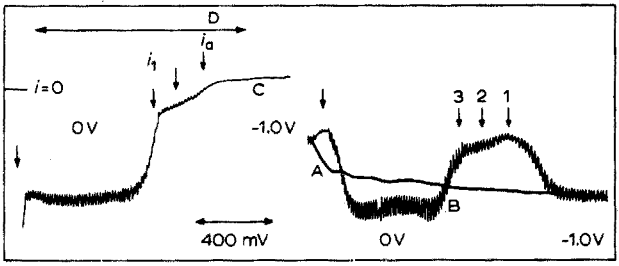


Fig. 11. A comparison of the d.c. and a.c. polarographic waves of sodium diethyldithiocarbamate. Phosphate buffer, pH 6.9; $5 \cdot 10^{-4} M$ sodium diethyldithiocarbamate. (A) and (B) a.c., (C) d.c. polarographic curve, (D) extent of absorption. (A) Supporting electrolyte, (B) and (C) dithiocarbamate solution. (1–3) peaks on a.c. curve; (i_a,i_1) d.c. waves; arrows show corresponding potentials. Curves recorded from +0.3 V to more negative potentials, 200 mV/absc., h = 68 cm.

In a solution containing $2 \cdot 10^{-4} M$ dithiocarbamate, peak 1 was twice as high as peak 3. With increasing concentration, peak 3 increased whereas peak 1 became only a little higher. This agrees with the assignment of peak 1 to the adsorption pre-wave i_a which above $2 \cdot 10^{-4} M$ also does not increase with the concentration of I. At concentrations above $5 \cdot 10^{-4} M$, the a.c. curves show no irregularities which would correspond to the anomalous behaviour shown on the d.c. curves.

When the commutator method of KALOUSEK[15,16] with rectangular voltage polarization was used, and the auxiliary potential was chosen in the potential region of the limiting current of wave i_1, a cathodic current increased in the potential region of the adsorption pre-wave i_a. To prevent complications solutions, $2 \cdot 10^{-4} M$ in 0.1 M sodium hydroxide were studied.

Reactions with metal ions

Addition of cadmium(II) to solutions of diethyldithiocarbamate (I) in 0.1 *M* sodium hydroxide resulted in a decrease of the anodic wave of I, accompanied by the formation of a white precipitate. The anodic wave disappeared when the ratio of Cd: dithiocarbamate was 1:2, hence the formation of a compound Cd(dithiocarbamate)$_2$ is assumed.

Similarly, addition of mercury(II) resulted in a decrease of the anodic wave of I and the formation of a white precipitate with a stoichiometry corresponding to Hg-(dithiocarbamate)$_2$. Polarographic curves were complicated presumably because the reaction was slow and unreacted mercury(II) ions caused a small increase in a cathodic current. The possibility of a redox reaction cannot be excluded.

The addition of lead(II) in 0.1 *M* sodium hydroxide resulted in a decrease of the anodic wave of I, which was reduced to zero when the ratio of Pb^{2+}: dithiocarbamate was 1:2. A cathodic wave at −0.80 V reaching its maximum height at the same stoichiometric ratio may be due to a partially soluble complex. The complicated behaviour was not examined further.

DISCUSSION

The one-electron anodic process observed for dialkyldithiocarbamates follows the scheme (A), (B):

$$\underbrace{R_2NCSS^-}_{H^+} \xrightleftharpoons[pK_1]{} R_2NCSS^- + H^+ \tag{A}$$

$$R_2NCSS^- + Hg^0 \rightleftharpoons R_2NCSSHg + e \tag{B}$$

The value of pK_1 has been shown[9] to be less than 4; hence above pH 6, the half-wave potentials were pH-independent, because equilibrium (A) was shifted to the right. The reversibility proved by logarithmic analysis and comparison with waves of mercury(II) salts[7] was confirmed by means of the commutator. The results of controlled-potential electrolysis indicate that the primary electrolysis product is quickly transformed to (R$_2$NCSS)$_2$ Hg(II). STRICKS AND CHAKRAVARTI[7], based on their observation of waves of the mercury(II) salts, suggested that the consecutive process is a rapid decomposition according to scheme (C):

$$2\ R_2NCSSHg \rightarrow (R_2NCSS)_2Hg \downarrow + Hg^0 \tag{C}$$

The irregular behaviour of the waves of diethyldithiocarbamate in the region from −0.4 V to +0.2 V is interpreted as the formation of an adsorption layer which differs in the orientation of the molecules at the surface, in crystallographic and physicochemical properties, or in chemical composition from the film which gives rise to the pre-wave i_a. The film breaks down regularly and is rebuilt, as was shown by the shape of the i–t curves. It is notable that these fluctuations of current are observed rather in the latter two-thirds of the drop-time. At the beginning of the drop-life the change in the area of the surface of the mercury drop is most pronounced, but at this stage the film of electrolysis products has not built up. The breaking of the film with resulting streaming of the solution[7] is one of the reasons for deviations from linear concentration dependence (Fig. 2). The other is that the recording instrument cannot follow the rapid changes in current and the recorded current does not correspond to the mean value. Formation of the breakable film can be prevented or delayed by addition of surface-active agents such as gelatin or ethanol (in high concentration) which are preferentially adsorbed.

These irregularities were not observed for the dibenzyl derivative II, which therefore can be assumed not to form such breakable films. On the other hand, dibenzyldithiocarbamate resembles many other sulphur compounds[17–20] in the formation of a current i_1 limiting at concentrations about $5 \cdot 10^{-4}\,M$ and in the formation of a wave i_2 at more positive potentials. Whereas wave i_a corresponds to a surface coverage in which the mercury compound formed covers an area of 50–100 Å^2 (depending on the structure of the compound formed), the limiting current of wave i_1 corresponds to a coverage of 5–10 Å^2 per adsorbed molecule. Apart from the possibility of formation of a mono- and a multilayer, it is possible to assume that between -0.7 V and -0.5 V the mercury compound molecules lie flat on the surface whereas between -0.5 V and $+0.1$ V, they are oriented perpendicularly and are attached only by the reactive grouping to the metallic surface. The occurrence of wave i_2 can be interpreted by the impenetrability of the film formed between -0.5 V and $+0.1$ V to further electrode process. Only when the adsorbate is desorbed at $+0.1$ V can the limiting current increase to reach the diffusion-controlled value. The properties of the adsorbate formed by the dibenzyl derivative II, in particular its mechanical stability, seem to differ from those of the adsorbate formed by compound I.

The a.c. polarographic results also indicate the adsorption of the products of the anodic electrode processes over a broad potential range. The absence of irregularities for the diethyl derivative seems to indicate that in the alternating electrical field, the conditions are unsuitable for the formation of the breakable film.

When the polarographic behaviour of dialkyldithiocarbamates is compared with that of monoalkyldithiocarbamates[13], the first, one-electron process shows a similarity. For both groups of compounds, wave i_1 is accompanied by an adsorption pre-wave and has other common properties.

On the other hand, monoalkyl derivatives give a further step, corresponding to a two-electron process, which is absent from the waves of the dialkyl compounds. The waves of the dialkyl compounds are complicated by formation of adsorbed layers, which show a limiting value at a concentration of about $5 \cdot 10^{-4}M$; this is shown by monoalkyl compounds only in strongly alkaline media.

The differences in the behaviour of mono- and dialkyl compounds may be caused by the polar effects of the alkyl groups, by their steric effects and in particular by the possibility of formation of the anion $R\text{–}N{=}CSS^{2-}$, which is possible for monoalkyl- but not for dialkyldithiocarbamates. This difference would also explain the reactivity of monoalkyl derivatives in alkaline media where the dialkyl compounds are stable, in their reaction with metal ions, and the different reaction paths in the reaction with iodine[21]; the greater reactivity of dialkyl derivatives compared to monoalkyl derivatives in acidic media must be due to a difference in protonation of the dithiocarbamate ion.

It has been shown[22] that the C–N bond in the metal complexes of dithiocarbamates shows a greater double bond character than in the anion. The loss of a proton from the metal complex of monoalkyldithiocarbamates enables a further bond to be formed to the divalent metal, and results in the formation of a 1:1 complex. An increase in the oxidation state of mercury in the 1:1 complex and formation of such complexes for dialkyldithiocarbamates is improbable, as these compounds cannot lose a proton and the complex would be positively charged.

The formation of a compound in which dialkyldithiocarbamate reacts with metal ion in stoichiometric ratio corresponding to the oxidation state of the metal is also found in the structures of zinc and iron compounds.

Analytical applications

Analysis of dialkyldithiocarbamates. Add the sample to 0.1 M sodium hydroxide solution containing 60% ethanol (or use an aqueous solution containing 0.02% gelatin in place of the ethanol) so that the final concentration of dithiocarbamate is between $5 \cdot 10^{-5} M$ and $8 \cdot 10^{-4} M$. Record the polarographic curve, measure the total wave-height and evaluate using a calibration curve; when higher sensitivity is requested, cathodic stripping[23,24] can be used.

Mixtures of monoalkyldithiocarbamates and dialkyldithiocarbamates. To determine a simple monoalkyldithiocarbamate in the presence of a simple dialkyldithiocarbamate, transfer the sample to a buffer solution of pH 3.5–5. Under these conditions dialkyl derivatives decompose rapidly, whereas the monoalkyldithiocarbamates decompose relatively slowly. Record the anodic wave 20–30 min after preparation of the reaction mixture. The wave height is proportional to the concentration of monoalkyldithiocarbamate.

The determine a simple dialkyldithiocarbamate in the presence of a simple monoalkyldithiocarbamate, heat the sample to 70° for 2–3 h in 2 M sodium hydroxide solution. Under these conditions monoalkyldithiocarbamates decompose and dialkyl derivatives remain practically unchanged. Purge the reaction mixture with oxygen-free nitrogen to prevent oxidation and to remove the isothiocyanate formed in the cleavage of monoalkyldithiocarbamate (which can produce electroactive monothiocarbamate). Record the anodic wave in the cooled mixture. The wave height gives the dialkyldithiocarbamate concentration, but it is preferable to prepare a calibration curve using the same procedure.

The authors thank Professor R. BELCHER for his interest and encouragement and to Dr. I. SMOLER for recording the *i–t* curves. D.J.H. also thanks Professor M. STACEY for the provision of a research grant; P.Z. thanks the Science Research Council for a Senior Visiting Fellowship.

SUMMARY

Dialkyldithiocarbamates give only a one-electron anodic wave. The various adsorption phenomena are probably caused by varying orientation of the mercury compounds on the electrode surface; the irregular *i–t* curves recorded at -0.04 V and the anomalous behaviour of the anodic current between $+0.2$ V and -0.4 V can be interpreted as the behaviour of an adsorbed film at the electrode. Analytical measurements are best made in 60% ethanolic 0.1 M sodium hydroxide media at concentrations of about 10^{-5} M dialkyldithiocarbamate; a method is given for the analysis of the monoalkyl and dialkyl compounds in mixtures.

RÉSUMÉ

Les dialkyldithiocarbamates ne donnent qu'une onde anodique à un électron. Les divers phénomènes d'adsorption sont probablement dus à une orientation variable des composés mercuriques à la surface de l'électrode. Les courbes irrégulières i–t enregistrées à -0.04 V et le comportement anormal du courant anodique entre $+0.2$ V et -0.4 V peuvent être attribués à la formation d'un film adsorbé sur l'électrode. Les mesures analytiques doivent être faites de préférence en milieu à 60% d'hydroxyde de sodium 0.1 M dans l'alcool et des concentrations environ 10^{-5} M de diéthyldithiocarbamates. Une méthode est proposée pour l'analyse des composés monalkyle et dialkyle dans des mélanges.

ZUSAMMENFASSUNG

Dialkyldithiocarbamate geben nur eine anodische Einelektronen-Stufe. Die verschiedenartigen Adsorptionsphänomena werden wahrscheinlich durch wechselnde Orientierung der Quecksilberverbindungen auf der Elektrodenoberfläche verursacht. Die irregulären i–t-Kurven, die bei -0.04 V aufgezeichnet werden, und das anormale Verhalten des anodischen Stroms zwischen $+0.2$ V und -0.4 V können durch das Verhalten eines adsorbierten Films auf der Elektrode gedeutet werden. Analytische Messungen werden am besten in 60%igem äthanolischen 0.1 M Natriumhydroxid bei Konzentrationen von etwa 10^{-5} M Dialkyldithiocarbamat durchgeführt. Es wird eine Methode für die Analyse der Monoalkyl- und Dialkylverbindungen in Mischungen angegeben.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

PART XIV*. ANODIC WAVES OF ETHYLENE-1,2-BISDITHIOCARBAMATE AND REACTIONS WITH HEAVY METALS

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(Received September 26th, 1967)

The polarographic behaviour of compounds containing two identical electroactive groups[1,2] usually resembles the behaviour of a similar compound bearing only one of the groups but may be different if the mutual interaction of the groups is strong. When the behaviours are similar, the presence of the second group may slightly modify the behaviour of the first group and act as a substituent, or the two groups may react simultaneously with the electrode in the same manner.

For ethylene-1,2-bisdithiocarbamate, which bears two carbamate groups, the presence of measurable waves in 0.2 M sodium hydroxide has been reported[3,4], but no attempt was made to interpret the course of the electrode process. In the present paper it is shown that the two dithiocarbamate groups (at least at lower pH values) are actually independent and react simultaneously with the electrode surface. The behaviour of this ethylenediamine derivative resembles to some extent that of simple monoalkyldithiocarbamates[5]. The considerably more pronounced adsorption phenomena cause the curves to be more complicated and ill-developed.

In connection with both the interpretation of mercury compound formation at the surface of the electrode and of the study of the metal compounds derived from ethylene-1,2-bisdithiocarbamate used as pesticides, the polarographic method was used to investigate the reaction of this dithiocarbamate with some metal ions in aqueous solutions. Although the 1:1 M^{2+}: ethylenebisdithiocarbamate compounds are well known, there has been little mention of other complexes formed by ethylene-1,2-bisdithiocarbamate. It has been stated[6,7] only that the manganese derivative may be reacted with a metal salt to give a further compound.

The present study was restricted to high pH values, because of the possibility of using exchange reactions under these conditions that would allow the analysis of pesticides. Whereas at the electrode surface both groups react simultaneously, in the homogeneous reaction first one and then the other dithiocarbamate group participates.

Some results of this investigation were previously reported briefly[8].

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[*] Part XIII: *Anal. Chim. Acta*, 41 (1968) 51.
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EXPERIMENTAL

Apparatus

The polarograph, Kalousek vessel, capillary, pH meter and spectrophotometer were the same as described previously[5].

Chemicals

Disodium ethylene-1,2-bisdithiocarbamate was crystallized from a solution of commercial NABAM in industrial methylated spirit (Robinson Bros. Ltd., West Bromwich). Ether was added to precipitate the dithiocarbamate, which was filtered off, and recrystallised twice by dissolving in ethanol and precipitating with ether. The product was a hexahydrate (m.p. 82°).

Pure manganese and zinc ethylene-1,2-bisdithiocarbamates were prepared by adding solutions of manganese or zinc salts to a solution of disodium ethylene-1,2-bisdithiocarbamate. The precipitate was filtered off and dried over silica gel.

All reagents were AnalaR grade.

Solutions

0.01 *M* stock solutions of disodium ethylene-1,2-bisdithiocarbamate in distilled water were unstable, turning pink after 4–5 h. Stock solutions were therefore prepared fresh before each experiment.

Experimental techniques

Polarographic studies, and examination of the reactions with metal ions were carried out as described previously[5].

RESULTS

Polarographic behaviour of disodium ethylene-1,2-bisdithiocarbamate

The polarographic curves of ethylene-1,2-bisdithiocarbamate (I) are very complicated (Fig. 1); only some of their characteristic features can be discussed. Below pH 10, an adsorption pre-wave i_a is present which limits at a concentration of about $5 \cdot 10^{-5}$ *M*. This wave is followed at more positive potentials by wave i_1, reaching the limiting height at concentrations of about $2.5 \cdot 10^{-4}$ *M*. The shape of this wave is almost discontinuous at the negative threshold, as predicted for waves of insoluble mercury salts[9]. In 0.1 *M* sulphuric acid this wave is accompanied by a wave i_1' (which probably corresponds to the same type of process as that occurring with wave i_1, but in the presence of an adsorbate) and by wave i_2 at positive potentials. Shifts of half-wave potentials of waves i_a, i_1 and i_2 (Fig. 2) were measured at lower concentrations of dithiocarbamate I ($2 \cdot 10^{-4}$ *M*).

At higher pH values, further adsorption processes affect the wave shape (Fig. 1), causing, at pH 6–10 in the potential range between −0.3 V and +0.2 V, a continuous increase of current. Nevertheless, even if the limiting current is not developed, the total limiting current at +0.2 V is a linear function of concentration. In 0.1 *M* sodium hydroxide solution the small wave i_a is overlapped by the wave i_A, limiting at about $3 \cdot 10^{-4}$ *M*, followed by wave i_B limiting at $8 \cdot 10^{-4}$ *M*. At more negative potentials a region of continuously increasing current (between −0.4 V and −0.1 V)

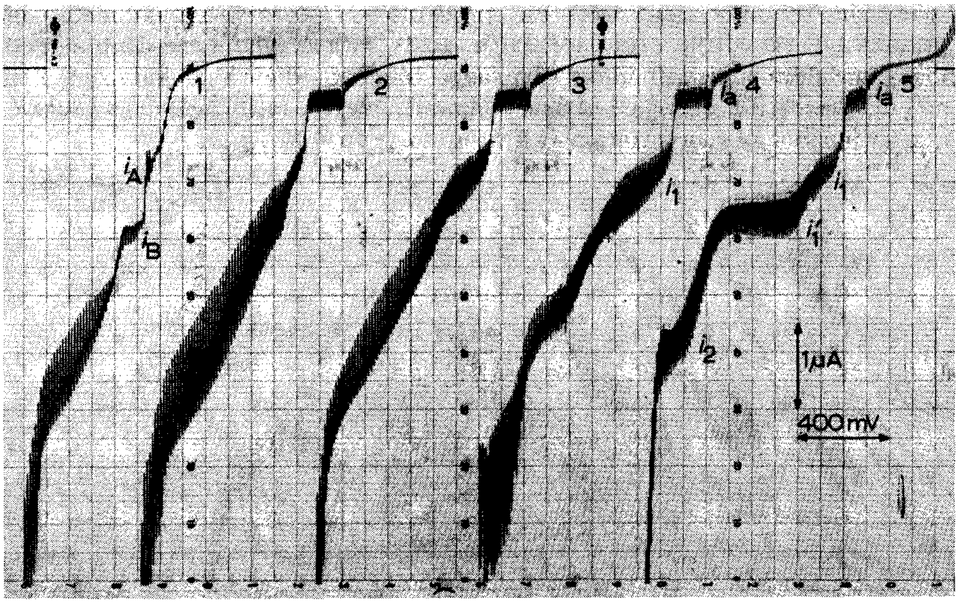


Fig. 1. The anodic waves of disodium ethylene-1,2-bisdithiocarbamate in various supporting electrolytes. (1) 0.1 *M* NaOH; (2) Borate buffer (pH 9.2); (3) Phosphate buffer (pH 6.9); (4) Acetate buffer (pH 4.7); (5) 0.1 *M* H_2SO_4. Disodium ethylene-1,2-bisdithiocarbamate, $5 \cdot 10^{-4}$ *M*. Curves recorded from -1.0 V towards more positive potentials, S.C.E., 100 mV/absc., $h = 68$ cm.

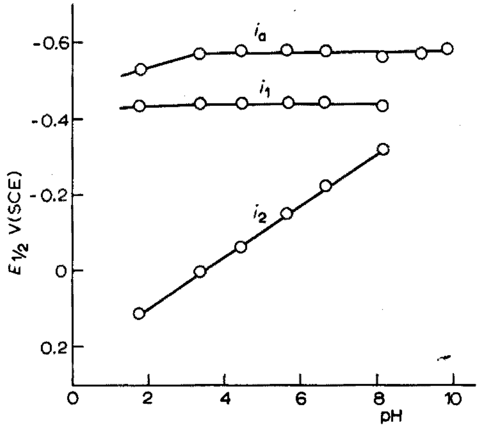


Fig. 2. The pH dependence of the half-wave potentials of the waves of disodium ethylene-1,2-bisdithiocarbamate, $2 \cdot 10^{-4}$ *M*. Britton–Robinson buffers, S.C.E.

occurs and at concentrations above $5 \cdot 10^{-4} M$ another discontinuous wave at -0.07 V (not shown in Fig. 1) appears. The total limiting current at 0.00 V is linearly proportional to concentration.

Dependence on mercury pressure confirmed that at a concentration of $5 \cdot 10^{-4}$ *M* waves i_a and i_1 are adsorption-controlled, whereas the total limiting current at $+0.2$ V (at pH 6.8) is diffusion-controlled.

Addition of ethanol or dimethylformamide improved the shape of the waves by reducing the adsorption effects (Fig. 3); addition of solvents, such as dimethylsulphoxide and acetonitrile, or surface-active agents, such as gelatin and dextran, gave no worthwhile improvement in the wave shape. In 0.1 M sodium hydroxide containing 90% of ethanol (Fig. 4) or 50% of dimethylformamide, the easily measured wave was a linear function of concentration at least up to $5 \cdot 10^{-4}$ M.

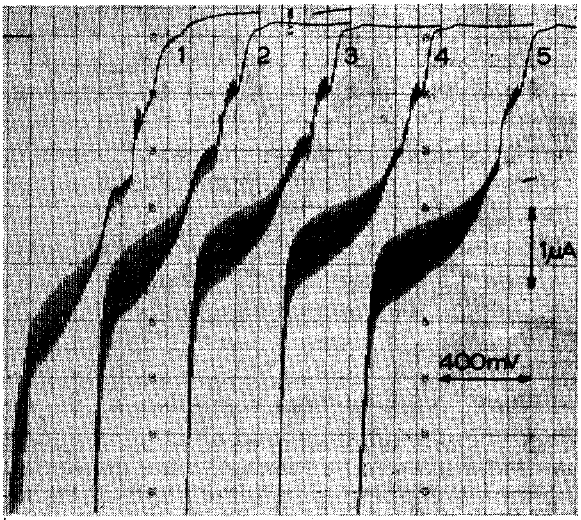


Fig. 3. The effect of ethanol on the waves of disodium ethylene-1,2-bisdithiocarbamate ($5 \cdot 10^{-4}$ M). 0.2 M NaOH (Curve 5, 0.01 M NaOH), ethanol: (1) 0; (2) 30; (3) 50; (4) 80; (5) 99%. Curves recorded from −1.0 V towards more positive potentials, 100 mV/absc., S.C.E., h = 68 cm.

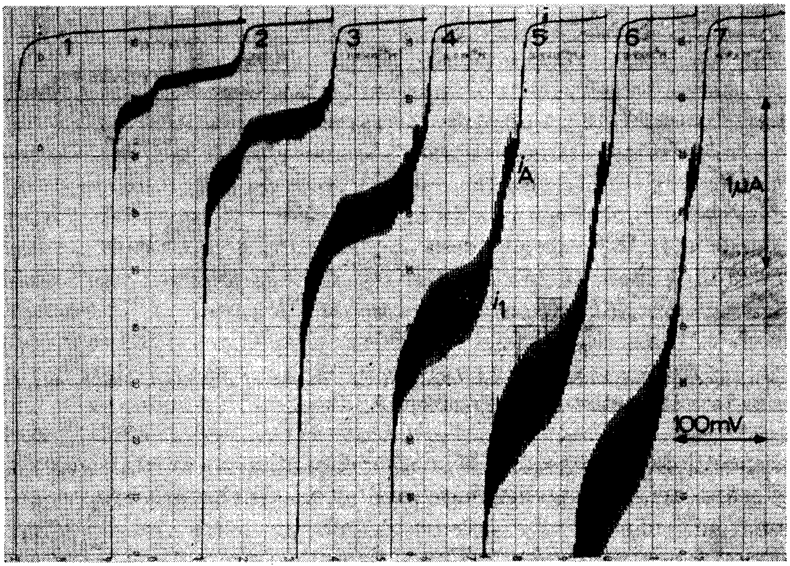


Fig. 4. The effect of concentration on the height of the waves of disodium ethylene-1,2-bisdithiocarbamate in a 90% ethanolic medium, 0.1 M in NaOH. Disodium ethylene-1,2-bisdithiocarbamate: (1) 0; (2) 0.5; (3) 1.0; (4) 2.0; (5) 2.9; (6) 3.8; (7) 4.8 ($\cdot 10^{-4}$ M). Curves recorded from −1.0 V towards more positive potentials, 100 mV/absc., S.C.E., h = 68 cm.

Comparison of wave-heights (Fig. 5) indicates that the ratio of total wave-heights at $4.9 \cdot 10^{-4}$ M is 1.0 : 1.75 : 3.55 for diethyl : n-butyl : ethylene-1,2-bisdithiocarbamate and at $7.4 \cdot 10^{-4} M$ the ratio is 1.0 : 1.84 : 3.55. The wave-height of the bisdithiocarbamate was thus almost twice that of a monoalkyldithiocarbamate.

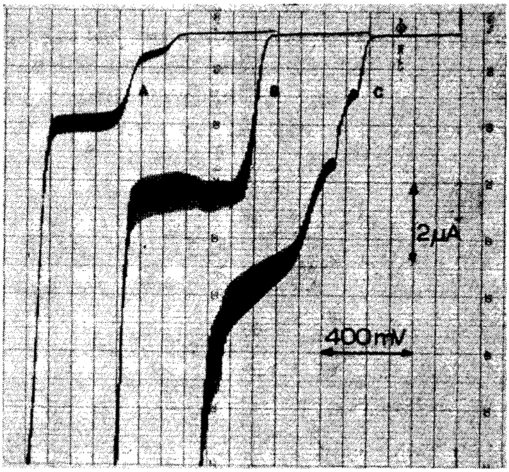


Fig. 5. Comparison of the height of the waves of typical mono- and dialkyldithiocarbamates with the height of the waves of disodium ethylene-1,2-bisdithiocarbamate. (A) Sodium diethyldithiocarbamate. (B) Sodium n-butyldithiocarbamate. (C) Disodium ethylene-1,2-bisdithiocarbamate. 60% EtOH, 0.1 M NaOH, dithiocarbamate $8.0 \cdot 10^{-4}$ M. Curves recorded from −1.0 V towards more positive potentials, 100 mV/absc., S.C.E., h = 60 cm.

Reaction with heavy metals

Addition of a cadmium salt solution to a solution containing disodium ethylene-1,2-bisdithiocarbamate in aqueous 0.1 M sodium hydroxide resulted in the formation of a white precipitate, a decrease of the anodic wave and an increase of a cathodic wave at −1.6 V (Fig. 6). This cathodic wave reached its maximum height when the ratio of Cd^{2+}: dithiocarbamate reached 1:1 (Fig. 7). With increasing excess of cadmium ions the precipitate turned pale yellow and the height of the total anodic current and of the cathodic wave at −1.6 V decreased. The anodic wave of the dithiocarbamate and the cathodic wave at −1.6 V disappeared when the mole ratio of Cd^{2+}: dithiocarbamate reached 2:1. The height of the small anodic wave at −0.15 V did not decrease with increasing excess of cadmium(II).

When, instead of titration as above, the two-fold molar excess of cadmium ions was added in one portion to the solution of dithiocarbamate in the same reaction medium, the solution developed a white turbidity and showed no anodic wave but only a very small cathodic wave at −1.6 V. After standing for 20 min, the precipitate separated out, and started to turn yellow; the cathodic wave at −1.6 V then disappeared but the anodic wave at −0.15 V increased. Within 1 h, the flocculation of the yellow precipitate was complete.

Copper(II) ions behaved similarly to cadmium, but instead of one wave, two cathodic waves appeared, at −0.71 V and −0.90 V. The total height of these waves reached its maximum when the ratio of Cu^{2+}: dithiocarbamate was 1:1. The height

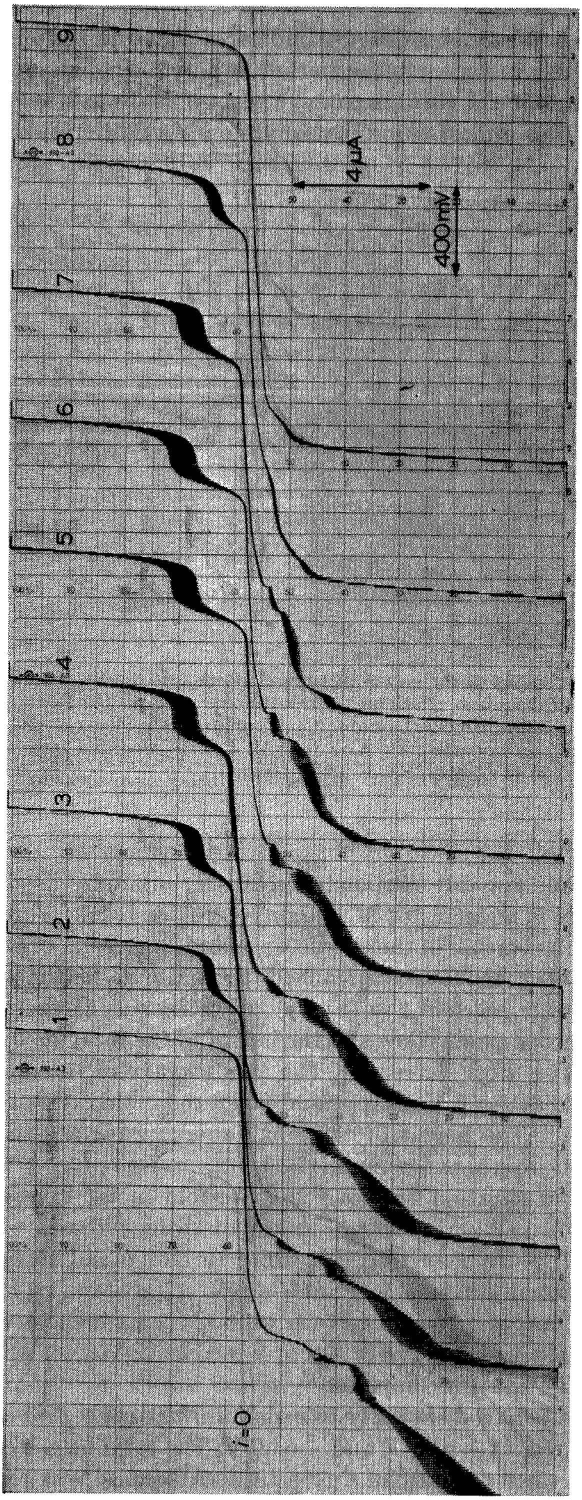
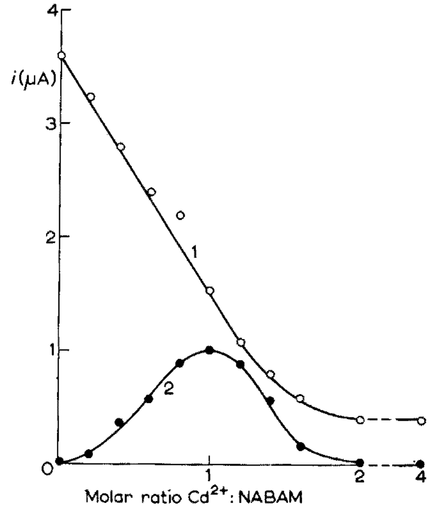


Fig. 6. Addition of cadmium to disodium ethylene-1,2-bisdithiocarbamate. 10 ml of 0.1 M NaOH, $5 \cdot 10^{-4}$ M disodium ethylene-1,2-bisdithiocarbamate. Addition of $4 \cdot 10^{-3}$ M Cd^{2+} soln. to give mole ratio of Cd^{2+}: ethylene-1,2-bisdithiocarbamate: (1) 0; (2) 0.4; (3) 0.6; (4) 0.8; (5) 1.0; (6) 1.2; (7) 1.4; (8) 1.6; (9) 2.0. Curves recorded from −2.0 V towards more positive potentials, 100 mV/absc., S.C.E., h = 40 cm.

of the cathodic and anodic waves decreased practically to zero, when the ratio of Cu^{2+}: dithiocarbamate was 1.7 : 1.

On addition of a solution of lead ions the anodic waves of dithiocarbamate I decreased and a cathodic wave at −1.63 V appeared which increased in height until the ratio of Pb^{2+}:dithiocarbamate was 1 : 1 (Fig. 8). At higher concentrations of lead ions the behaviour differed from that observed with cadmium(II) and copper(II) ions in the formation and increase of a plumbate wave at −0.7 V. The anodic waves and the cathodic wave at −1.63 V reached their minimum value when the ratio of Pb^{2+}: dithiocarbamate was about 2.2 : 1.



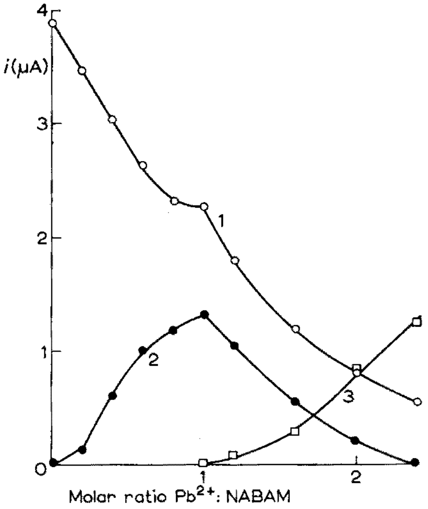


Fig. 7. Addition of cadmium to disodium ethylene-1,2-bisdithiocarbamate. (1) Total height of anodic waves; (2) height of cathodic wave. Conditions as Fig. 6.

Fig. 8. Addition of lead to disodium ethylene-1,2-bisdithiocarbamate. (1) Total height of anodic waves; (2) height of cathodic wave at −1.63 V; (3) height of cathodic wave at *c.* −0.7 V. Conditions as Fig. 6.

Addition of solutions of zinc, manganese, nickel or cobalt ions to a solution of dithiocarbamate in aqueous 0.1 *M* sodium hydroxide solution caused no decrease in the height of the anodic waves. Zinc gave a reduction wave at −1.3 V because of zincate ions; manganese, nickel and cobalt formed hydroxides or oxides. In purely aqueous solution, however, cobalt and nickel do form ethylene-1,2-bisdithiocarbamate compounds[10].

DISCUSSION

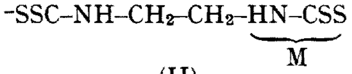
The anodic waves of disodium ethylene-1,2-bisdithiocarbamate (I) correspond to mercury compound formation. Although the complexity of the polarographic curves prevented the complete elucidation of the electrode processes taking place at the various waves, it can be concluded that in principle the processes involved are similar to those which govern the waves of simple monoalkyl- and dialkyldithiocarbamates[5,11]. The main reason for the differences is that the curves of the ethylene derivative are more affected by adsorption phenomena than the curves of simple alkyl dithiocarbamates.

An analogy with monoalkyl dithiocarbamates[5] is shown at lower concentrations ($2 \cdot 10^{-4} M$) of the ethylene derivative; below pH 9, two 2-electron processes can be observed for the latter. The shifts of the half-wave potentials of waves i_1 and i_2 with pH under these conditions (Fig. 2) resemble those for waves i_1 and i_2 of monoalkyldithiocarbamates (*cf.* Fig. 3, Part XII[5]). The fact that two 2-electron steps are observed indicates that the scheme (A)–(D) suggested previously[5] is in principle followed and that the solution of ethylene derivative $(SSC\text{–}NH\text{–}(CH_2)_2\text{–}HN\text{–}CSS)^{2-}$ of a concentration C_B behaves like a solution of a monoalkyl derivative $(R\text{–}NH\text{–}CSS)^-$ of a concentration $2C_B$. This indicates that the two carbamate groupings of the ethylene derivative I behave like separate independent reaction centres and that mercury compound formation at the electrode surface can proceed at both groups practically simultaneously, rather than in a series of consecutive processes in which first one $-NH\text{–}CSS^-$ and then the other $-NH\text{–}CSS^-$ group would react. In the latter case the presence of four more or less separated one-electron processes would be expected.

The simultaneous interaction of both $-NH\text{–}CSS^-$ groups with mercury at the electrode surface is further indicated by the adsorption phenomena. The wave i_a reached its limiting value in solutions containing about $5 \cdot 10^{-5} M$ ethylene derivative I, whereas for monoalkyl-[5] and dialkyldithiocarbamates[11] the corresponding wave i_a reached its limiting value in $1 \cdot 10^{-4} M$ solutions. Similarly, wave i_1 was observed to reach its limiting value below pH 9 in about $2.5 \cdot 10^{-4} M$ solution of I whereas the wave i_1 in dibenzyldithiocarbamate reached it at $5 \cdot 10^{-4} M$. Furthermore, the concentration limit of wave i_A in 0.1 M sodium hydroxide solutions was found at $3 \cdot 10^{-4} M$ for ethylene derivative I and $5 \cdot 10^{-4} M$ for monoalkyl derivatives[5].

At concentrations of I higher than about $2 \cdot 10^{-4} M$, further adsorption processes complicate the course of the polarographic curves. A possible explanation of the continuous increase in current at potentials more positive than about -0.3 V (Fig. 1) without the formation of a limiting current can be tentatively explained by the participation of an electrode process the rate of which increases with increasingly positive potentials (*e.g.* a mercury compound formation through the first adsorbed layer). For a better understanding a thorough investigation of i–t curves under these conditions would be necessary.

The formation of the metal compound, when the electrode is the reaction partner, where the reaction seems to take place simultaneously at both carbamate groupings, follows a different path from the reactions of the bisdithiocarbamate I with metal ions in solution, at least in alkaline media. Experimental data on the homogeneous reactions (Figs. 6–8) indicate complex formation between bivalent metal (M^{2+}) ions and dithiocarbamate I in the ratio 1:1 for cadmium(II), copper(II) and lead(II) ions. These complexes are to some extent soluble, and give rise to cathodic waves at more negative potentials than those of the metal ions in hydroxide media. They also give anodic waves characteristic for the dithiocarbamate grouping. This behaviour would be difficult to explain if the participation of both dithiocarbamate groupings in the interaction with a single metal ion in the 1:1 complex was assumed. On the other hand, if we assume that in such a complex the metal ion is bound only by one dithiocarbamate grouping (II), the free dithiocarbamate group would participate in increasing solubility and would be responsible for the interaction with mercury at the electrode and for formation of the anodic wave.



$$^{-}SSC{-}NH{-}CH_2{-}CH_2{-}\underbrace{HN{-}CSS}_{M}$$

(II)

The 1:2 complex of bisdithiocarbamate with cadmium, copper and lead, in which the ratio of the bivalent metal to dithiocarbamate group was 1:1, was apparently more stable than the analogous complexes of the simple monoalkyldithiocarbamates[5]. The situation for cadmium ions seems most straightforward; the anodic waves were reduced to zero when the ratio Cd^{2+}: bisdithiocarbamate I was 2:1. The decomposition of the 2:1 complex to form cadmium sulphide took place only slowly. The small anodic wave at -0.15 V formed under such conditions may be due to some decomposition product of the 2:1 complex.

Formation of complexes of bisdithiocarbamate I in hydroxide solutions depends on the tendency of the particular metal ion to participate in competitive reactions. Hence, manganese, nickel and cobalt form the oxides or hydroxides and zinc forms zincate, rather than react with dithiocarbamate I. For lead, when the ratio Pb^{2}: dithiocarbamate I is less than 1:1, a complex of type II is preferentially formed. When this ratio exceeds 1:1, competition occurs and both the 2:1 lead: dithiocarbamate complex and plumbate are formed, as indicated by the simultaneous decrease of the anodic wave of the dithiocarbamate and increase of the plumbate wave (Fig. 8).

ANALYTICAL APPLICATIONS

Based on the experimental evidence of the electrode processes discussed above, it is possible to suggest analytical procedures for the dithiocarbamates derived from ethylenediamine which are most frequently used as pesticides. The suggested procedure allows direct determination of dithiocarbamates in the concentration range $1 \cdot 10^{-5}M$–$5 \cdot 10^{-4}M$. This sensitivity is sufficient for analysis of commercially available preparations, but would be unsatisfactory for the determination of residues in plants without preliminary accumulation of the active component. However, the latter type of analysis is rarely required, for dithiocarbamates are harmless to animals. Hence the sensitivity of the developed procedures is generally satisfactory for all practical applications.

The methods developed could be used not only for rapid analysis of commercial products but also for studying the chemical reactions taking place in the production of these pesticides and to study the kinetics and mechanisms of the acid cleavage, used in connection with the determination of the evolved carbon disulphide, which is currently used for the analyses of ethylenebisdithiocarbamates. A polarographic kinetic study of the type used for alkyldithiocarbamates[12] would make it possible to establish logically the optimum reaction conditions for the evolution of carbon disulphide instead of the present empirical approach.

Determination of disodium ethylene-1,2-bisdithiocarbamate (NABAM)

Transfer the sample to a solution of 0.1 *M* sodium hydroxide in 90% ethanol so that the final concentration of the dithiocarbamate is between $1 \cdot 10^{-5} M$ and $5 \cdot 10^{-4} M$. For higher concentrations of the dithiocarbamate I, use an aqueous solution of 0.1 *M* sodium hydroxide. Record the anodic waves, measure the total wave-height (Fig. 4) and evaluate by means of a calibration curve constructed from polarographic curves recorded in the same media as the sample.

Determination of zinc ethylene-1,2-bisdithiocarbamate (ZINEB)

The use of dilute sodium hydroxide has been suggested[3,4] to convert ZINEB to zincate ions and ethylene-1,2-bisdithiocarbamate ions, the anodic waves of which can be used for analysis. We have shown that the reaction is quantitative in 0.1 *M*, 0.5 *M* and 1.0 *M* sodium hydroxide solutions. However, the U.V. spectra of these solutions after 24 h showed that decomposition had occurred in the more dilute hydroxide solutions and hence 1.0 *M* sodium hydroxide was preferable.

For analysis of preparations, transfer the sample to a solution of 1.0 *M* sodium hydroxide, record and measure the anodic wave and evaluate by means of a calibration curve prepared either by using a pure sample of disodium salt of I or a standard sample of ZINEB.

If analyses for residual ZINEB in crops etc. are required, extract the dithiocarbamate from the plant material (about 100 g) by homogenizing with 10 ml of 1 *M* sodium hydroxide. Record and measure the anodic wave and evaluate by means of calibration curve, prepared by adding standard amounts of disodium or zinc salts of the dithiocarbamate I to the plant material. Dithiocarbamate can be determined in the required range (0.3 to 3 p.p.m. of the wet weight of vegetable tissue, giving concen-

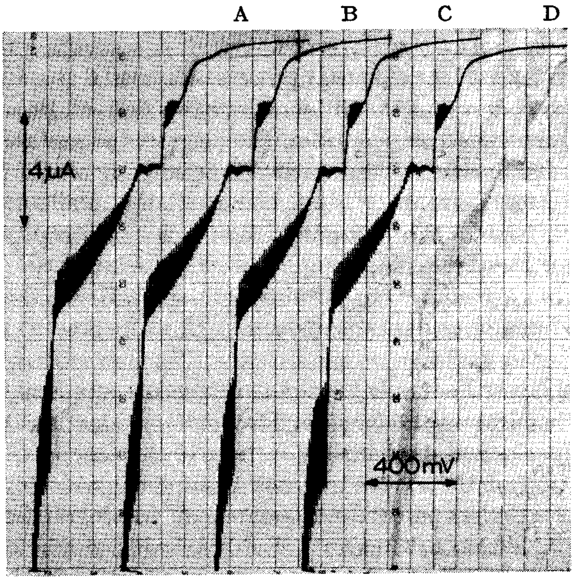


Fig. 9. Liberation of free ethylene-1,2-bisdithiocarbamate from manganese ethylene-1,2-bisdithiocarbamate. 0.1 g pure manganese ethylene-1,2-bisdithiocarbamate added to (A) 20 ml 0.1 *M* NaOH, (B) 20 ml 0.5 *M* NaOH, (C) 20 ml 0.1 *M* NaOH. After 5 min, 0.5 ml sample of each solution taken and added to 10 ml 0.1 *M* NaOH. Polarograms recorded as A, B and C respectively. (D) The theoretical equivalent amount of disodium ethylene-1,2-bisdithiocarbamate. Curves recorded from − 1.0 V towards more positive potentials, 100 mV/absc., S.C.E., *h* = 40 cm.

trations in the range $1 \cdot 10^{-4} M$ to $1 \cdot 10^{-5} M$). For greater sensitivity of measurement NANGNIOT[4] has suggested the use of hanging mercury drop.

Determination of manganese ethylene-1,2-bisdithiocarbamate (MANEB)

Although NANGNIOT[13] has observed that the determination of MANEB by polarography is difficult because of its insolubility, it was shown in the present work that the ethylene-1,2-bisdithiocarbamate ion can be liberated from MANEB by the action of sodium hydroxide, a dark-brown precipitate also being formed. The reaction yield after 5 min was practically 100% in 1.0 *M* sodium hydroxide, 98% in 0.5 *M* and 94% in 0.1 *M* sodium hydroxide (Fig. 9). Again the solution in 1.0 *M* sodium hydroxide showed the least changes in wave-height with time. The procedure is therefore the same as for ZINEB. The use of a linear calibration curve constructed by converting standard amounts of pure MANEB into ethylene-1,2-bisdithiocarbamate ion allowed determinations in the range $3 \cdot 10^{-6} M$ to $3 \cdot 10^{-4} M$; thus, when necessary, the method can be used even for residue analysis.

The authors thank Mr. A. STEVENSON and Mr. M. J. V. WAYMAN of Robinson Bros. Ltd., West Bromwich for samples of NABAM, ZINEB and MANEB, and Professor R. BELCHER for his interest and encouragement. D. J. H. also thanks Professor M. STACEY for the provision of a research grant; P.Z. thanks the Science Research Council for the provision of a Senior Visiting Fellowship.

SUMMARY

The presence of two 2-electron anodic steps on polarographic curves of ethylene-1,2-bisdithiocarbamates together with the shifts of the half-wave potentials with pH and the adsorption phenomena, indicate a simultaneous reaction of both dithiocarbamate groupings at the electrode surface. In the homogeneous alkaline solutions, cadmium(II), copper(II) and lead(II) ions form an intermediate 1:1 compound with ethylene-1,2-bisdithiocarbamate in which only one dithiocarbamate group reacts. A 1 *M* sodium hydroxide solution is most suitable for the determination of the ethylene-1,2-bisdithiocarbamate anion liberated from zinc or manganese derivatives in the analysis of pesticides ZINEB and MANEB. Waves of disodium ethylene-bisdithiocarbamates (NABAM) allow $1 \cdot 10^{-5} M$ solutions to be analysed.

RÉSUMÉ

La présence de deux vagues anodiques à 2 électrons des courbes polarographiques des éthylène-1,2-bisdithiocarbamates et leur comportement vis-à-vis du pH et des phénomènes d'adsorption indiquent une réaction simultanée des deux groupements dithiocarbamates à la surface de l'électrode. En solution alcaline, les ions cadmium(II), cuivre(II) et plomb(II) forment un composé intermédiaire 1:1 avec l'éthylène-1,2-bisdithiocarbamate dans lequel un seul groupe dithiocarbamate réagit. Une solution d'hydroxyde de sodium 1 *M* convient le mieux pour le dosage de l'anion éthylène-1,2-bisdithiocarbamate, libéré de dérivés du zinc et du manganèse, dans l'analyse des pesticides ZINEB et MANEB. Les vagues des éthylène-bisdithiocarbamates (NABAM) permettent d'analyser des solutions $1 \cdot 10^{-5} M$.

ZUSAMMENFASSUNG

Das Auftreten von zwei 2-elektronischen anodischen Schritten bei polarographischen Kurven von Aethylen-1,2-bisdithiocarbamaten zusammen mit Verschiebungen des Halbstufenpotentials in Abhängigkeit vom pH-Wert und Adsorptionserscheinungen weisen auf eine gleichzeitige Reaktion beider Dithiocarbamat-Gruppierungen an der Elektrodenoberfläche hin. In homogenen alkalischen Lösungen bilden Cd^{2+}, Cu^{2+} und Pb^{2+} ein 1:1-Zwischenprodukt mit Aethylen-1,2-bisdithiocarbamat, bei welchem nur eine Dithiocarbamatgruppe reagiert. Bei der Analyse von Pesticiden ist eine 1 *M* NaOH-Lösung am geeignetesten zur Bestimmung des Aethylen-1,2-bisdithiocarbamatanions, das durch Zink- oder Manganderivate freigesetzt wird. 10^{-5} *M* Lösungen können analysiert werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SOME VANADIUM(V) COMPLEXES AS REAGENTS FOR THE PHOTOMETRIC DETERMINATION OF ALCOHOLS

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(Received August 4th, 1967)

Vanadium 8-hydroxyquinolinate has been used for the photometric determination of alcohols[1–9], and the reaction of vanadium 8-hydroxyquinolinate with alcohols has been discussed by several authors[10–13]. It has been reported that some other vanadium complexes give rise to a red coloration in the presence of alcohols[14–18], and some of these complexes have been proposed for the detection of alcohols[16]. The formation constant of the ester of vanadium 5,7-diiodo-8-hydroxyquinolinate with cetyl alcohol has been determined photometrically in *o*-dichlorobenzene[13]. More recently, in a quantitative study on the synergetic extraction of vanadium with 8-hydroxyquinoline in the presence of alcohol[19], the present authors have estimated the formation constant of esters of vanadium 8-hydroxyquinolinate with various aliphatic alcohols. The photometric determination of alcohol is based on the following equilibrium in an organic phase:

$$ROH + VOA_2OH \rightleftharpoons VOA_2OR + H_2O \qquad (1)$$

where A and ROH denote the ligand and alcohol respectively. Unfortunately the equilibrium (1) is not much favored to the right[13,19]. Thus the formation of the ester VOA_2OR is not quantitative and the sensitivity is largely dependent on the equilibrium constant (1). This paper is devoted to a study of some vanadium complexes and corresponding esters with the emphasis on simple and sensitive methods for the photometric determination of alcohols.

Spectral characteristics of vanadium complexes and the corresponding esters

The values of the wavelengths of maximum absorbance (or of the shoulder) of various vanadium complexes and the corresponding esters are given in Table I. As can be seen from Table I, all of the esters studied possess maximum absorbance (or the shoulder) at 445–480 nm regardless of the ligands. On the other hand, the maximum absorbance (or the shoulder) of the vanadium complexes is found at different wavelengths with different ligands. When the absorbance spectra of a complex and the corresponding ester overlap, unreacted complex should preferably be stripped with sodium carbonate or dilute sodium hydroxide solution before photometry of the resulted ester. The absorbance spectrum of a vanadium 2-methyl-8-hydroxyquinolinate ester has a plateau at about 445–480 nm, while the vanadium complex itself has no noticeable absorption in the region. Therefore alcohols in organic solvents can be very conveniently determined by means of this complex without a stripping process.

Partition of vanadium complexes and their esters between the aqueous and organic phases

Of the complexes listed in Table I, the esters of vanadium complexes of 8-hydroxyquinoline, acetylacetone, maltol, tropolone and 4-isopropyltropolone can hardly be stripped with saturated sodium carbonate or dilute sodium hydroxide solution, while a significant amount of decomposition occurs with the other esters when stripped with these solutions. In the case of the vanadium complexes with maltol, acetylacetone, thenoyltrifluoroacetone, salicylaldehyde and salicylaldoxime, the corresponding esters partition favorably in the organic phase*. Thus with the latter complexes alcohols in the aqueous solution and in the organic solvents can be conveniently determined by means of a procedure involving a single partition process: only the ester produced is extractable into organic solvents and stripping process can be avoided.

TABLE I

WAVELENGTH OF MAXIMUM ABSORBANCE OF VANADIUM COMPLEXES AND THE CORRESPONDING ESTERS

Ligand	λ_{max} *of complex (nm)*	λ_{max} *of ester (nm)*
Tropolone	505	470
4-Isopropyltropolone	505	470
Maltol	490	445
8-Hydroxyquinoline	550	450–480
2-Methyl-8-hydroxyquinoline	385	450–480
Acetylacetone	—	450
Thenoyltrifluoroacetone	—	450
Salicylaldehyde	550	450–470
Salicylaldoxime	550	450–480
Kojic acid	—	430

Color development and stability of the resulted ester

Complete color development of vanadium 2-methyl-8-hydroxyquinolinate with alcohol in 1:1 benzene–chloroform mixture takes about 30 min at room temperature.

The color is stable for at least 24 h. The effect of pH on the extraction of esters with vanadium maltolate and acetylacetonate in the presence of *n*-butanol is shown in Fig. 1. The optimum pH range for the extraction of both esters is 2.4–2.5. The formation of esters is complete after *ca.* 30 min and no variation of the absorbance is observed during prolonged extraction for 30–120 min. It may be noted that the time required for the complete esterification is somewhat different for different alcohols. As expected, much time is needed for the esterification of tertiary alcohols and of alcohols with small partition coefficients between the aqueous and organic phases. For the vanadium maltolate, at pH 1.3, the extraction of the ester is at a maximum for about 10 min and prolonged extraction causes the decomposition of the ester and the oxidation of maltol by pervanadyl ion. Figure 2 shows the effects of time on the

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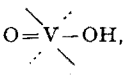
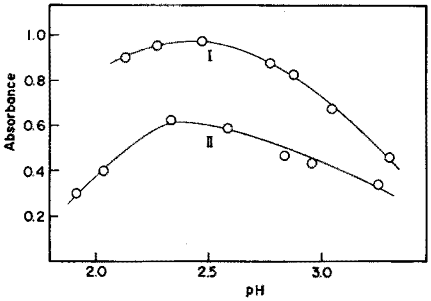
* In the extraction of vanadium with a ligand which forms a functional group  $O{=}V{-}OH$, synergy is observed in the presence of alcohol[19].

color development of vanadium with maltol in the aqueous solution. At pH 1.3, maximum absorbance is obtained immediately after mixing and the absorbance decreases on standing and finally the color almost disappears, probably because of reduction of vanadium with maltol; at pH 2.6, maximum absorbance is obtained 10 min after mixing, after which the color is stable for at least 1 h. On the other hand, the esters of vanadium maltolate and acetylacetonate are stable for at least 4 h.



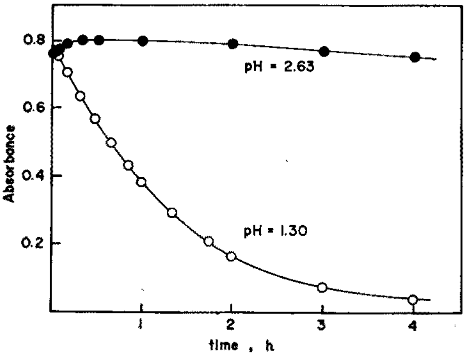


Fig. 1. Effect of pH on the extraction of ester. Extraction time: 30 min. (I) Vanadium maltolate: 25 ml of aqueous solution containing $2 \cdot 10^{-2}$ M vanadium, 10^{-2} M maltol and 6.0 mg of alcohol are shaken with equal volume of benzene. Absorbance is read at 445 nm. (II) Vanadium acetylacetonate: 25 ml of aqueous solution containing $2 \cdot 10^{-3}$ M vanadium, 10^{-1} M acetylacetone and $5 \cdot 10^{-2}$ g of alcohol are shaken with equal volume of benzene. Absorbance is read at 450 nm.

Fig. 2. Effect of time on the absorbance of vanadium maltolate. Vanadium: $2 \cdot 10^{-4}$ M; maltol: 10^{-3} M; absorbance is read at 490 nm.

Formation constant of esters

Esterification of vanadium complex in the organic phase is written as equilibrium (1). Since the concentration of water has little effect on the position of equilibrium, the formation constant of the ester may be given by the following[13]:

$$K_{est} = [VOA_2OR]/[VOA_2OH]\ [ROH] \qquad (2)$$

This constant can be determined either photometrically or by means of a method involving extraction. Details of the data treatment have been given elsewhere[19,20]. The obtained values are tabulated in Table II.

Thus, vanadium 8-hydroxyquinolinate and maltolate are both sensitive reagents for alcohol and the latter provides a convenient means for the photometric determination of alcohol without a stripping process, the unesterified complex being

TABLE II

FORMATION CONSTANT OF *n*-BUTANOL ESTERS OF VANADIUM COMPLEXES

Vanadium complex	*Solvent*[a]	*Formation constant*
8-Hydroxyquinolinate[19]	Benzene	$10^{2.97 \pm 0.10}$
2-Methyl-8-hydroxyquinolinate	Benzene–chloroform (1:1)	4 ± 2
Maltolate	Benzene	$10^{3.8 \pm 0.2}$

[a] The solvent is not anhydrous but saturated with water.

difficult to extract into the organic phase. On the other hand, though a method with vanadium 2-methyl-8-hydroxyquinolinate is not sensitive, a very simple method of alcohol determination can be established with this complex. Some procedures *without stripping* are given below; these allow the determination of alcohol in the concentra-

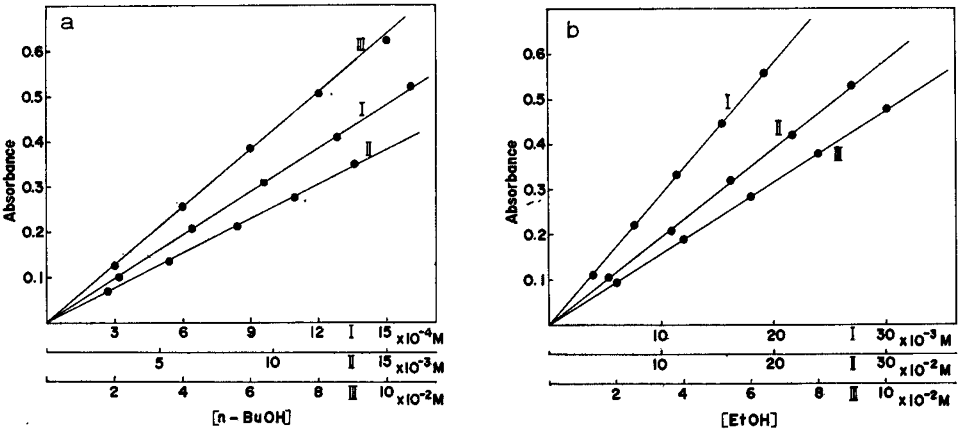


Fig. 3. Some examples of calibration curves for: (a) *n*-butanol, (b) ethanol. (I) in aq. soln. with vanadium maltolate; (II) in aq. soln. with vanadium acetylacetonate; (III) in organic solvent with vanadium 2-methyl-8-hydroxyquinolinate.

TABLE III

EFFECT OF DIFFERENT KINDS OF ALCOHOL

Alcohol	*Concn. (M)*	*Abs.*	*Concn. (M)*	*Abs.*
A. Reaction in the organic phase				
	Vanadium 8-hydroxyquinolinate		*Vanadium 2-methyl-8-hydroxyquinolinate*	
Methyl	10^{-3}	0.860	$1.01 \cdot 10^{-1}$	0.582
Ethyl	10^{-3}	0.800	$1.03 \cdot 10^{-1}$	0.476
n-Propyl	10^{-3}	0.915	$1.08 \cdot 10^{-1}$	0.532
Isopropyl			$1.08 \cdot 10^{-1}$	0.220
n-Butyl	10^{-3}	0.980	$1.01 \cdot 10^{-1}$	0.627
Isobutyl	10^{-3}	0.970	$1.01 \cdot 10^{-1}$	0.700
sec-Butyl	10^{-3}	0.470	$1.01 \cdot 10^{-1}$	0.274
tert-Butyl	10^{-3}	0.105	$1.01 \cdot 10^{-1}$	0.043
n-Amyl	10^{-3}	1.09		
n-Octyl	10^{-3}	1.11		
B. Reactions involving partition				
	Vanadium acetylacetonate		*Vanadium maltoate*	
Methyl	$1.10 \cdot 10^{-1}$	0.077	$1.34 \cdot 10^{-2}$	0.150
Ethyl	$5.40 \cdot 10^{-2}$	0.105	$6.38 \cdot 10^{-3}$	0.185
n-Propyl	$2.72 \cdot 10^{-2}$	0.227	$3.27 \cdot 10^{-3}$	0.353
Isopropyl	$2.72 \cdot 10^{-2}$	0.081	$3.26 \cdot 10^{-3}$	0.173
n-Butyl	$1.36 \cdot 10^{-2}$	0.347	$1.61 \cdot 10^{-3}$	0.519
Isobutyl	$1.36 \cdot 10^{-2}$	0.342	$1.61 \cdot 10^{-3}$	0.495
sec-Butyl	$1.36 \cdot 10^{-2}$	0.201	$1.61 \cdot 10^{-3}$	0.242
tert-Butyl	$1.36 \cdot 10^{-2}$	0.025	$1.61 \cdot 10^{-3}$	0.031

tion range of 10^{-1}–10^{-4} M (see *Recommended procedures*). Typical calibration curves are given in Figs. 3a and 3b.

Effect of kind of alcohol

Table III shows the effect of the variation of alcohols on the absorbance. When the same total concentration of isomeric butanol is used, the absorbance decreases as follows: primary > secondary > tertiary. This can be plausibly interpreted as the increase of the steric hindrance of the side chain of the alcohol, the inductive effect of the methyl group and the decrease in the partition coefficient of the isomers between the aqueous and organic phases (normal $\simeq$ iso > secondary > tertiary).

Insofar as normal alcohols are concerned, the sensitivity is roughly proportional to the partition coefficient of the alcohol in the methods involving partition (methods with acetylacetonate and maltolate); from methanol to *n*-butanol, the sensitivity increases gradually (see Table III and Ref. 19).

EXPERIMENTAL

Reagents

Saturated chloroform solution of vanadium 2-methyl-8-hydroxyquinolinate. Solution A: 466.8 mg V_2O_5 in 250 ml of 5% perchloric acid solution. Solution B: 7.97 g of 2-methyl-8-hydroxyquinoline in 500 ml of 2% perchloric acid solution. Mix 25 ml of solution A and 50 ml of solution B in a separatory funnel, adjust the pH to 4.1 with sodium acetate solution, dilute to *ca.* 250 ml with distilled water and then extract the complex with 200 ml of purified chloroform. Dehydrate the organic layer with purified anhydrous sodium sulfate.

Vanadium maltolate solution. Mix 25 ml of 10^{-2} M vanadium solution in 5% perchloric acid and 20 ml of aqueous $5 \cdot 10^{-2}$ M maltol* solution, dilute to *ca.* 80 ml with distilled water, adjust the pH to 2.45 with sodium hydroxide and finally dilute to 100 ml with distilled water. Prepare the solution just before use.

Vanadium acetylacetonate solution. Mix 25 ml of 10^{-2} M vanadium solution in 5% perchloric acid and 20 ml of aqueous 0.5 M acetylacetone solution, dilute to *ca.* 80 ml with distilled water, and proceed as for the above maltolate solution.

The chloroform and benzene were free from alcohol.

Appropriate amounts of alcohols were dissolved in water or in organic solvent. All alcohols used were of guaranteed grade and distilled two times, and fractions distilled at constant temperature were collected. All other chemicals were of guaranteed grade and used without further purification.

Apparatus

Beckman DU Spectrophotometer, Horiba Model-P pH meter, Iwaki KW mechanical shaker.

Recommended procedures

(*a*) *Method with vanadium 2-methyl-8-hydroxyquinolinate (simple method of low sensitivity).* To 20 ml of saturated chloroform solution of this complex, add 5 ml of

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* This reagent was extracted from leaves of *Evodiopanax innovans* and purified by recrystallization and sublimation in vacuum.

organic solvent containing an alcohol. After 1 h at room temperature, measure the absorbance at 495 nm against a blank.

(*b*) *Method with vanadium maltolate (simple and sensitive method).* To 15 ml of the vanadium maltolate solution in a separatory funnel, add 10 ml of aqueous solution containing an alcohol. Shake the solution with 25 ml of benzene for 30 min at room temperature. Separate the organic layer and dehydrate it with purified anhydrous sodium sulfate. Measure the absorbance at 445 nm against a blank similarly treated.

(*c*) *Method with vanadium acetylacetonate (method of medium sensitivity).* Proceed as in method (*b*), but measure the absorbance at 450 nm.

The authors wish to thank Professor S. YASUE (Faculty of Pharmacy, Nagoya Municipal University) for the sample of maltol and Professors Y. OKA and T. NOZOE (Faculty of Science, Tohoku University) for samples of tropolone and 4-isopropyltropolone.

SUMMARY

Vanadium(V) complexes with an acidic hydroxy group attached to the metal form the corresponding esters with alcohols. These esters show a characteristic absorption at 445–480 nm, so that alcoholic hydroxy groups can be determined photometrically. The formation constants of the *n*-butanol esters of vanadium maltolate and 2-methyl-8-hydroxyquinolinate were determined in benzene or benzene–chloroform (1:1). Simple methods are described for the determination of alcohol in the concentration range 10^{-1}–10^{-4} M.

RÉSUMÉ

Les complexes de vanadium(V) avec un groupe hydroxy acide lié au métal donnent les esters correspondants avec des alcools. Ces esters présentent une absorption caractéristique à 445–480 nm, permettant le dosage photométrique des groupes hydroxy alcooliques. On a déterminé les constantes de formation des esters *n*-butanol du maltolate de vanadium et méthyl-2-hydroxy-8-quinoléate dans le benzène ou un mélange benzène–chloroforme (1:1). Des méthodes simples sont décrites pour le dosage de l'alcool à des concentrations allant de 10^{-1} à 10^{-4} M.

ZUSAMMENFASSUNG

Vanadin(V)-Komplexe mit einer sauren Hydroxy-Gruppe am Metall bilden Ester mit Alkoholen. Diese Ester zeigen eine charakteristische Absorption bei 445–480 nm, so dass alkoholische Hydroxy-Gruppen photometrisch bestimmt werden können. Die Bildungskonstanten des *n*-Butanolesters von Vanadinmaltolat und 2-Methyl-8-hydroxychinolinat in Benzol oder Benzol–Chloroform (1:1) wurden bestimmt. Zur Bestimmung von Alkohol im Konzentrationsbereich von 10^{-1}–10^{-4} M werden einfache Methoden beschrieben.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE APPLICATION OF X-RAY DIFFRACTION ANALYSIS TO URANIUM CERAMICS

PART II. QUANTITATIVE ANALYSIS OF THE URANIUM CARBIDES

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(Received October 12th, 1967)

The need for a fissile material possessing better properties than those of uranium dioxide with regard to thermal conductivity for instance, has attracted considerable attention to the carbides of uranium as nuclear fuels[1]. A proper study of these materials requires analytical methods for the determination of their composition. Chemical analysis gives the amount of uranium and free and total carbon, but these data are not sufficient to give quantitative information about the phases present in an uranium–carbon alloy. Microscopical methods allow the different phases present to be detected, but X-ray diffraction methods can give more precise quantitative data and improved limits of detection. In spite of the great number of papers concerning the hydrolysis of the uranium carbides, which are often contradictory[2,3], it seems impossible to use this technique for quantitative work.

The only attempt to determine these carbides by X-ray diffraction has been reported by ATODA *et al.*[4]. In the present investigation the determination of trace and major amounts of UC and UC_2 in binary and multicomponent systems was studied by different analytical diffraction techniques: direct methods, internal and external standard technique, active dilution method.

EXPERIMENTAL

Apparatus and operating conditions

A standard Philips diffractometer, including a proportional counter and pulse-height discrimination was used. The X-ray radiation was obtained from a copper anode tube with a nickel filter at 50 kV and 20 mA. The divergence and scatter slits were usually 1° but 4° for low concentrations; the receiving slit was 0.1 mm. A counting time of 100 sec was used.

Sample preparation

The characteristics of the uranium carbides used, are shown in Table I. In spite of the high oxygen content (up to 7500 p.p.m.) of several carbides, no trace of UO_2 was observed. Lattice parameter measurements carried out on the UC samples containing 0.52 and 0.16% O_2 gave values of 4.9600 and 4.9603 $\pm$ 0.0002 Å respectively. This is the commonly accepted value for stoichiometric UC (maximum O_2 content

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about 500 p.p.m.). Together with the result for the combined carbon of the UC, which contained 0.52% O_2, of 4.78 wt%, this means that a UCO phase can be excluded and that most of the oxygen is present as amorphous UO_2 and probably a small part adsorbed.

TABLE I

CHARACTERISTICS OF THE URANIUM CARBIDES USED

Sample no.	*Compound*	*Origin*	*Total Carbon (%)*	*Free Carbon (%)*	*U (%)*	*O_2 (%)*	*N_2 (%)*	*H_2 (%)*
1	UC	Atomergic Chemetals	5.02	0.03	94.35	0.57	0.0690	0.0167
2	UC "pre-reacted* pellets"	Nukem	4.78	<0.01	94.80	0.52	0.0162	0.0065
3	UC arc-melted	Nukem	4.71	<0.01	95.10	0.16	0.0065	0.0037
4	UC arc-melted	Nukem	4.85	<0.01	94.80	0.39	0.0187	0.0093
5	UC_2	Atomergic Chemetals	9.59	0.76	89.70	0.75	0.1200	0.0158
6	UC_2	Nukem	9.98	1.26	89.50	0.33	0.0153	0.0029

* UC obtained by a special fabrication method of Nukem (Nuklear-Chemie und Metallurgie GmbH, Wolfgang, Main).

In the UC material delivered by the Atomergic Chemetals Co. a small amount of UC_2 was present, while X-ray examination of the UC_2 samples revealed the presence of small quantities of UC and free carbon (graphite), which amount was about 1% (see Table I). To avoid oxidation of the carbides, grinding and mixing was carried out under hexane, and sieving in a dry (15% relative humidity) argon atmosphere. The particle size of the powders used to set up calibration curves was less than 22 μ. All samples were pressed into disks (at 7 tons per cm^2 for 2 min), adding about 10% in weight of Mowiol* (a polyvinyl alcohol). Pressing the samples into disks, a preferred orientation effect was noted. Especially the [200] reflexion of UC and the [002] and [110] reflexion of UC_2, became more intense (factor 2) compared to an unorientated power sample. It was found, however, that this effect was reproducible, when a constant pressure and the same pressing time were used for all samples. A reproducibility test, with 10 disks each of pure samples of U, UO_2, UC and ThO_2, in which the peak intensities of the [110] reflexion of uranium and the [111] reflexions of the other compounds were measured, showed average percentage deviations of 1.58% for UC, 1.80% for U, 1.30% for ThO_2 and 1.85% for UO_2.

RESULTS

Determination of the binary mixture UC–UC_2

Direct method. If the two components UC and UC_2 of a multicomponent mixture

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are considered, it can be shown that for a particular reflexion [hkl] of the UC phase or UC_2 phase:

$$\frac{I_{UC[111]}}{I_{UC_2[101]}} = \frac{(1+\cos^2 2\theta/\sin^2\theta\cos\theta\cdot A.T.U.v.F^2)_{UC}}{(1+\cos^2 2\theta/\sin^2\theta\cos\theta\cdot A.T.U.v.F^2)_{UC_2}}\cdot\frac{\varrho_{UC}\cdot x_{UC}}{\varrho_{UC_2}\cdot y_{UC_2}} = K\frac{x_{UC}}{y_{UC_2}} \quad (1)$$

where $(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$ = Lorentz polarization factor,

A = the absorption factor (constant for the Bragg–Brentano diffractometer arrangement),
v = the multiplicity factor,
T = the Debye Waller temperature factor,
F = the structure factor,
U = the unit cell volume,
ϱ = the theoretical density,
K = a proportionality constant,
$I_{UC\,[111]}$ or $I_{UC_2[101]}$ = the integrated intensity of the two reflexions,
x_{UC} or y_{UC_2} = the weight fractions of UC and UC_2 in the mixture.

Thus in a mixture where UC and UC_2 are present, the ratio of their percentages by weight is proportional to the ratio of the intensity of the reflexions chosen as analytical lines.

If only UC and UC_2 are present, then $y_{UC_2} = 100 - x_{UC}$, and substituting in eqn. (1), the weight percentage of UC becomes

$$x_{UC} = 100\cdot\frac{I_{UC[111]}}{K\,I_{UC_2[101]}+I_{UC[111]}} = \frac{100}{1+K\dfrac{I_{UC_2[101]}}{I_{UC[111]}}} \quad (2)$$

In our case, however, $x_{UC}+y_{UC_2}$ is <100, since the UC–UC_2 samples used contained oxygen and free carbon, the total amount of which in the UC–UC_2 mixtures varied between 1.8 and 2.1%, depending on the materials used. This means that the factor 100 in eqn. (2) must be replaced by 98.2 or 97.9, respectively. The proportionality constant K was determined experimentally with mixtures of known concentrations of UC and UC_2. A K factor of 0.69 ± 0.03 was found. The precision, when synthetic samples were analysed, was about 2%.

Another direct method (without calibration curves) is possible by taking the expression for the theoretical analysis curve for a mixture of 2 components:

$$I_1/(I_1)_0 = x_1\mu_1/\{x_1(\mu_1-\mu_2)+\mu_2\} \quad (3)$$

where

$I_1/(I_1)_0$ = the ratio of the intensity of component 1 in the mixture over component 1 in the pure state,
x_1 = the weight fraction of component 1,
μ_1 and μ_2 = the mass absorption coefficients of component 1 and 2 respectively.

Since μ_1 and μ_2 can easily be calculated, the weight fraction x_1 can be calculated simply by measuring the intensity of a reflexion of component 1 in the mixture and of the same reflexion of the pure component 1.

The results obtained from several synthetic samples are given in Table II. The mass absorption coefficients were obtained by interpolating VICTOREEN's[5] data. This method is still valid even if UO_2 is also present in the UC–UC_2 mixture, since the mass absorption coefficients of UC_2 and UO_2 are close together (μ_m using Cu Kα radiation, for UC_2 and UO_2 are respectively 335 and 326 g^{-1} cm^2).

Calculations were made to establish, when U and C (graphite) were also present, upto what amount eqn. (3) could still be used, to obtain the same precision as had been obtained for the binary UC–UC_2 mixture. It was found that for concentrations of uranium upto 50% and for concentration of graphite (C) upto 10%, the theoretical intensity–concentration relationship could be applied for the determination of the uranium monocarbide. The advantage of these direct methods compared to the "calibration curve method", is that, once the proportionality constant K has been established, only the two analytical lines in the unknown sample have to be measured. When the x_1 method is used, the analytical line in the unknown specimen and the same line of the pure compound must be measured.

TABLE II

COMPARISON BETWEEN THEORETICAL AND FOUND VALUES OF UC DETERMINED BY MEANS OF THE EXPRESSION FOR THE THEORETICAL ANALYSIS CURVE

Composition (%)	*Found* (%)	*Relative error* (%)	*Composition* (%)	*Found* (%)	*Relative error* (%)
90.0	89.0	1.1	30.0	28.0	6.6
70.0	71.1	1.5	20.0	21.3	6.5
50.0	48.5	3.0	10.0	9.4	6.0

External standard method. The calibration curves for UC–UC_2 mixtures in the 10–100% concentration range and for small concentrations (0–15%) of UC_2 in UC were found to be rectilinear. For the latter curve, the integrated intensity of the [101] and [002] peaks of UC was measured. The precision obtained was about 3%.

Determination of UC in mixtures of UO_2 and U using the internal standard technique

In the well-known internal standard method[6], the ratio of the intensity of the compound to be determined to the intensity of the internal standard is matched against predetermined working curves. Thoria was found to be a suitable internal standard. The [111] reflexions of UC and thoria were chosen as analytical lines. A straight-line calibration graph was obtained upto 50% UC. A precision of about 3% relative was obtained in the analysis of synthetic samples.

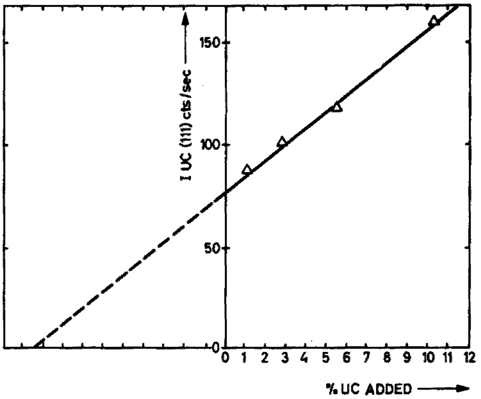
Disadvantages of the internal standard method are that dilution of the sample takes place, and that it is often difficult to find a suitable internal standard, which must be free of interferences from the constituents of the sample.

Determination of UC and UC_2 by the method of active dilution

Another technique for analyzing binary and multicomponent systems, especially if there is no suitable compound available for the internal standard, is the method of dilution with an active matrix; this means that the sample is diluted with a known amount of the component of interest. For a system where all the components present possess mass absorption coefficients which are close together (*e.g.* oxides and carbides of uranium), eqn. (4) may be used to solve for the composition x.

$$I_x/I_{x+a}=x/x+a \tag{4}$$

where a is the weight percentage added, and I_x and I_{x+a} are, respectively, the intensities of the reflexions of compound x, before and after adding the compound. This equation, however, assumes a straight relationship between intensity and concentration, which is theoretically true only if the mass absorption coefficients of the components are equal. In the case of uranium carbides, whose mass absorption coefficients are not equal but are similar (335 and 350 $g^{-1}\,cm^2$ for UC_2 and UC respectively), a better precision can be obtained by making different additions and plotting I_{x+a} as a function of the added quantity (see Fig. 1). In Fig. 1, the quantity sought is the absolute value of the x axis intercept. This latter method was used for the determination of small amounts of UC in the UC_2 samples; results were 9.6 ± 0.3% and 6.5 ± 0.3 % UC respectively for sample no. 5 (Atomergic Chem) and for sample no. 6 (Nukem).



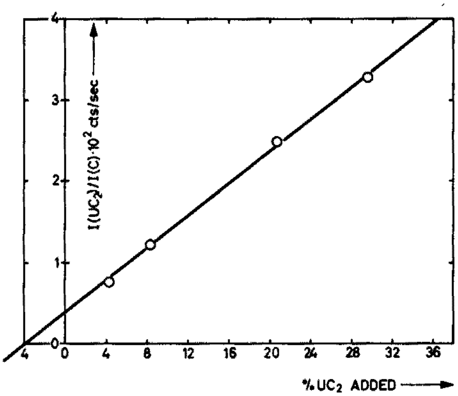


Fig. 1. Determination of UC by a simplified version of the active dilution method.

Fig. 2. Calibration curve for the determination of UC_2 in C by the active dilution method.

However, if the mass absorption coefficient of one of the components in the system is quite different from the rest, a second component has to be measured in the sample. Suppose the sample contains a second component B, the weight fraction of which is x_B. If an amount $|a|$ of component A (to be determined) is added to the sample, then the weight fraction of component A (per 1 g of initial sample) is: $x_A+a/1+a$ and of component B: $x_B/1+a$.

Then

$$I_A/I_B=K\cdot(x_A+a)/x_B \tag{5}$$

A plot of I_A/I_B as a function of $|a|$ will be a straight line, not passing through the origin. The quantity x_A is the absolute value of the x-axis intercept[7]. This method was applied to the determination of UC_2 in C (Fig. 2) and of C in UC_2. The method could be of interest for the analysis of fuel elements for high-temperature gas-cooled reactors of the Dragon type[8]. A precision of 5% relative, in the 0–10% concentration range, was obtained, for the determination of UC_2 in C.

Limits of detection

The limits of detection of UC_2 in UC and of UO_2 in UC were found to be 0.04

and 0.03%, respectively. These limits of detection were calculated for a counting time of 100 sec, with samples containing 0.5% UO_2 or UC_2; the minimum content detectable was defined as that concentration which yields an intensity equal to 3 times the standard deviation of the background intensity. This definition, however, takes no account of the instrumental errors: instability of generating and detecting units, errors due to sample preparation, etc. Lavrentiev and Vainshtein[9] have derived the following formula for the limit of detection, taking into consideration these errors.

$$LD = 2.8/I_{\mathrm{P}} \cdot \{I_{\mathrm{B}}/T + v_{\mathrm{i}}^2 \cdot I_{\mathrm{B}}^2\}^{\frac{1}{2}} \tag{6}$$

where

I_{P} = the analytical line intensity referred to unit concentration,
I_{B} = the background intensity,
T = the counting time,
v_{i} = the instrumental error.

From this formula, it follows that the limit of detection is determined by both statistical and instrumental errors of measurement, hence it is impossible to increase sensitivity indefinitely, by increasing the counting time infinitely. In the present case, where v_{i} is about 10^{-2}, and the counting time is 100 sec, the same results for the limits of detection for both definitions were obtained.

Considerations about the stoichiometry of "UC_2"

Several investigations have shown that "UC_2" cannot normally be prepared as a fully stoichiometric compound, but usually has the composition $UC_{1.8-1.9}$[10-12]. Since the quantity of UC present in the UC_2 samples used could be determined by the active dilution method, it was possible to calculate the stoichiometry of the "UC_2" samples from the results of the total and free carbon analysis. Suppose x is the weight fraction of UC in the "UC_2", y the percentage of combined carbon of the "UC_2" phase and CC the percentage of combined carbon in the sample (which contained also small amounts of UC and C) as determined by chemical analysis, then

$$4.8x + (1-x)y = CC \tag{7}$$

or

$$y = (CC - 4.8x)/(1-x) \tag{8}$$

The variance of error for y will be given by the equation:

$$V[y] = \left(\frac{\partial y}{\partial CC}\right)^2 V[CC] + \left(\frac{\partial y}{\partial x}\right)^2 V[x] \tag{9}$$

where V is the variance of the variable between brackets and it is assumed that the errors coming from CC and x are independent of one another.

Derivation of y followed by division by y^2 yields:

$$\frac{V[y]}{y^2} = \frac{V[CC]}{(CC-4.8x)^2} + \frac{V[x]\ (CC-4.8)^2}{(1-x)^2\ (CC-4.8x)^2} \tag{10}$$

The variances are equivalent to the squares of the standard deviations.

In the samples used, x is equal to or lower than 0.1, hence $1-x \sim 1$, and $CC - 4.8x \sim CC$. As a first approximation, the variance can be calculated from the equation:

$$V[y]/y^2 = V[CC]/(CC)^2 + V[x](CC-4.8)^2/(CC)^2 \tag{11}$$

When it is taken into account that $\sigma_C = 0.02$ (standard deviation of the combined carbon determination), that $\sigma_x = 0.005$ (standard deviation of the addition diffraction method for the UC phase determination) and that in the samples used $CC - 4.8$ is about 5, then $\sigma_y (\equiv \sqrt{V[y]})$ is equal to about 0.03. The composition of the two UC_2 samples, calculated in this way, was found to be $UC_{1.96 \pm 0.01}$ for the Nukem sample and $UC_{2.03 \pm 0.01}$ for the Atomergic Chem sample.

Since the UC_2 samples contained relatively high amounts of oxygen and nitrogen, the influence of these elements on the stoichiometry of the UC_2 samples was considered. If it is assumed that no oxygen and nitrogen adsorption has taken place, but that these elements are completely involved in the UC-lattice, to form compounds of the type $UC_{1-x}O_x$ for the Nukem UC_2 sample (nitrogen content negligible) or $UC_xO_yN_z$ for the Atomergic Chem UC_2 sample where $x + y + z = 1$, then the maximum error occurs. This means that the UC in the two UC_2 samples is then respectively $UC_{0.95}O_{0.05}$ and $UC_{0.86}O_{0.12}N_{0.02}$. When this correction was applied, values of $UC_{1.97}$ and $UC_{2.04}$ were found. However UC_2 can contain up to about 2% dissolved oxygen at about 1550°[13]; if all the oxygen found in the present dicarbides was dissolved, forming a $UC_{2-y}O_y$ compound (not very probably), then according to eqn. (7), the amount of combined carbon of the UC phase must be about 11 wt %, which is of course impossible. Therefore, the most likely explanation is that the oxygen in these dicarbides is present both as amorphous UO_2 and for a smaller part adsorbed. It must, however, be noted that most of the oxygen was introduced during the grinding procedure of the starting material. The oxygen content of the sample no. 6, for instance, was about 600 p.p.m. before grinding, while after grinding under hexane the obtained powder contained 3300 p.p.m. O_2. This means that although UC_2 has always been found to be substoichiometric, with a commonly accepted value for the combined carbon of 8.6 ± 0.1 wt % ($UC_{1.86 \pm 0.02}$), the amount of combined carbon of the UC_2 used in the present study was 9.00 ± 0.04 and 9.28 ± 0.04 wt % corresponding respectively to $UC_{1.96 \pm 0.01}$ and $UC_{2.03 \pm 0.01}$.

DISCUSSION

Determination of UC and UC_2 in binary and multicomponent systems gave satisfactory results; in general, a relative standard deviation of about 2% was obtained. This is slightly worse than that found for the analysis of the oxides of uranium[14]; the decrease in precision can probably be ascribed to inhomogeneity in the prepared mixtures, since the mixing procedures were carried out under hexane to avoid oxida-

TABLE III

COMPARISON OF PRECISION OBTAINED BY THE DIFFERENT DIFFRACTION METHODS USED

Method	*Relative error*
K-method	2%
x_1-method	about 6% (0–50% concentration range) 1 to 2% (50–100% concentration range)
External standard method	2%
Internal standard method	3%
Active dilution method	3 to 5% (0–10% concentration range) 2 to 3% (10–100% concentration range)

tion of the carbides. The precision obtained by the different methods used is given in Table III.

For the analysis of mixtures of uranium carbides, the direct methods are much faster than the external standard technique. However, if the uranium carbide mixtures contain other compounds whose mass absorption coefficients differ significantly, the internal standard method must be employed. The active dilution method can also be used, but is of advantage only if one or two analyses for a particular component are desired.

Uranium monocarbides of different origin (arc-melted, sintered) were studied, but no notable difference in intensity of the reflexions was obtained (differences in intensity of fused UO_2 samples and UO_2 obtained by reduction have been found previously[14]).

X-Ray diffraction methods for the quantitative phase determination of uranium carbides are particularly helpful as a rapid means of nondestructive determination, when the material under examination is required for some other purpose. Limitations arise from the fact that only crystalline compounds are detectable and that limits of sensitivity are about 0.04%. Chemical analysis of the uranium carbides is a destructive method, and gives only the combined carbon content but not the amount of the phases present.

We are grateful to Professor A. MICHEL for his direction of these investigations, to Mrs. CECCARELLI and Mr. COLOMBO for the chemical analysis of the uranium carbides and to Mr. H. LAURENT, Head of the Analytical Chemistry Division, for many helpful discussions during the performance of this work.

SUMMARY

Different X-ray diffractometer methods are proposed for the determination of uranium carbides in binary and multicomponent mixtures (direct methods, internal standard and active dilution method). The relative standard deviation was found to be 2%. Limits of detection for UC_2 and UO_2 in UC were about 0.04%. Calculations showed that the UC_2 in the samples used contained 9.00 and 9.28 ± 0.04 wt% of combined carbon, corresponding to $UC_{1.96\pm0.01}$ and $UC_{2.03\pm0.01}$.

RÉSUMÉ

Différentes méthodes d'analyse diffractométrique ont été utilisées en vue de déterminer les carbures d'uranium dans des mélanges de deux ou plus de composés (méthode directe, emploi d'un étalon interne ou de l'addition normalisée). L'écart type relatif est en général de l'ordre de 2%. Les limites de détection de UC_2 et de UO_2 dans UC atteignent des valeurs d'environ 0.04%. Les calculs ont montré que les UC_2 contenu dans ceux-ci renfermaient respectivement 9.00 et 9.28 ± 0.04% de carbone combiné correspondant aux formules $UC_{1.96\pm0.01}$ et $UC_{2.03\pm0.01}$.

ZUSAMMENFASSUNG

Es wird eine Röntgen-Beugungsmethode vorgeschlagen zur Bestimmung von

Urancarbiden in binären und Mehrkomponenten-Mischungen. Die relative Standardabweichung beträgt 2%, die Nachweisgrenze für UC_2 und UO_2 in UC etwa 0.04%. Berechnungen zeigten, dass das UC_2 in den verwendeten Proben 9.00 und 9.28 ± 0.04 Gew.% gebundenen Kohlenstoff enthält. Das entspricht den Formeln $UC_{1.96\pm0.01}$ und $UC_{2.03\pm0.01}$.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SOME INTERFERENCES IN THE ATOMIC ABSORPTION SPECTROPHOTOMETRY OF CALCIUM

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(Received October 18th, 1967)

Atomic absorption spectrophotometry has been widely applied to the determination of traces of calcium in a variety of materials[1], but as in the flame photometric determination, numerous substances influence the production of calcium atoms in the flame. The depressive effects of phosphate, sulphate and aluminium have been studied in detail, and the use of large amounts of lanthanum or strontium salts to overcome these effects is universally appreciated. The effects of other species, particularly of alkali and the other alkaline earth metals, are less well documented. Much of the information that is available from flame photometric studies is confused by spectral effects. Atomic absorption spectrophotometry provides a means of ascertaining their chemical interference free from spectral effects. In previous work[2], a detailed study of chemical interferences in the atomic absorption spectrophotometry of magnesium gave valuable information about the mechanism of atom production in the flame and the nature of the interference effects. This paper extends the investigation to calcium under similar conditions. The results obtained, in conjunction with those obtained for magnesium[2], have enabled an improved explanation of alkaline earth interactions in flames to be formulated.

EXPERIMENTAL

Apparatus

This was as described previously[2], except that a calcium hollow cathode lamp (Hilger and Watts) was used.

Instrumental conditions

These were selected for flame and instrumental stability rather than sensitivity, and were constant throughout the experiments.

Flame

As for magnesium, the absorbance of calcium was markedly dependent on propane flow rate (Fig. 1). Great care was taken to ensure a constant rate.

The position of the light beam in the flame could be changed as described previously[2]. Unless otherwise stated, experiments were carried out with the burner 0.2 cm below its fully raised position, *i.e.* with the centre of the light beam 0.5 cm

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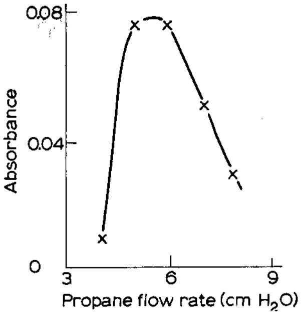
above the flame base. Each recorded point is the mean of 5 absorbance readings. Distilled water was sprayed between readings. At least 30 min were allowed for the burner and lamp to stabilise at the working conditions.

	Wavelength (Å)	*Slit width (mm)*	*Lamp current (mA)*	*Air pressure (psi)*	*Gas flow rate (cm H_2O)*
Air–propane	4225	0.1	8	14	5.5 (see Fig. 1)
Air–acetylene				12.5	21.3

Investigation of interferences

The absorbances of aqueous solutions of calcium (20 p.p.m., added as its chloride) were measured in the presence of various amounts of sodium silicate, phosphoric acid, sulphuric acid, disodium EDTA (at various pH values), nitric acid, acetic acid, 8-quinolinol (dissolved in 0.3 *M* acetic acid), hydrochloric acid, and the chlorides of aluminium, barium, iron, lanthanum, magnesium, sodium and strontium.

Chemicals were as described previously[2].



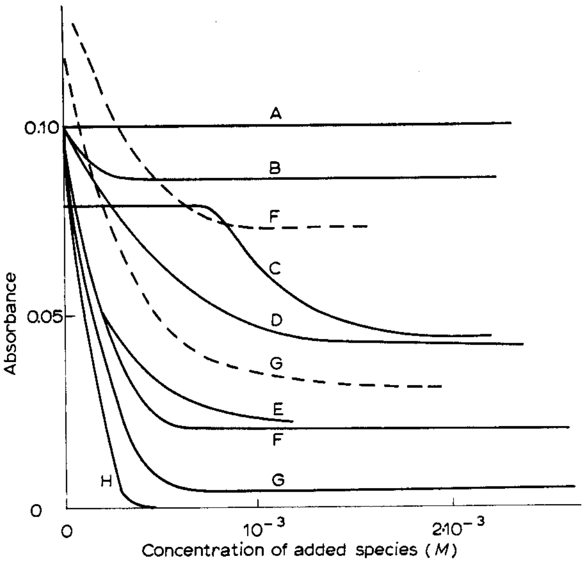


Fig. 1. Variation of calcium absorbance with propane flow-rate, burner fully raised. Solution: 20 p.p.m. Ca in 0.1 *N* HCl.

Fig. 2. The effect of anions and complexing agents on calcium absorbance. Solutions: 20 p.p.m. Ca in presence of (A) HCl, (B) 8-quinolinol or acetic acid, (C) H_3PO_4 + 1000 p.p.m. Sr, (D) HNO_3, (E) EDTA, (F) H_2SO_4, (G) H_3PO_4, (H) SiO_4^{4-}. Full lines, air–propane flame; dotted lines, air–acetylene flame.

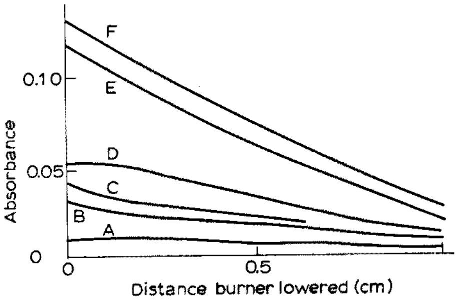
RESULTS

The effects of different concentrations of a number of anions on the calcium absorbance in an air–propane and an air–acetylene flame are shown in Fig. 2. Figure 3 shows the flame profiles of calcium in the presence of amounts of these anions sufficient to attain the plateau regions shown in Fig. 2. It confirms previous observations[3,4] that the relative magnitudes of the depressive effects of sulphate and phosphate decrease high in the flame, although the absorbance at this height is also much lower. The relative magnitudes of the depressive effects decrease in this order:

$$SiO_4^{4-} > PO_4^{3-} > SO_4^{2-} > \text{EDTA} > NO_3^- > CH_3COO^- = \text{8-quinolinol} > Cl^-.$$

The effect of EDTA was virtually the same at all pH values studied.

The effects of different concentrations of various cations on the absorption of calcium in the air–propane flame are shown in Fig. 4. The corresponding flame profiles are shown in Fig. 5. Only for aluminium is there general agreement about the effect[5,6].



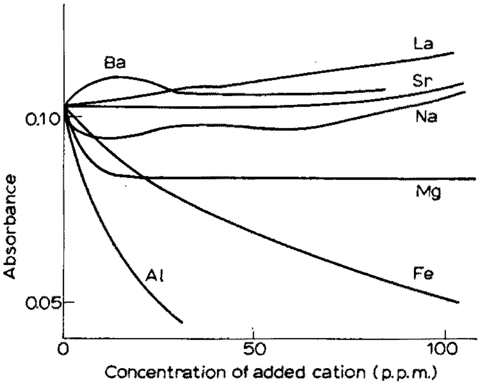
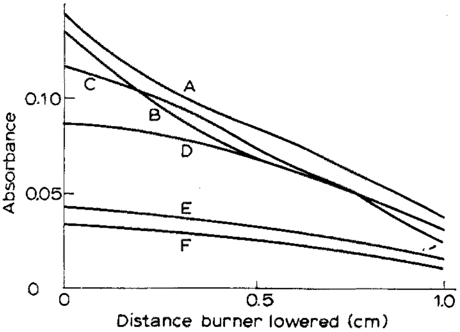


Fig. 3. Flame profile of Ca (20 p.p.m.) in presence of (A) H_3PO_4, (B) H_2SO_4, (C) EDTA, (D) HNO_3, (E) HCl, oxalic acid, acetic acid, (F) $CaCl_2$ alone, in air–propane flame.

Fig. 4. The effect of cations on the absorbance of 20 p.p.m. Ca, all as their chlorides, in 0.1 *M* HCl.



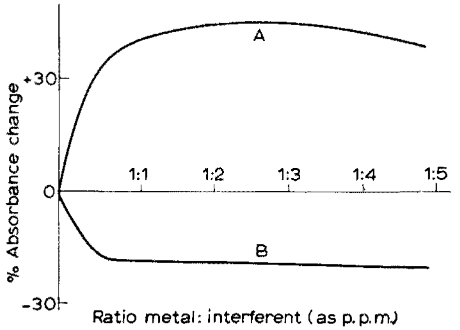


Fig. 5. Flame profile of Ca (20 p.p.m.) in presence of (A) La (100 p.p.m.), (B) Sr (100 p.p.m.), (C) Na (100 p.p.m.), (D) Mg (100 p.p.m.), (E) Fe (150 p.p.m.), (F) Al (50 p.p.m.).

Fig. 6. Effect of Mg on Ca absorbance and *vice versa*. (A) 0.5 p.p.m. Mg, (B) 20 p.p.m. Ca.

DISCUSSION

The depressive effects of the anions (and of aluminium and iron) can best be explained by the resistance of the calcium salts of these species to producing calcium atoms in the relatively cool flames. Many calcium salts will decompose to form calcium oxide particles in the flame, which will be the sole source of calcium atoms. These atoms have been postulated[2] to arise from interaction of flame radicals with the surface of the oxide particle *e.g.*:

$$CaO(s) + H^{\cdot}(g) \rightleftharpoons Ca(g) + {}^{\cdot}OH(g) \tag{1}$$

However, experiments with a platinum wire in a bunsen flame established that whereas many calcium salts did decompose to the oxide, calcium sulphate, silicate and phosphate were hardly affected by the flame. This resistance to chemical reactions in the flame suggests that in their rapid passage through the flame, these particles are only slowly (if at all) converted to oxide, and are also likely to be quite resistant to radical interaction before conversion to oxide. The greater their resistance to these effects, the slower is the production of calcium atoms, so that the concentration of calcium atoms will be least in the lowest regions of the flame. DAVID[6] found that, although phosphate depressed calcium absorbance in all parts of the air–acetylene flame, the most striking depression was at the flame base. The absorbance then rose rapidly with increasing height in the flame, until it reached almost 50% of the absorbance obtained in the absence of phosphate. It also explains why the relative magnitudes of the depressive effects decrease in the higher regions of the flames[3,4,7]. The magnitudes of the depressive effects are less in the air–acetylene flame than in the air–propane flame, because of the increased rate of radical interaction at the higher temperature.

As the production of vapour-phase calcium species is controlled by a reaction of radicals with solid particles, reaction must take place at the surface of these particles. The larger the particles, the smaller is the surface-to-volume ratio, so that the relative rate of production of calcium atoms will be less. This could account for the bending of calibration curves towards the concentration axis, which was found for more than 50 p.p.m. of calcium. The effect will be most noticeable when the surface interaction is slow, *e.g.* as with calcium phosphate particles. ALKEMADE AND VOORHUIS[7] found that the effect of phosphate was relatively less for smaller calcium concentrations, *i.e.* for smaller residual particles. BAKER AND GARTON[8] also concluded that the degree of interference was related to particle size.

Cation effects

As with magnesium, the alkaline earth elements have an effect on the absorbance of calcium in the air–propane flame. In a previous paper[2] it was concluded that the enhancing effect of calcium on magnesium was related to the production of gas-phase calcium atoms, because the enhancement was greater in the presence of sulphate than in the presence of phosphate, as is the production of calcium atoms (*cf.* Fig. 2). It was suggested that an interaction such as:

$$Ca(g) + MgO(g) \rightleftharpoons Mg(g) + CaO(g) \tag{2}$$

could account for this effect, but it has been shown[9] that this interaction would be rare because of the low concentrations of these species in the flame. A better explanation, therefore, is the interaction of calcium atoms with the solid magnesium oxide particles:

$$Ca(g) + MgO(s) \rightarrow Mg(g) + CaO(s) \tag{3}$$

As solid calcium oxide is more difficult to convert to gaseous atoms at 2000°K than solid magnesium oxide (ΔH_0 (2000°K) = -195 kcal/mole for CaO and -181 kcal/mole for MgO)[10] reaction (3) would be thermodynamically favourable. This mechanism implies that the enhancement of magnesium atom production occurs at the expense of calcium atom production. Figure 6 shows that this enhancement is indeed paralleled by a decrease in calcium atom production.

Reaction (3) is most likely to occur immediately after the calcium atom has been formed by reaction (1), *i.e.* when the calcium atom is very near to the particle surface. Indeed, the reaction can be considered to be a direct consequence of the lesser electronegativity of calcium compared to magnesium. When the hydrogen atom reacts with the oxide ion, the magnesium ion is more likely to accept the electrons produced by the reaction.

Strontium had no effect on calcium absorbance until high strontium concentrations were reached. This was expected because calcium and strontium had almost the same effect on magnesium absorbance[2], and also have the same Pauling electronegativity. Barium had little effect on calcium atom production; this is similar to its effect on magnesium. This may be because barium oxide boils at *ca.* 2000° and so would be appreciably volatile in the air–propane flame, unlike the other alkaline earth oxides. Lanthanum, as would be expected with its very stable oxy-species, enhances calcium atom production. The depressive effect of sodium, which has also been observed in the hotter oxy–hydrogen flame[11], is difficult to explain. Ionisation is not likely to be an important factor because calcium atoms are not appreciably ionised at this temperature. It is also interesting that none of the interfering elements (except barium) produced peaks corresponding to those observed for magnesium[2].

The depressive effect of iron is similar to, but less than that of aluminium[12], and thus probably arises from the formation of a spinel $CaO \cdot Fe_2O_3$. Iron had no enhancing effect, unlike its effect on magnesium[2,13] and unlike its effect in the presence of sulphate[14].

The efficiency of various cations in removing anionic interferences ($Mg < Sr < La$)[15,16] is thus due to 3 effects.

(*a*) The preferential precipitation of the interfering anion with the added cation[17]. A large excess of all cations will be similarly effective in freeing calcium from the effect of the anion.

(*b*) A general reduction in calcium atom production because of the much increased particle size in the flame.

(*c*) An enhancement (La), depression (Mg) or no change (Sr) of the production of calcium atoms by the large excess of added cation.

The authors thank Professor R. BELCHER for his interest in this work, and Professor C. DUVAL for study leave granted to C.R.

SUMMARY

The effects of anions, cations and complexing agents on the absorbance of calcium in the air–propane flame are investigated. Mechanisms for the various enhancing and depressive effects are suggested.

RÉSUMÉ

On a examiné l'influence des anions, cations et agents complexants sur l'absorption du calcium dans la flamme air–propane. Des mécanismes sont proposés concernant les divers effets dépressifs et autres.

ZUSAMMENFASSUNG

Die Einflüsse von Anionen, Kationen und Komplexbildnern auf die Absorption des Calciums bei der Flammenabsorptionsspektralphotometrie unter Verwendung einer Luft–Propan-Flamme werden untersucht. Mechanismen für die verschiedenen Anregungs- und Absorptionseffekte werden vorgeschlagen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DEVELOPMENT OF FLUORIDE-SENSITIVE MEMBRANE ELECTRODES

PART I. MEMBRANES CONTAINING THORIUM, LANTHANUM OR CALCIUM FLUORIDE

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(Received October 26th, 1967)

Very few direct electrochemical methods are available for the determination of the fluoride ion. Some spontaneous current methods have been suggested in which aluminium[1-4], zirconium[5], and single-crystal silicon[6] anodes are used, and amounts of fluoride down to about 2 p.p.m. have been determined, but none of these electrodes seems to be very satisfactory in regard to reproducibility or selectivity for practical applications.

At the time that this work was started, no fluoride-selective electrodes had been studied. Because there is an outstanding need for reliable and simple methods of determining low concentrations of fluoride ion and of detecting the end-points in titrations of fluoride with metal ion solutions, a potentiometric study of the membrane type of electrode was undertaken.

Many different types of membrane electrode have been used in potentiometric studies with, for example, paraffin wax or collodion as the base material carrying the active precipitate. For applied purposes, the technique used by PUNGOR, HAVAS AND TOTH[7-9] appears to give the most reproducible values of potentials as well as the best mechanical properties for the electrode. In this technique, the required precipitate is dispersed in a silicone rubber base material and the membrane is prepared by cold polymerization in the presence of a suitable catalyst. Electrodes sensitive to sulphate, chloride, iodide, as well as various cations, have been made and thoroughly studied by PUNGOR, TOTH AND HAVAS[7-9]. Most of these electrodes behave formally like a glass electrode in regard to the dependence of the potential on pX, and they follow the Nernst equation, at least approximately, over certain ranges of concentration of the required ion. The selectivity and sensitivity of the silver iodide electrode are particularly notable, for a viable change in potential is obtained with as little as 10^{-8} *M* iodide solution. No fluoride-sensitive electrodes of this type have previously been reported.

The major problem in the production of the fluoride electrodes was the choice of an insoluble precipitate for incorporation in the membrane. It is extremely important that the precipitate should have a very low solubility product and be of good crystalline form, *i.e.* that it should possess the characteristics of a good weighing

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form for the ion required. However, while there is little argument about silver iodide being the best available weighing form for iodide and barium sulphate the best for sulphate, there is no such unanimity in the case of fluoride. Undoubtedly, the most crystalline weighing form for fluoride is lead chlorofluoride but this would be useless for selective electrodes since it contains two anions and its slight solubility might also pose problems. Accordingly, the choice of precipitate seemed to lie between thorium fluoride, calcium fluoride and rare earth fluorides. Since all of these fluorides tend to form gelatinous precipitates, it was necessary to improve conventional methods of precipitation, as well as to study the eventual electrode behaviour.

EXPERIMENTAL

Preparation of membrane electrodes

The precipitate was generally used in a 1:1 weight ratio with the silicone rubber materials, with cold polymerization. The membranes were usually *ca.* 0.3 mm thick and were sealed to the end of a 10-mm diameter glass tube with silicone rubber adhesive.

Measurement of potential

An E.I.L. Vibron pH meter Model 39A was used for all measurements. In all cases, the system measured was as follows:

$Ag/AgCl/KCl$ solution–$10^{-3}M$ F^-/membrane/xM F^-–KCl solution/$AgCl/Ag$.

MEMBRANES CONTAINING THORIUM FLUORIDE

Thorium fluoride was chosen for the first experiments because of its insolubility ($pK_{s0} = \sim 25$)[10], though its precipitation characteristics were known to be poor. A study was made of the effects of the anion attached to thorium, the form and excess of fluoride, the pH of precipitation, the temperature and the acid used. The precipitates were examined under an electron microscope. In virtually all the precipitation methods tested, the particles were found to be amorphous and the particle size generally lay in the range 0.2–2 μ. When urea was used to effect precipitation from homogeneous solution, long needle-shaped crystals were obtained (particle size 13–30 μ). The most uniform crystals (cubic, particle size 5–20 μ) were obtained from mixtures at 95° containing thorium acetate, ammonium nitrate, nitric acid, urea and fluoroboric acid in an amount 10% in excess of that required to precipitate thorium fluoride quantitatively.

Electrodes prepared from precipitates obtained by all these methods showed essentially the same behaviour. Although there was a reproducible and rapidly established negative change in potential with decreasing concentrations of fluoride ion, the electrodes were in no way selective to fluoride. Probably it was a galvanic potential arising from the adsorption of the electrolyte on the membrane surface, that was being measured. It was proved that the potential was not due to diffusion across the membrane; essentially the same readings were obtained whether or not a silver layer was placed between membrane layers. After the pretreatment of the electrodes, which was done analogously to the pretreatment of silver iodide electrodes, a certain amount of fluoride was desorbed when the electrodes were soaked in water;

the fluoride in the washing liquid could be readily detected by the 8-hydroxyquinoline test[11].

In the case of the silver iodide electrode, it appears not to be critical whether the incorporated precipitate is prepared with an excess of silver or iodide[8], but for the barium sulphate and silver chloride electrodes the precipitates were originally prepared with an excess of anion[7]. Accordingly, in the first stages of this work, an excess of fluoride was always used for precipitation. When these electrodes showed the unselective negative potential change, further tests were made with precipitates prepared from an excess (10–100%) of thorium(IV). These precipitates were very finely divided (particle size 0.2–2 μ with aggregates up to 20–30 μ) even when the precipitation was done in the presence of ammonium nitrate. Unfortunately, membranes which incorporated these precipitates behaved in essentially the same way as the previous membranes. Membranes containing precipitates from equivalent amounts of thorium(IV) and fluoride also behaved similarly.

In an attempt to elucidate the causes of these unsatisfactory results, a typical thorium fluoride membrane and a silver iodide membrane were compared by electron microprobe studies. In the case of silver iodide, the particles of precipitate were very closely packed together and large, whereas in the case of thorium fluoride, the particles were rather sparsely distributed, despite the fact that about the same weight ratio of the two precipitates was incorporated in the membranes. These results provide some confirmation of the statement[8] that the specific volume of the precipitate is very important for the correct functioning of the electrode.

In further preparations, thorium fluoride was precipitated in the presence of *p*-ethoxychrysoidine, which substance has been shown[8] to cause a 10-fold increase in the specific volume of silver iodide. Membranes containing precipitates made from a 25–35% excess of thorium in the presence of *p*-ethoxychrysoidine and washed with water only, were found to respond selectively to fluoride. However, these electrodes proved to be rather insensitive to fluoride and the measured potentials were not reproducible, probably because of swelling in the membrane layer. The tendency of thorium and fluoride to form different complexes may also explain some of the difficulties found with these electrodes.

MEMBRANES CONTAINING LANTHANUM FLUORIDE

Very few gravimetric procedures based on lanthanum fluoride are available[12,13]; precipitates prepared by the method of POPOV AND KNUDSON[13] proved to be very gelatinous. Accordingly, different methods of precipitation were studied in the same way as for thorium fluoride. The most crystalline precipitates were obtained from mixtures containing nitric and formic acids, sodium fluoride, lanthanum acetate and urea at 95°.

Precipitates were made with excess of lanthanum or fluoride and with equivalent amounts of the two ions. Only when membranes were made from precipitates prepared with an excess of lanthanum did the electrode show a selective response for fluoride. When lanthanum fluoride was precipitated in the presence of *p*-ethoxychrysoidine from sodium fluoride with a 30% excess of lanthanum acetate, the properties of the fluoride-selective electrodes prepared became relatively reproducible, and their responses approximated to the theoretical values over the range 10^{-2}–10^{-4} *M* fluoride (Fig. 1). Below this range, sensitivity was very poor; immersing the electrodes in 10^{-1} M fluoride or in other strong electrolyte often destroyed their selective properties.

These electrodes proved to have quite rapid response times and could be stored in water or in $10^{-3}M$ fluoride without loss in activity for up to 1 week. However, since their production was unreliable, these studies were temporarily abandoned in favour of other types of precipitate.

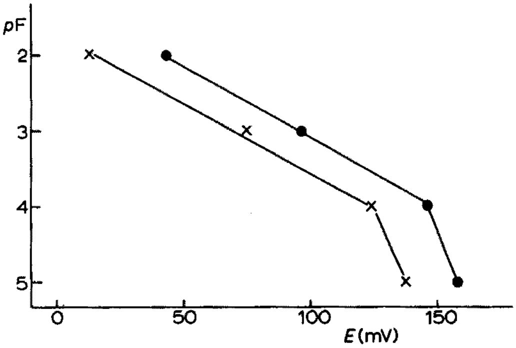

Fig. 1. E *vs.* pF curves for different membranes prepared from lanthanum fluoride (made with a 30% excess of La^{3+}).

Some electrodes were prepared from commercially available pure lanthanum fluoride but these proved to be almost entirely unresponsive to changes in ion concentration. Pretreatment of the membrane, or of the precipitate before incorporation into the membrane, with either fluoride or lanthanum(III) effected no improvement in behaviour.

Other membranes were prepared from commercially available yttrium, cerium(III) and samarium fluorides, but none was selective for fluoride and most were entirely unresponsive to changes in ion concentration. These results, however, indicate the importance of the method of preparing the precipitate which is to be incorporated into the membrane. The commercial method of preparation probably finishes with an ignition process which deactivates the particles for electrochemical purposes.

After this work had been completed, the Orion fluoride-sensitive electrode became commercially available. This electrode contains a single crystal of lanthanum fluoride doped with europium(II), and can be used over the 10^{-1}–$10^{-6}M$ fluoride range[14]. It has recently been examined by LINGANE[15] for end-point detection in titrations of fluoride with lanthanum(III), calcium(II) or thorium(IV) solutions. The range of this electrode is three magnitudes greater than that of the best membrane electrode obtained in the present work. Further work is in progress on the lanthanum fluoride membrane electrode to improve its reliability and range.

MEMBRANES CONTAINING CALCIUM FLUORIDE

Calcium fluoride is one of the more reputable weighing forms for fluoride ($pK_{so} = 10.5$)[10], though it tends to be gelatinous; for gravimetric purposes, it has often been coprecipitated along with another calcium salt so that it can be easily filtered.

As with the other types of membrane electrode, membranes prepared from precipitates made with excess of anion were entirely inselective, but those with an excess of cation showed some promise. A closer examination of the effect of varying the excess of calcium(II) used in the preparation of the precipitate was made.

Two procedures were used. In method I, an excess of calcium chloride at pH 2.7 was treated at 95° with fluoboric acid and the precipitate was digested at 95° for 2 h. In method II, an excess of calcium chloride was added gradually to sodium fluoride in 10% acetic acid at 95°, urea was added and the precipitate was digested as before. The use of calcium nitrate instead of chloride did not affect the precipitate or the performance of the final membrane.

Method I gave round particles of size 3–6 μ whereas method II gave cubic particles of size 1.5–4 μ. Figure 2 shows crystals prepared by the two methods; it should be noted that calcium fluoborate is very soluble and, indeed, calcium(II) can be used to speed the hydrolysis of the fluoborate ion. When the excess of calcium in Method I was varied between 0 and 50%, it was found that precipitates made from less than 10% excess fluoride were inselective when incorporated in membrane electrodes. Precipitates from 10–45% excess calcium behaved selectively to changes in fluoride concentration but the slope of the E–pF plot over the range 10^{-2}–$10^{-4}M$ fluoride was only about 0.03±0.005 V. Electrodes prepared from precipitates from greater than 50% excess calcium behaved very erratically. With this method, the addition of *p*-ethoxychrysoidine during the precipitation improved the response time of the electrode but did not affect the particle size or the sensitivity.

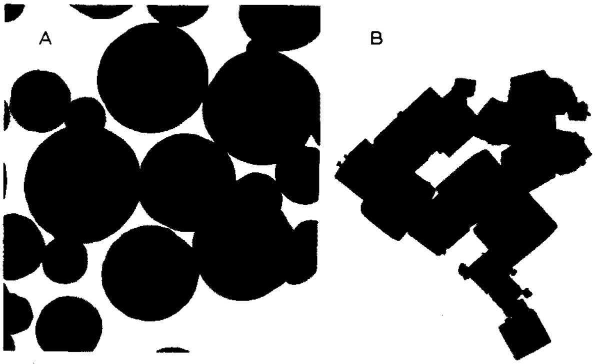

Fig. 2. Different preparations of calcium fluoride as seen under electron microscope. (A) From $CaCl_2$ and HBF_4 at pH 2.7. (B) From $CaCl_2$ and NaF in acetic acid–urea medium.

Precipitates made by Method II were tested in the same way. Here, the sensitivity as well as the response time of the membrane electrodes were improved by the addition of *p*-ethoxychrysoidine during the precipitation, although the particle size was again virtually unaffected. Increase in the excess of calcium(II) used for precipitation tended to improve the sensitivity of the final membrane; precipitates from 45% excess calcium gave membranes which possessed *ca.* 80% of the theoretical sensitivity for changes in fluoride ion over the range 10^{-2} to $10^{-4}M$ (Fig. 3, lines 1–3). Below $10^{-4}M$ fluoride, the potential of the electrodes showed no simple linear dependence on pF. The incorporation of some carbon into the membrane with the calcium fluoride improved the response considerably in the 10^{-4}–$10^{-5}M$ decade (Fig. 3, line 4) and also improved the response time.

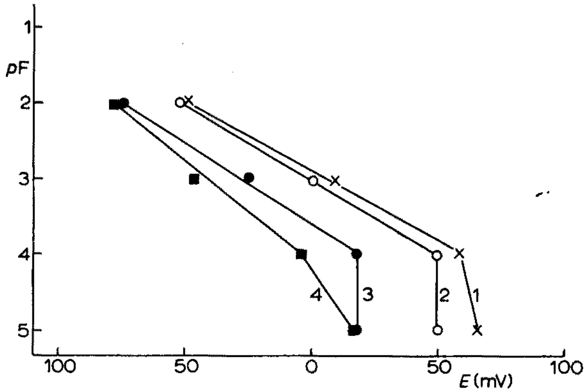

Fig. 3. E *vs.* pF curves for different membranes prepared from calcium fluoride (made with 45% excess of Ca^{2+}). Curves 1–3 were obtained with CaF_2 only in the membrane; for curve 4, graphite was also incorporated.

A disadvantage of the electrodes was their tendency to swell during storage in water or saturated calcium fluoride solution; after such storage for two weeks, the electrodes had lost *ca.* 20% of their sensitivity as indicated by the decrease in slope of the E–pF plot. This may have been due to the rather hygroscopic nature of the calcium fluoride after oven-drying. Membranes prepared from ignited calcium fluoride were virtually unresponsive to changes in fluoride concentration.

Attempts to make a fluoride-sensitive electrode by incorporating powdered fluorspar in the membrane failed, as did tests with a large single crystal of fluorspar, despite pretreatment with calcium(II) solutions. Obviously the natural substances are too inert to have any possibilities.

CONCLUSIONS

Of the various precipitates studied for the production of a fluoride-sensitive membrane electrode, thorium fluoride electrodes proved to be unreproducible even under optimum conditions, probably because of variable complex formation. Both lanthanum fluoride and calcium fluoride electrodes proved to give selective responses for fluoride. The response of the lanthanum fluoride electrodes over the 10^{-2}–$10^{-4}M$ fluoride range corresponded more nearly to the theoretical slope according to the Nernst equation, than did the calcium fluoride electrode; this may be due to the difference in solubility products of the two precipitates. It has been shown by PUNGOR *et al.*[7–9] that, for membrane electrodes, the lower limit of detection of an ion is closely related to the solubility of the salt incorporated in the membrane. The pK_{so} value[10] for calcium fluoride is *ca.* 10 and, according to LINGANE[15], *ca.* 17 for freshly precipitated lanthanum fluoride. From these values, the theoretical lower limit of detection is *ca.* 10^{-4} g-ion/l, and this is the value which was found experimentally.

This study has shown the vital importance of the method of preparing the precipitate. If an excess or an equivalent amount of fluoride is used, the final membranes are non-selectively ion-responding, probably by an adsorption effect. If an excess of the metal ion is used, then the final electrode generally responds selectively to fluoride, provided that a correct proportion of precipitate (50–60%) is incorporated. The fluoride electrodes were found to have a much higher resistance than the silver iodide electrode but this could be partially overcome by mixing graphite with the silicone rubber along with the precipitate.

Some preliminary studies on the behaviour of membranes containing mixed fluorides have been made. For example, an electrode made from barium fluoride spiked with lanthanum fluoride showed a moderate response at the $10^{-5}M$ fluoride level. Further work along these lines is in progress. Other rare earth fluorides will also be investigated.

We are grateful to Prof. E. PUNGOR, Veszprém, for valuable advice and discussions and for granting leave of absence (1965–66) to one of us (K.T.); and to Prof. M. STACEY, F.R.S., and Prof. R. BELCHER for their interest in this work. The work was made possible by a Science Research Council grant, which is gratefully acknowledged.

SUMMARY

Fluoride-sensitive membrane electrodes of the PUNGOR type are described. In these electrodes, a fluoride precipitate is incorporated in a silicone rubber membrane; fluorides of thorium, lanthanum and other rare earths, and calcium have been examined. The method of preparing the precipitate is important; an excess of metal is vital for correct functioning of the final electrode. The most reliable results were obtained with calcium fluoride electrodes, though their sensitivity was less than that of the best lanthanum fluoride electrodes. With these electrodes, linear responses are obtained in the 10^{-2}–$10^{-4}M$ fluoride range.

RÉSUMÉ

On décrit des électrodes à membranes au fluorure de type Pungor. Un précipité de fluorure est incorporé dans une membrane de caoutchouc silicone; on a essayé les fluorures de calcium, thorium, lanthane et autres terres rares. La façon de préparer le précipité est importante; un excès de métal est vital pour un fonctionnement correct de l'électrode finale. Les meilleurs résultats ont été obtenus avec des électrodes au fluorure de calcium bien que leur sensibilité soit inférieure à celle des meilleures électrodes au fluorure de lanthane. On a obtenu des résultats linéaires au moyen de ces électrodes pour des concentrations en fluorure de 10^{-2} à 10^{-4} M.

ZUSAMMENFASSUNG

Fluoridempfindliche Membran-Elektroden des Pungor-Typs werden beschrieben. Bei diesen Elektroden wird ein Fluorid-Niederschlag innerhalb einer Silikon–Gummi-Membran gebildet. Die Fluoride des Thoriums, Lanthans und an-

derer Seltener Erden und des Calciums wurden geprüft. Die Herstellung des Niederschlages ist wichtig, da ein Überschuss des Metalls für die einwandfreie Funktion der Elektrode wesentlich ist. Die zuverlässigsten Ergebnisse wurden mit Calciumfluorid-Elektroden erhalten, obwohl ihre Empfindlichkeit geringer war als die der besten Lanthanfluorid-Elektroden. Mit diesen Elektroden wurden lineare Beziehungen im Bereich von 10^{-2} – 10^{-4} M Fluorid gefunden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF METALLIC IRON, NICKEL AND COBALT IN REDUCED ORES AND OXIDES

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(Received October 20th, 1967)

A research programme required that metallic iron, nickel and cobalt be determined in the presence of mixtures of oxides of all 3 elements; suitable chemical procedures for the determination of metallic nickel and cobalt under such conditions are not available from the literature. X-ray diffractometry has been used[1,2] for the analysis of mixtures of metals and oxides, but when the 3 metals are present, metallic phases of indefinite composition may be formed and a quantitative characterisation of the system may not be possible. Further, the reduction of individual particles of oxides can produce a metallic shell containing an oxide core; subsequent subdivision of this assembly to dimensions suitable for X-ray diffractometry can introduce difficulties.

Chemical procedures have been developed for the determination of metallic iron in the presence of iron oxides. The principal requirement of these procedures is to dissolve the metallic iron selectively and without significant attack on the iron oxides present. The procedures have been based generally on the oxidation of iron by readily reducible ions in aqueous solution or by halogens in non-aqueous media; HABASHY[3] used copper(II) with a mercury catalyst and MORRIS[4] used mercury(II), TKACHENKO *et al.*[5] used mercury(II) in ethanol, ROONEY AND STAPLETON[6] used iodine–ethanol, CLASSEN[7] used bromine–ethanol and KRAFT AND FISCHER[8] used bromine–methanol.

Suitable procedures should be applicable to reduced ores containing large or small amounts of metallic phases, present either as large or finely divided metallic particles. Preliminary studies indicated that the method of HABASHY[3] attacked nickel and cobalt oxides. The procedures based on mercury(II) were found to require finely divided samples and the residual mercury in solution was inconvenient in the subsequent nickel and cobalt determinations. Consequently, the bromine–methanol method of KRAFT AND FISCHER[8] was studied for the determination of metallic nickel and cobalt in the presence of oxides. The procedure would dissolve sulphides[9] as well as metals; however, sulphides were at very low concentration in the samples of interest, and if present an appropriate correction can be made. Iron, nickel and cobalt in the resultant solution were determined directly by atomic absorption spectrophotometry[10–12].

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EXPERIMENTAL

Reagents and apparatus

Iron, mild steel turnings (Ni 0.009%, Co 0.012%). Nickel sheet (B.D.H. Ltd.; Co < 0.005%, Fe < 0.1%). Cobalt pellets (B.D.H. Ltd). Fe_2O_3 (Johnson Matthey, Ltd.; Ni 0.0001%, Co < 0.0001%). $NiO + Ni_2O_3$ (B.D.H. Ltd.; Co < 0.002%, Fe < 0.01%). Co_2O_3 (B.D.H. Ltd.; Fe < 0.01%, Ni < 0.004%). FeO, prepared by heating iron(II) oxalate in nitrogen at 700° for 1 h[8].

Methanol (Mallinckrodt, water < 0.20% w/v) was used with hydrogen peroxide (30% w/v), bromine and hydroxylamine hydrochloride, all of which were AnalaR products (B.D.H. Ltd.).

An atomic absorption spectrophotometef (Techtron, Melbourne), was used for the final measurements.

Recommended procedure

Transfer 500 mg of dry sample (powder of 100 B.S. mesh; malleable, one dimension less than 1 mm) to a dry 150-ml Erlenmeyer flask (B24 neck). Prepare a calibration series for the range 0–12% Fe, 0–4% Ni and 0–0.4% Co.

Insert an air condenser (12 cm × 2 cm I.D.), add 50 ml of 5% (v/v) bromine in methanol, cover with a watch glass and boil gently until dissolution of the metallic phases is complete; this takes at least 15 min. Cool, filter on a Whatman No. 540 paper into a 250-ml Erlenmeyer flask and wash with 50 ml of methanol. Add 20 ml of 50% (v/v) hydrochloric acid and 5 ml of 75% (w/v) hydroxylamine hydrochloride solution and mix well. Stand until the reduction of bromine is complete. Add 3% (w/v) hydrogen peroxide until the straw colour of the chloroferrate complex is fully developed. Boil gently for 5 min to decompose excess hydrogen peroxide, cool and dilute with water to 200 ml.

Make atomic absorption spectrophotometric measurements for iron at 2483.27 Å, nickel at 2320.03 Å and cobalt at 2407.25 Å, using a premixed air–acetylene flame and a laminar flow burner.

RESULTS AND DISCUSSION

The time required for complete dissolution of the metallic component of the samples varied from 15 min for 100%–100 B.S. mesh samples to 120 min for samples with not more than 1-mm malleable particles present.

KRAFT AND FISCHER[8] showed that bromine–methanol selectively dissolved metallic iron from iron–iron oxide mixtures, and that Fe_3O_4 and FeO added as individual phases were unattacked.

A series of tests was carried out on a partly reduced lateritic nickel ore sample (total Fe, Ni, Co, 16.7, 1.75, 0.19% respectively; metallic Fe, Ni, Co, 10.06, 1.28, 0.105%, respectively; sample 100%–100 B.S. mesh), with reaction times varying from 15 to 180 min. Within this time range, the results for metallic iron, nickel or cobalt were independent of reaction time, which indicated that dissolution of the oxides present did not occur. However, as a variety of oxides can be present in reduced ore samples it was necessary to carry out more comprehensive tests.

A study was designed to determine the solubility of iron, nickel or cobalt oxides in bromine–methanol. To simulate the conditions of the determination, each element was added in the metallic state to appropriate oxide mixtures. In each experiment the reaction time was 120 min, and the amounts of the two elements other than that added as metal were determined in the solution. In initial tests, the dissolution of some oxide material was observed. However, this was found to be caused by water (either adsorbed or present as hydroxyl groups) which formed hydrobromic acid and hypobromous acid. Therefore, the oxides used in subsequent tests were heated to 780° in a nitrogen atmosphere to remove free and combined water. The study demonstrated that there was no significant oxide reaction with the bromine–methanol reagent (see Table I).

TABLE I

THE INFLUENCE OF OXIDE ADDITIONS ON THE VALUES DETERMINED FOR METALLIC IRON, NICKEL AND COBALT

Taken		*Found*		
Metal (200 mg)	*Oxides (400 mg total addition)*	*Element in solution (mg)*		
		Fe	*Ni*	*Co*
Fe		n.d.[a]	0.018	0.024
Fe	Fe^{2+}, Fe^{3+}	n.d.	0.018	0.024
Fe	Ni^{2+}, Ni^{3+}	n.d.	0.018	0.024
Fe	Co^{3+}	n.d.	0.018	0.024
Fe	Fe^{2+}, Fe^{3+}, Ni^{2+}, Ni^{3+}, Co^{3+}	n.d.	0.018	0.020
Ni		0.068	n.d.	<0.002
Ni	Fe^{2+}, Fe^{3+}	0.068	n.d.	<0.002
Ni	Ni^{2+}, Ni^{3+}	0.068	n.d.	<0.002
Ni	Co^{3+}	0.068	n.d.	<0.002
Ni	Fe^{2+}, Fe^{3+}, Ni^{2+}, Ni^{3+}, Co^{3+}	0.068	n.d.	<0.002
Co		<0.002	0.140	n.d.
Co	Fe^{2+}, Fe^{3+}	<0.002	0.134	n.d.
Co	Ni^{2+}, Ni^{3+}	<0.002	0.140	n.d.
Co	Co^{3+}	<0.002	0.140	n.d.
Co	Fe^{2+}, Fe^{3+}, Ni^{2+}, Ni^{3+}, Co^{3+}	<0.002	0.140	n.d.

[a] n.d. = not determined.

Although bromine–methanol had been shown to be a selective solvent for metallic iron, nickel or cobalt individually in the presence of their mixed oxides, it was necessary to demonstrate that there were no extraneous reactions when all 3 elements were present both as metals and oxides. Accordingly, oxides of the individual elements were partially reduced with hydrogen at 800°, and the metallic contents were determined by the proposed method. The analysis was then repeated in the presence of suitable amounts of the other 2 elements, added both as metal and oxide. The results are presented in Table II, and demonstrate that recovery of the metallic elements is not influenced by these additions.

After it was observed that free and combined water produced increased dissolution of metal oxides, the possible influence of water present in the bromine–methanol reagent was studied. The water content of the methanol used was determined by titration with Karl Fischer reagent and found to be 0.024% (maximum specification, 0.20%). Accordingly, a series of bromine–methanol solutions with incremental additions of water was prepared and dissolution of iron(III) oxide in these mixtures was measured after a reaction period of 120 min; the results are presented in Table III. Within the range of water contents studied, a progressive increase in the water content produced a corresponding increase in the dissolution of iron(III) oxide. The results indicated that no difficulties would be encountered with adequate experi-

TABLE II

THE INFLUENCE OF OTHER METALS AND METAL OXIDES ON THE OBSERVED METALLIC CONTENT OF A PARTIALLY REDUCED OXIDE

Partially reduced oxide (500 mg sample)	*Added mixture of metals and metal oxides (mg)*	*Metallic content observed*
Fe/FeO	—	8.3% Fe
Fe/FeO	15 Ni, 35 NiO, 5 Co, 45 CoO	8.3% Fe
Ni/NiO	—	2.78% Ni
Ni/NiO	4 Fe, 46 FeO, 5 Co, 45 CoO	2.77% Ni
Co/CoO	—	0.175% Co
Co/CoO	4 Fe, 46 FeO, 15 Ni, 35 NiO	0.174% Co

TABLE III

THE INFLUENCE OF WATER ON THE DISSOLUTION OF IRON(III) OXIDE IN 5% (v/v) BROMINE–METHANOL

(500 mg Fe_2O_3, 50 ml 5% (v/v) Br_2–CH_3OH)

% Added water	0.0	0.1	0.5	1.0	2.0
% Fe_2O_3 dissolved	0.00	0.09	0.57	1.20	2.66

TABLE IV

RESULTS OBTAINED WITH A REDUCED NICKEL ORE AND STANDARD ALLOYS

Sample taken	*Found*		
	% Metallic Fe	*% Metallic Ni*	*% Metallic Co*
Nickel ore 16.7% total Fe, 1.75% total Ni, 0.19% total Co (51% SiO_2, 5% Al_2O_3, 18% MgO)	10.06[a] ($1\sigma \equiv 0.028$)	1.28[a] ($1\sigma \equiv 0.015$)	0.105[a] ($1\sigma \equiv 0.003$)
NBS 101d (45 mg) + Nickel sheet (455 mg) 6.27% Fe (92% Ni, 0.7% Cr)	6.27[a] ($1\sigma \equiv 0.050$)	n.d.[b]	n.d.
BCS 254 2.08% Ni (94% Fe, 0.5% V, 1.3% Mo, 0.5% Cr)	n.d.	2.08[a] ($1\sigma \equiv 0.046$)	n.d.
NBS 126a 0.30% Co (36% Ni, 63% Fe, 0.4% Mn)	n.d.	n.d.	0.301[a] ($1\sigma \equiv 0.002$)

[a] mean of 5 results.
[b] n.d. = not determined.

mental technique and reagents, *i.e.* with water removed from ore samples, dry glassware, and methanol with a water content of less than 0.05%.

A series of standard alloys and a reduced nickel ore were analysed by the proposed procedure (Table IV). The ore used for this test had been ground to 100 B.S. mesh; the reproducibility obtained on samples containing larger particles would be limited by the sampling procedure. The reproducibility and accuracy are satisfactory, thus confirming the validity of the proposed procedure.

Appreciation is expressed to the Research Manager, The Broken Hill Proprietary Company Ltd., for permission to publish this work.

SUMMARY

A procedure is described for the determination of metallic iron, nickel and cobalt in reduced ores and oxides. The metallic phases are dissolved in bromine–methanol solution, excess of bromine is destroyed by reaction with hydroxylamine hydrochloride and the analysis is completed by atomic absorption spectrophotometry. Solution of oxide phases is not observed if free or combined water is removed from the samples. Results are presented for an ore and standard alloys.

RÉSUMÉ

On décrit un procédé pour le dosage du nickel, du cobalt et du fer métalliques dans des minerais et oxydes réduits. Les phases métalliques sont dissoutes dans une solution brome–méthanol. L'excès de brome est détruit par le chlorhydrate d'hydroxylamine; le dosage est finalement effectué par spectrophotométrie par absorption atomique. Des solutions de phases oxydes ne sont pas formées si l'eau libre ou combinée est séparée des échantillons. Des résultats sont donnés pour un minerai et des alliages étalons.

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben zur Bestimmung von metallischem Eisen, Nickel und Cobalt in reduzierten Erzen und Oxiden. Die metallischen Phasen werden in einer Lösung aus Brom und Methanol gelöst, der Überschuss des Broms wird durch Reaktion mit Hydroxylaminhydrochlorid zerstört und die Analyse mit Hilfe der atomaren Absorptionsspektralphotometrie durchgeführt. Ein Lösen der oxidischen Phasen wird nicht beobachtet, wenn freies oder gebundenes Wasser aus den Proben entfernt wird. Ergebnisse werden für ein Erz und Standardlegierungen angegeben.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF BIURET IN UREA AND MIXED FERTILIZERS

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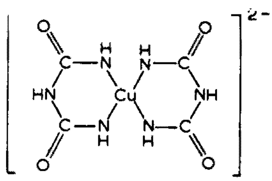
(Received November 1st, 1967)

The photometric methods for the determination of biuret are, in general, based on the reaction of biuret with copper in basic solution (the well known biuret reaction). The excess of copper is kept in solution by tartrate.

According to AIDA *et al.*[1] the red-coloured reaction product is:



Several standard methods of analysis based on this principle have been published[2–6]. Biuret also forms coloured reaction products with nickel, cobalt and cadmium. SVERAK[7] describes a method based on the reaction with nickel, which, however, is less sensitive.

In this laboratory a comparative study has been made[8] of the methods given in references 2–5 and the DSM standard method. The first four methods are almost identical; the DSM method differs from them in that the concentration of the reagent is considerably lower, so that the blank is also much lower. The latter method is thus to be preferred if small amounts of biuret have to be determined. In the removal of turbidity excellent results were obtained by adding solutions of Carrez I and II[8]. A precipitate of $K_2Zn_3[Fe(CN)_6]_2$ was obtained which settled rapidly and was easy to filter. This method is greatly superior to precipitation of iron hydroxide[5].

There is no detailed information in the literature about the influence of acidity, copper and tartrate concentrations on the results, or about the effect of constituents of urea solutions and mixed fertilizers. In the present paper these points are further investigated.

The sensitivity of the methods mentioned above is not very adequate for concentrations of 0.5% or less. At this concentration and with a sample weight of 1 g, the absorbance is about 0.06 while the blank is as high as 0.44. Frequently, the authors were faced with the problem of determining very small concentrations of biuret with a high relative accuracy. The photometric method did not suffice in these cases and therefore another method was developed. Again use was made of the copper–biuret complex. This complex behaves like an anion and may therefore be concentrated on

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an anion-exchanger and thus separated from any cation (excess copper included) and from neutral substances like urea. After elution with a suitable salt solution, the copper bound to biuret may be determined by compleximetric titration. It was found that a very accurate method could be based on this principle. For an exact determination of biuret in process solutions and end-products of a urea factory, this method certainly is superior to the photometric method. This separation procedure may well be used as a concentration step, so that the sensitivity may be enhanced considerably. This paves the way to the determination of traces of biuret.

PHOTOMETRIC DETERMINATION OF BIURET

A systematic study was made of the influence of alkalinity and of the copper and tartrate concentrations. The possible interference of urea, phosphate, nitrate, sulphate and chloride was also examined. The methods chosen were the DSM method and that of the AOAC. The latter method is almost identical with those of refs. 3, 4 and 5. The difference between the methods used concerns the final concentrations of base, copper and tartrate (Table I).

TABLE I

CONCENTRATION OF REAGENTS IN THE METHODS OF DSM AND AOAC

Reagent	*DSM method*	*AOAC method*
Base	0.1 *M* KOH	0.2 *M* NaOH
K Na tartrate	0.014 *M*	0.036 *M*
$CuSO_4$	0.0048 *M*	0.012 *M*

TABLE II

CHANGE IN pH ON ADDITION OF KOH

KOH (mg eq.)	*Method*	
	DSM	*AOAC*
0	4.8	4.7
1	11.6	9.9
5	12.6	12.1
10	12.8	12.4
20	13.1	12.9

Influence of alkalinity

Into 50-ml measuring flasks were introduced 0 and 10 mg of biuret and different quantities of potassium hydroxide. The prescribed quantities of tartrate and copper sulphate were kept constant. After making up to the mark and mixing, the absorbance was measured with a Unicam SP 600 spectrophotometer at a wavelength of 555 nm in 4-cm cells. The results are shown in Fig. 1. For a complete development of the copper–biuret colour a pH of 12 has to be reached (Fig. 1 and Table II). At still higher pH values the absorbance remains constant. The absorbance of the blank gradually increases with increasing alkalinity. It is of primary importance to have a reproducible blank, especially with the AOAC method, where the concentration of copper is 2.5 times as high as in the DSM method. The influence of the blank in the AOAC method appears from the curve for the determination of 10 mg of biuret (Fig. 1, dotted curve). The absorbance of the blank here is four times the absorbance of the copper–biuret complex. This means that small deviations in the blank cause rather large errors in the biuret value. The alkalinities of the blank and the sample solution must be almost equal. With several kinds of samples this will not be easy to realize.

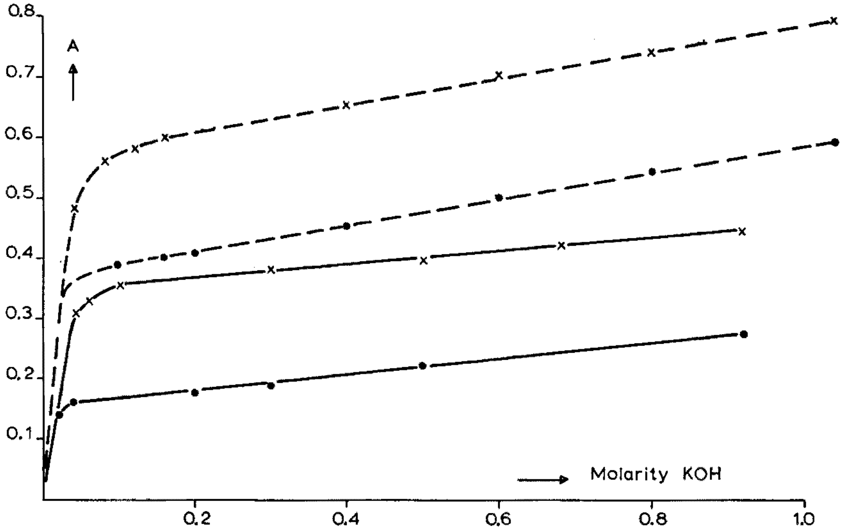


Fig. 1. Influence of alkalinity. ———DSM method, — — — — AOAC method. ● and ×, 0 and 10 mg of biuret respectively.

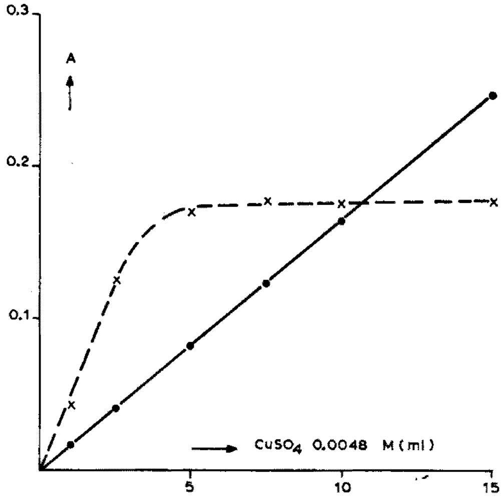


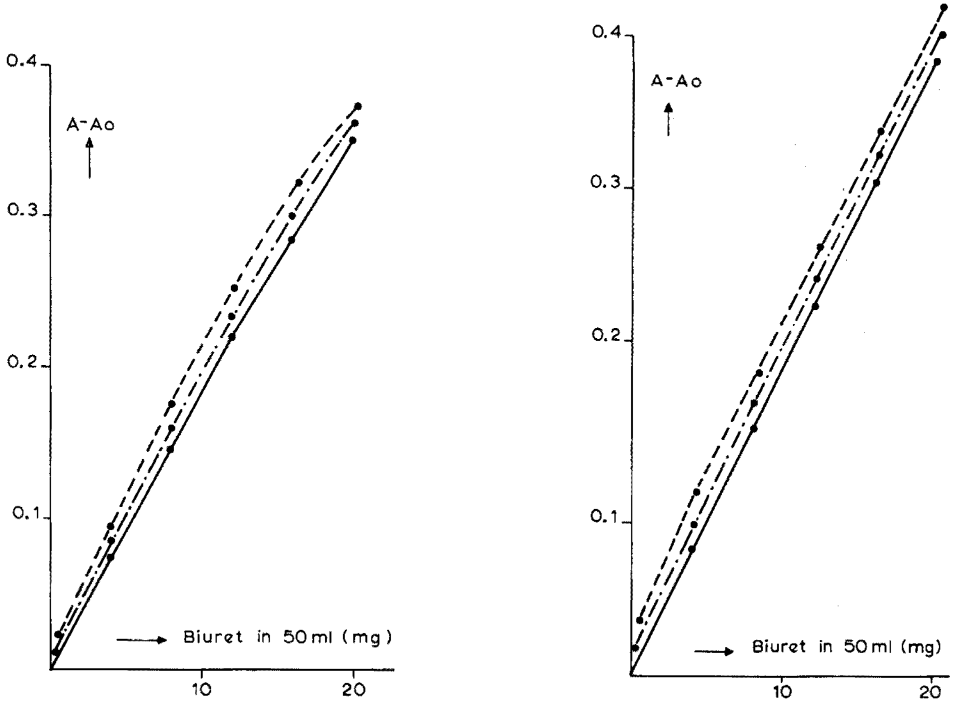
Fig. 2. Influence of copper. —×—×— absorbance of copper–biuret complex; ——— absorbance of blank.

Influence of copper concentration

To 0 and 10 mg of biuret the prescribed quantities of base and tartrate and different quantities of copper sulphate were added. After making up to the mark and mixing, the absorbance was measured. Figure 2 shows the results obtained with the DSM method (the AOAC method yields the same picture). It appears that in this case 5 ml of 0.005 *M* copper sulphate suffices for optimal colour development. Larger quantities of copper produce a proportional rise of the blank whereas the absorbance of the copper–biuret complex remains constant; thus the accuracy of the determination diminishes. Accordingly, the quantity of copper sulphate should be adapted to the expected quantity of biuret.

Interference by urea

With both methods, standard curves were constructed for concentrations of 0–20 mg of biuret in 50 ml. The experiments were repeated with addition of 4 and 8 g of urea, which had been crystallized twice and contained 0.007 % biuret (determined titrimetrically after separation from urea with an ion exchanger); the biuret content was taken into account. In the construction of the curves use was made of the blank obtained without addition of urea. The results are given in Figs. 3 and 4, which show that in the presence of urea higher absorbance values are found. If this is not taken into account, the figures for the biuret content will be *too high*. The relative error at a biuret content of 0.1% is about 20%.



Figs. 3–4. Interference by urea: (3) DSM method; (4) AOAC method. ———— standard curve; — · — · — · standard curve with addition of 4 g of urea; – – – – – – standard curve with addition of 8 g of urea.

This fact has not been reported in any previous publication on this subject.

It may be concluded that for every gram of urea in 50 ml of solution a correction of −0.0034 absorbance units has to be made, which corresponds to 0.17 mg of biuret. In many cases this correction will suffice. For an exact determination, especially at low biuret values, it is recommended to use standard curves with known quantities of urea free from biuret.

Interference by components of mixed fertilizers

Most mixed fertilizers contain ammonium, calcium, magnesium and potassium in the form of nitrates, phosphates, sulphates and/or chlorides. Ammonium interferes by forming a deep blue copper–ammonia complex. On the other hand, precipitates of calcium phosphate and magnesium hydroxide may be formed. These interferences may be overcome by removal of the cations by means of a strongly acid cation exchanger, as is prescribed in the AOAC method (it should be noted that only this method gives detailed information about the pretreatment of samples of mixed fertilizers). In the present work only the influence of nitrate, sulphate, phosphate and chloride (added as sodium salts) was studied. The results are shown in Table III.

TABLE III

INFLUENCE OF NITRATE, PHOSPHATE, SULPHATE AND CHLORIDE ON THE PHOTOMETRIC METHOD

Component	*Added to 100 ml (mg)*	*DSM method*		*AOAC method*	
		mg biuret		*mg biuret*	
		Added	*Found*	*Added*	*Found*
NO_3^-	1000	5.0	5.1	10.0	9.9
SO_4^{2-}	1000	5.0	5.3	10.0	9.9
Cl^-	1000	5.0	4.9	10.0	9.8
PO_4^{3-}	100	5.0	4.7	5.0	4.7
Added as NaH_2PO_4	200	5.0	4.2	5.0	4.1
PO_4^{3-} added as aqueous solution at pH 12	1000	5.0	5.3	5.0	5.3

Nitrate, sulphate and chloride may be present in rather large quantities. The influence of the acidity in the presence of phosphate is clearly visible. According to the AOAC method, the acid eluate of the cation exchanger is neutralized to methyl red. Phosphate is then present as NaH_2PO_4, and with as little as 100 mg of phosphate the results are already somewhat low. The permissible amount of phosphate is enlarged if a pH value of 12 is used.

COMPLEXIMETRIC DETERMINATION OF BIURET

Recommended procedure

To a solution of the sample, 5 ml of 0.05 *M* copper sulphate, ammonia to a final concentration of 0.9 *M*, and sodium hydroxide to a final concentration of 0.3 *M* were added. The ultimate volume should be *ca.* 100 ml (ammonia kept the excess of copper in solution). This solution was passed through a column filled with the strongly basic anion-exchanger Dowex 1-X4 (OH form, 50–100 mesh, column diameter 22 mm, height 200 mm) and washed with 120 ml of wash solution (also 0.9 *M* in ammonia and 0.3 *M* in sodium hydroxide). Subsequently, the copper–biuret complex was eluted with 100 ml of 2 *M* potassium nitrate, and next with 100 ml of 0.2 *M* nitric acid. To the eluate were added the indicator glycine thymol blue, enough hydrochloric acid (s.g. 1.19) to form a yellow colour (colour change from red-violet via blue and green to yellow), and enough urotropine to turn the colour blue (pH 5.5–6). Subsequently, the copper was titrated with 0.01 *M* EDTA, to a colour change from blue to yellow (1 ml of 0.01 *M* EDTA ≡ 2.062 mg of biuret).

The whole column should be charged with copper–biuret complex once before use, because the exchanger may contain sites that absorb copper irreversibly.

Influence of the reagents

The concentrations of ammonia and sodium hydroxide in the prepared sample and in the washing liquid are not very critical. Every new batch of ion-exchanger should be checked by analysing a sample of known biuret content. A column can be used for at least 200 determinations. A quantity of 5 ml of 0.05 *M* copper sulphate suffices for samples containing not more than 40 mg of biuret. The quantity of the washing liquid (120 ml) is adapted to this.

Urotropine may contain traces of metals influencing the colour change of the indicator. Purification can be effected by means of a cation-exchanger in the ammonium form.

Interferences

Urea is not bound by the ion-exchanger, hence biuret in the p.p.m. range can be determined by taking large quantities of urea (*i.e.* 25 g). Up to 0.5 g of ammonium carbonate or carbamate does not interfere.

The influence of phosphate, nitrate, sulphate and chloride on the results was investigated by adding different quantities of these materials to 5 mg of biuret. The results are shown in Table IV. It appears that large quantities of anions interfere, which is easily understandable, since they are bound by the anion-exchanger and enter into competition with the copper–biuret complex. The sum of nitrate, phosphate, sulphate and chloride must not be more than 4 mg eq. of which not more than 1 mg eq. should be sulphate.

TABLE IV

INTERFERENCE BY NITRATE, PHOSPHATE, SULPHATE AND CHLORIDE IN THE TITRIMETRIC METHOD

Component	*Added (mg)*	*mg biuret*	
		Added	*Fcund*
NO_3^-	100	5.00	4.96
	200	5.00	4.84
	300	5.00	4.69
SO_4^{2-}	50	5.00	4.93
	100	5.00	4.68
	200	5.00	4.49
PO_4^{3-}	100	5.00	5.06
	200	5.00	4.75
	300	5.00	4.12
Cl^-	100	5.00	5.08
	200	5.00	4.80

Therefore this procedure is not very suitable for the analysis of mixed fertilizers, unless a preliminary ether extraction of the biuret is performed in a Soxhlet device. This extraction is also useful for the photometric determination of low biuret contents in mixed fertilizers.

Accuracy and precision

Quantities of 2.5, 5, 10 and 40 mg of biuret were dissolved in 50 ml of water and determined. The results are shown in Table V.

Both the accuracy and the precision are very satisfactory. Even with 2.5 mg of biuret the relative standard deviation is only 1.9%.

TABLE V

ACCURACY AND PRECISION OF THE TITRIMETRIC METHOD

Biuret taken (mg)	2.5	5	10	40
Number of determinations	10	11	10	12
Mean	2.50^4	5.00^2	10.05	39.94
Standard deviation	0.048	0.08	0.20	0.14
Relative standard deviation	1.9	1.6	2.0	0.4

The authors are greatly indebted to Dr. L. BLOM, under whose direction this work was carried out, for his constant interest and advice.

SUMMARY

A new method has been developed for the determination of biuret in urea, based on the separation of the copper–biuret complex with the aid of an anion-exchanger, followed by titration of the bound copper with EDTA. This method may be used directly for the determination of biuret in solutions and in end-products of a urea factory, even with biuret contents down to 0.001%. The well-known photometric method cannot be used for less than 0.1% biuret contents; corrections are needed for the interference of urea, and ammonia and insoluble products have to be removed. Both methods are suitable for the determination of biuret in mixed fertilizers down to 0.5%, provided that cations are first removed on a cation exchanger. However, the photometric determination calls for special precautions with regard to acidity when phosphates are present.

RÉSUMÉ

Une nouvelle méthode est proposée pour le dosage du biuret dans l'urée, basée sur la séparation du complexe cuivre–biuret à l'aide d'un échangeur d'anions, suivie d'un titrage du cuivre combiné au moyen d'EDTA. Ce procédé peut être utilisé directement pour le dosage du biuret dans des solutions et dans les produits finals de fabrication d'urée, même pour des teneurs en biuret de 0.001%. La méthode photométrique usuelle ne permet pas de doser des teneurs en biuret inférieures à 0.1%; d'autre part des corrections sont nécessaires et l'urée, l'ammoniaque et des produits insolubles doivent être éliminés. Dans le cas de dosages dans des engrais les deux méthodes peuvent être utilisées, à condition que les cations soient éliminés au préalable à l'aide d'un échangeur de cations. Le dosage photométrique exige certaines précautions en ce qui concerne l'acidité, lorsque des phosphates sont présents.

ZUSAMMENFASSUNG

Eine neue Methode wurde zur Bestimmung von Biuret in Harnstoff entwickelt. Sie beruht auf der Abtrennung des Kupfer–Biuret-Komplexes mit einem Anionenaustauscher und anschliessender Titration des gebundenen Kupfers mit AeDTE. Diese Methode kann direkt zur Bestimmung von Biuret in Lösungen und in den Endprodukten einer Harnstoffabrikation verwendet werden, und zwar hinab bis zu Gehalten von 0.001%.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE EFFECT OF CATALYSTS ON THE THERMAL DECOMPOSITION OF SODIUM SUPEROXIDE

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(Received September 22nd, 1967)

For a number of years considerable interest has been expressed in compounds containing unfamiliar oxidation states of oxygen, *i.e.*, the alkali metal superoxides and ozonides. Comprehensive reviews of the chemistry and applications of inorganic superoxides and ozonides have appeared[1,2]. Limited data, however, is available in the literature on the thermal decomposition of these compounds, and on the effect of catalysts on the decomposition process.

The thermal decomposition of sodium superoxide has been considered to proceed *via* a two-step process as illustrated by the following reactions:

$$2\ NaO_2 \rightarrow Na_2O_2 + O_2 \qquad (1)$$

$$Na_2O_2 \rightarrow Na_2O + \tfrac{1}{2}O_2 \qquad (2)$$

SHECHTER AND SHAKELY[3] have noted that sodium superoxide is "not thermally stable at 100°". At this temperature, however, their early studies indicate that the decomposition rate is slow. VOL'NOV[4,5] on the other hand, has reported that sodium superoxide is converted to the peroxide at 250° and the oxide is not formed until temperatures in excess of 311° are attained. RODE[6,7] has reported that the superoxide undergoes violent decomposition with the formation of the peroxide at 250° in oxygen, and at approximately 215° in dry, carbon dioxide-free air. Both Russian authors have noted that the decomposition is endothermic.

This paper describes an investigation of the thermal decomposition of sodium superoxide using the methods of simultaneous differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG). In addition, the DTA technique has been utilized to evaluate the effects of a number of metallic oxide catalysts and a pretreatment technique on the thermal decomposition of sodium superoxide.

EXPERIMENTAL

Apparatus

Differential thermal analysis data were obtained using a Stone apparatus, model DTA-11M. The cell geometry and construction of this instrument have been previously described[8,9]. A static self-generated atmosphere was employed in all tests; the temperature program rate was 10°/min and the reference material was aluminium oxide. A sample of pure sodium superoxide and a sodium superoxide

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sample diluted 1:1 with alumina were subjected to DTA and the thermograms were compared. Since there were no differences in the plots and since the inclusion of the diluent facilitated the cleaning of the test cell, all future samples included alumina as diluent. Because a comparison of the temperatures of the transitions was of prime interest, accurate weights of the test samples were not obtained. Rather the DTA sample holder was filled, and tapped several times to facilitate settling of the sample. Approximately equal volumes of the alumina reference material and test samples were used.

Because of the hygroscopic nature of the materials studied, it was necessary to take special precautions when loading the DTA sample holder to prevent contamination by atmospheric moisture. This was accomplished by fashioning a portable glove-bag from polyethylene. The bag was positioned over the sample holder and filled with dry nitrogen gas. A desiccant and the sample to be analyzed were placed inside and the entire enclosure was sealed with adhesive tape. After the sample holder had been loaded, the bag was removed. At the end of each run, the glove-bag was replaced, and the furnace, thus enclosed, was allowed to cool in the presence of the desiccant.

Simultaneous DTA, TG, and DTG data on the thermal decomposition of sodium superoxide were obtained using the Mettler Vacuum Thermanalyzer.

Materials

Sodium superoxide was obtained from the Mine Safety Appliances Company (*ca.* 98.0% purity). Metallic oxides were certified reagent-grade chemicals and were used without further purification or treatment. The polymeric phthalocyanine catalyst was synthesized by the condensation of pyromellitic dianhydride, urea, copper(I) chloride and boric acid according to the established procedure[10]. Pretreatment of several superoxide samples was effected by exposing vials of material in a desiccator containing water for specified periods of time.

RESULTS AND DISCUSSION

Decomposition of sodium superoxide

The DTA thermograms for several sodium superoxide samples containing various metal oxides are seen in Fig. 1. Only those catalyzed samples whose DTA thermograms were different from that of the uncatalyzed superoxide are shown. Examination of the curve for sodium superoxide reveals endothermic peaks at *ca.* 150 and 165° and a strong endotherm peaking at *ca.* 300°. Previously reported Russian work[4,11] substantiates the latter two peaks.

The endotherm beginning at 270° and peaking at 300° can be attributed to the decomposition of sodium superoxide to the peroxide according to reaction (1). To confirm this a sample of sodium superoxide was heated at 250° for 7 h and then analyzed. This analysis showed that the peroxide concentration increased while the superoxide content decreased. The superoxide concentration was determined by the method of SEY'B AND KLEINBERG[12]. A standard permanganate titration was used for the determination of the peroxide content. The results of a typical analysis are given in Table I.

It is interesting to note that VOL'NOV has reported that the thermogram of sodium superoxide displays only two endotherms[4] below 500°: at 145° and 278°. In order to confirm our initial experimental techniques and results, and to obtain a more complete record of the thermal decomposition, a sample of sodium superoxide and a sodium superoxide sample containing 1% by weight of copper(I) oxide catalyst were subjected to simultaneous DTA, TG, and DTG analysis[13]. These studies were performed using a temperature program rate of 4°/min and a dynamic atmosphere of dry air at a flow rate of 5.7 l/h. Aluminium oxide was the reference material and the sample holder was a platinum crucible[14]. The thermograms are shown in Figs. 2 and 3. The presence of 3 principal peaks at *ca.* 135°, 150° and 285° is indicated, in qualitative agree-

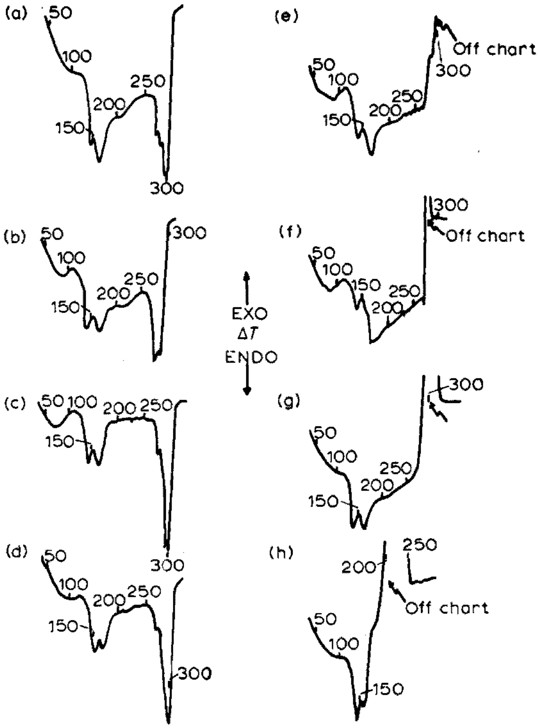

Fig. 1. DTA curves for sodium superoxide samples containing different catalysts. (a) Uncatalyzed; (b) PdO; (c) TiO_2; (d) CdO; (e) V_2O_5; (f) V_2O_3; (g) MnO_2; (h) polymeric copper phthalocyanine. Atmosphere: air (static); temperature rise rate 10°/min.

TABLE I

ANALYSIS OF SODIUM SUPEROXIDE BEFORE AND AFTER ISOTHERMAL DEGRADATION AT 250°

	Initial	*Final*
% NaO_2[a]	83.6	10.7
% Na_2O_2[b]	6.5	73.0
% Na_2O[c]	0.0	2.7
% NaOH[c]	9.2	12.2
% Na_2CO_3[c]	0.6	1.0

[a] Obtained by method of SEY'B AND KLEINBERG[12].
[b] Titration with permanganate.
[c] Determined from acid–base titration.

ment with the initial results. Because of the significant differences in experimental conditions (dynamic *vs.* static atmosphere, 4°/min temperature rise *vs.* 10°/min etc.) these temperatures, as would be expected, are slightly lower than those obtained with the Stone DTA apparatus.

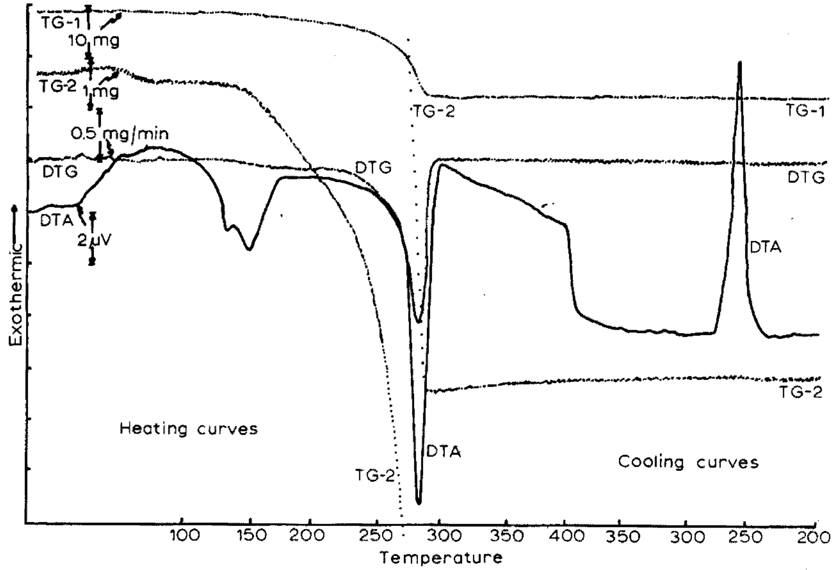

Fig. 2. Simultaneous DTA, TG and DTG plots for sodium superoxide. Sample wt. 70.1 mg; atmosphere: air at 5.7 l/h; temperature rise rate 4°/min.

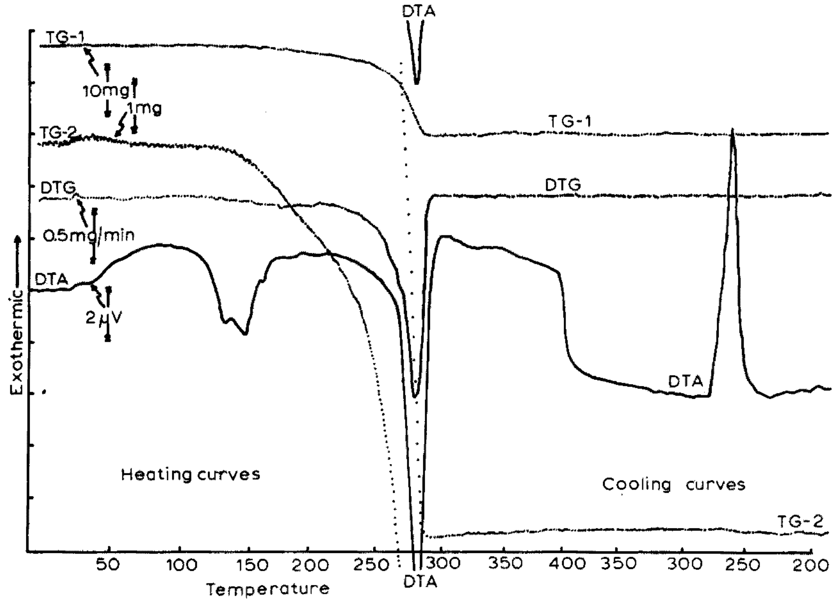

Fig. 3. Simultaneous DTA, TG and DTG plots for sodium superoxide sample containing 1% by weight copper(I) oxide. Sample wt. 100.0 mg; atmosphere: air at 5.7 l/h; temperature rise rate 4°/min.

The weight loss curve for sodium superoxide (Fig. 2, TG-1) simultaneously recorded with the DTA thermogram, exhibited only a slight decrease in weight at temperatures lower than 200°, with the principal break occurring in the 250° range. The expanded thermogravimetric curve (Fig. 2, TG-2 = 10 × TG-1) shows this break more clearly. From these curves it may be concluded that the decomposition of sodium superoxide involving the production of oxygen (weight loss) does not occur at a meaningful rate until temperatures near 250° are attained.

The curves for sodium superoxide containing 1% copper(I) oxide (Fig. 3) display identical peaks on the DTA and a similar break on the TG thermogram indicating that copper(I) oxide at this concentration level has no effect on the decomposition temperature of sodium superoxide under these conditions.

Examination of the DTG curves for the two samples reveals sharp peaks in both cases at *ca.* 285°. With the pure sample, the peak length represents a weight loss rate of 15.5 mg/min, while with the catalyzed material, the rate indicated is 19.0 mg/min. The addition of copper(I) oxide, therefore, does appear to cause a slight increase in the rate of decomposition of sodium superoxide.

These simultaneous analyses were performed to a temperature of 400°, at which time the furnace was turned off and the cooling curves were traced from 400° to room temperature. It is seen that the DTA cooling curve for sodium superoxide displays a strong exotherm at 260° while no comparable weight change is recorded at this temperature on the TG cooling curve (Fig. 2, TG-1 or TG-2). Since this exothermic peak occurs in the same temperature range as the endothermic peak on the heating curve which has been assigned to the decomposition of the superoxide to peroxide and oxygen, its presence indicates that the product(s) of the decomposition must undergo some physical transition at this temperature. This exotherm may correspond to the formation of a solid solution involving the peroxide. VOL'NOV[5] has indicated that sodium superoxide, sodium oxide and sodium hydroxide form solid solutions in this temperature range. The presence of the hydroxide may arise from trace amounts of water present in the original compound. If small amounts of water were present in the original sample, it is probable that the third peak noted at 150° on the Stone thermograms and at 135° on the Mettler curves, but not recorded by VOL'NOV, may be traced to the presence of impurities of the form $M_2O_2 \cdot 8H_2O$. The slight falling off of the curves below 100° also supports this view. The octahydrate of sodium peroxide has been reported to melt at 50–70° and to dehydrate[15] at 110–130°. Analysis of the original sodium superoxide (Table I) revealed the presence of peroxide contamination.

Effects of metallic oxide catalyst

DTA thermograms were obtained on sodium superoxide samples containing the various catalysts listed in Table II. Samples containing Cu_2O, Al_2O_3, NiO, Fe_3O_4, Fe_2O_3, Ag_2O and CdO gave thermograms essentially the same as pure sodium superoxide. Therefore, the DTA curves for these samples are not shown. Material containing PdO and TiO_2 (Fig. 1 (a) and (b)), however, gave thermograms in which the endotherm normally peaking at 300° in pure sodium superoxide, occurred at *ca.* 275°. These were the only two metallic oxide catalysts tested which lowered the temperature of the decomposition endotherm.

Completely different thermograms were obtained with superoxide samples containing vanadium and manganese oxides and the polymeric phthalocyanine (Fig. 1).

DTA plots containing these catalysts were characterized by uncontrollable exothermic reactions beginning *ca.* 270° in most cases. With the polymeric phthalocyanine catalyst this exotherm commenced about 170°. Because of this activity, samples containing these catalysts were subjected to isothermal kinetic analysis at 250°. The analyses of the products of the reactions revealed that a significant proportion of the catalysts had been solubilized by reaction. With the polymeric phthalocyanine catalysts, for example, a blue solution containing copper was obtained upon dissolution of the reaction product.

TABLE II

COMPOSITION OF SODIUM SUPEROXIDE SAMPLES INVESTIGATED BY DTA

Catalyst	*Formula*	*Catalyst concentration (% by weight)*	*Diluent*[a] *concentration (% by weight)*
None			49.7
Copper(I) oxide	Cu_2O	20.2	39.7
Vanadium(III) oxide	V_2O_3	15.5	51.5
Vanadium(V) oxide	V_2O_5	15.7	38.9
Palladium oxide	PdO	9.6	50.9
Titanium oxide	TiO_2	10.3	44.9
Nickel oxide	NiO	9.6	54.3
Iron(III) oxide	Fe_2O_3	9.0	50.2
Iron oxide (Magnetite)	Fe_3O_4	7.9	48.9
Manganese dioxide	MnO_2	10.1	46.0
Silver oxide	Ag_2O	11.4	50.0
Cadmium oxide	CdO	11.9	44.9
Polymeric copper phthalocyanine		12.7	39.7

[a] Al_2O_3.

Since the copper is not easily removed from the phthalocyanine without destroying the organic ring structure[16], it appears that the organic portion of the molecule has been attacked. This is an interesting observation in as much as the phthalocyanine nucleus is a relatively stable organic molecule. It must be noted however, that the catalyst used here was polymeric and contained a number of unreacted end groups[10] (probably carboxylic acid groups). The presence of these groups could increase the susceptibility to oxidative attack. Further work is being done with both monomeric and polymeric phthalocyanines to determine the exact nature of the reaction occurring with the superoxide.

Effect of preconditioning sodium superoxide

The DTA thermogram obtained for a sample of sodium superoxide which was first briefly exposed to a 100% humid atmosphere is shown in Fig. 4. Immediately obvious is the sharp exothermic peak at 80°. A similar exothermic effect in this temperature range has been observed with a number of peroxyhydrates ($M_2O_2 \cdot XH_2O_2$) and has been attributed to the dissociation of the crystallized hydrogen peroxide[19,20]. The monoperoxyhydrate of sodium peroxide, for example, has been reported[21] to decompose exothermically at 65°. Furthermore, the thermogram of the preconditioned sample displays a noticeable lengthening of the peak normally occurring at *ca.* 165° on the thermograms obtained. It has been reported that the diperoxyhydrate decomposes in this temperature range[22]. Thus the formation of both the mono- and diperoxyhydrates of sodium peroxide is suggested by the DTA data.

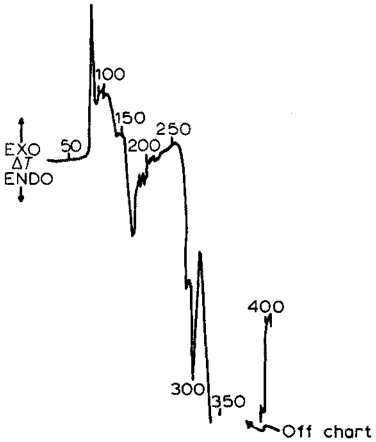

Fig. 4. DTA thermogram of sodium superoxide preconditioned by exposure to 100% humidity for 13 min. Atmosphere: air (static); temperature rise rate: 10°/min.

Mel'nikov *et al.*[15] in studying the reactions of water vapor with sodium superoxide have reported that at 20–25° the total active oxygen is liberated with the formation of sodium hydroxide. At temperatures less than 0°, these authors postulate the formation of sodium peroxide octahydrate:

$$2\ NaO_2 + 8\ H_2O \rightarrow Na_2O_2 \cdot 8\ H_2O + O_2$$

The octahydrate, however, decomposes[15] endothermically at 50–70°. The presence of the strong exotherm in this temperature range on our DTA plots would indicate that a species different from the hydrate has indeed been formed under our experimental conditions. This species is considered to be a peroxyhydrate of sodium peroxide. It should be noted that in the Russian experiments, water vapor was actually passed through the superoxide. The contact, therefore, was more complete and lasted for a considerably longer time period than our brief exposures. With longer exposure times, the formation of the hydrate and/or hydroxide no doubt will take place.

Based on the DTA data obtained in this work, the following reactions can be rationalized for the decomposition of sodium superoxide exposed briefly to 100% relative humidity:

The superoxide reacts with water vapor yielding mono- or diperoxyhydrates

$$4\ NaO_2 + 2\ H_2O \rightarrow 2\ Na_2O_2 \cdot H_2O_2 + O_2$$

or

$$2\ NaO_2 + 2\ H_2O \rightarrow Na_2O_2 \cdot 2\ H_2O_2$$

Upon heating, the peroxyhydrates dissociate to form hydrates of sodium peroxide

$$Na_2O_2 \cdot H_2O_2 \xrightarrow{\sim 80^\circ} Na_2O_2 \cdot H_2O + \tfrac{1}{2}O_2$$

$$Na_2O_2 \cdot 2H_2O_2 \xrightarrow{\sim 165^\circ} Na_2O_2 \cdot 2H_2O + \tfrac{1}{2}O_2$$

Dehydration of the formed hydrates then takes place upon further heating

$$Na_2O_2 \cdot H_2O \xrightarrow{\sim 290^\circ} Na_2O_2 + H_2O$$

The water released in the dissociation of the hydrate can react with the peroxide present resulting in complete disintegration of the sample

$$Na_2O_2 + 3\ H_2O \rightarrow 2\ NaOH + 2\ H_2O + \tfrac{1}{2}O_2$$

Because of the brief periods of exposure (less than 15 min) most of the initial reaction between the superoxide and the water vapor took place on the surface, and considerable amounts of sodium superoxide remained in the sample after exposure. The endotherm corresponding to the decomposition of the superoxide, therefore would be superimposed on that peak representing dehydration of the peroxide hydrate. The violent exotherm commencing at 300° (Fig. 4) was not obtained with dry untreated superoxide samples, and dramatically illustrates the effect of adsorbed water in bringing about the complete disintegration of the superoxide (and peroxide).

The authors thank the National Aeronautics and Space Administration for financial support. We are indebted to Dr. V. NACCI and Mr. S. HUSTON of the Civil Engineering Department of the University of Rhode Island for allowing the use of their Stone Differential Thermal Analysis unit. We also wish to thank Mr. H. P. VAUGHN of the Mettler Instrument Co. for his assistance in obtaining the DTA–TG–DTG thermograms.

SUMMARY

Simultaneous differential thermal, thermogravimetric and differential thermogravimetric analysis have been made on samples of sodium superoxide and sodium superoxide containing 1% (w/w) copper(I) oxide. Decomposition of the superoxide involving oxygen production (weight loss) does not occur at a meaningful rate until temperatures approach 250°. The effects of 12 metallic oxide catalysts and one metallo-organic catalyst on the decomposition of sodium superoxide have been studied by differential thermal analysis. Six metallic oxides had no effect while 3 oxides, (palladium oxide, titanium oxide and cadmium oxide) caused small but distinct changes in the DTA plots. A polymeric phthalocyanine, and the oxides of vanadium(III), vanadium(V) and manganese(IV) apparently reacted with the superoxide above 250°. Pretreatment of the superoxide by brief exposure to 100% humidity resulted in the formation of peroxyhydrates of sodium peroxide which upon dissociation produced water vapor in turn causing the release of oxygen from the superoxide and peroxide at lower temperatures than those experienced with untreated superoxide samples.

RÉSUMÉ

On a appliqué simultanément l'analyse thermique différentielle, thermogravimétrique et thermogravimétrique différentielle à des échantillons de superoxyde de sodium et de superoxyde de sodium contenant 1% d'oxyde de cuivre(I). La décomposition du superoxyde avec production d'oxygène (perte de poids) est négligeable jusqu'à 250°. On a examiné l'influence de 12 oxydes métalliques catalyseurs et d'un catalyseur organométallique sur la décomposition du superoxyde de sodium, par analyse thermique différentielle. Un prétraitement du superoxyde avec brève exposition à 100% d'humidité produit une formation de peroxyhydrates de peroxyde de sodium qui, après dissociation donne de la vapeur d'eau provoquant le dégagement d'oxygène du superoxyde et du peroxyde à des températures inférieures à celles mesurées avec des échantillons non traités.

ZUSAMMENFASSUNG

Natriumperoxid und Natriumperoxid-Proben, die 1 Gew. % Kupfer(I)-oxid enthielten, wurden gleichzeitig mit der DT-, TG- und DTG-Analyse untersucht, um katalytische Effekte auf die thermische Zersetzung von Natriumperoxid festzustellen. Die Zersetzung des Peroxids unter gleichzeitiger Bildung von Sauerstoff ist bis zu Temperaturen von 250° bedeutungslos. Der Einfluss von weiteren 12 metallischen oxydischen Katalysatoren und eines metallorganischen Katalysators wurde mit der DTA untersucht.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

N-BENZOYL-N-PHENYLHYDROXYLAMINE AND THE DETERMINATION OF TITANIUM

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(Received August 28th, 1967)

N-Benzoyl-N-phenylhydroxylamine (BPHA) was first synthesized by BAMBERGER[1] who recommended it as a possible analytical reagent. Since its re-introduction by SHOME[2] as a gravimetric reagent, BPHA has been used extensively for the determination of many metals[3]. Other N-acyl substituted phenylhydroxylamines have been synthesized and studied[4,5] but none shows any particular advantage (in ease of preparation, stability or reactivity) over BPHA as an analytical reagent. Spectrophotometrically, BPHA has been most successful for the determination of vanadium in 4–8 *M* hydrochloric acid solutions[6] and it, or similar compounds, has been widely used for the direct determination of small quantities of vanadium in ores, refractories, alloys, petroleum products, and biological materials.

Titanium is quantitatively precipitated by BPHA as a yellow compound of indefinite composition from 0.1–0.4 *N* hydrochloric acid; low results are obtained at higher acidities[2]. Spectrophotometrically, the titanium–BPHA complex is extracted into chloroform to give a yellow to orange colored extract whose color and intensity are very dependent upon the acid concentration of the initial solution. In recent years the benzoyl[7,8] and furyl[9] derivatives of phenylhydroxylamine have been used for the spectrophotometric determination of titanium. The present work reports the results of a detailed investigation of the conditions affecting the extraction of titanium–BPHA complexes and their use for the trace determination of titanium. In strongly acidic solutions (10–12 *M* hydrochloric acid), BPHA should prove as useful for the determination of titanium as it is for vanadium; with tin(II) chloride present only niobium (of a large number of metal ions tested) interferes seriously. The results obtained by the recommended procedure are compared with those obtained by other methods used for the trace analysis of titanium.

EXPERIMENTAL

Apparatus, reagents, and solutions

A Bausch and Lomb Spectronic 505 recording spectrophotometer was used to determine spectra of solutions and a Unicam SP 500 spectrophotometer was employed for measurements at a particular wavelength.

BPHA was prepared as previously described[10] and recrystallized from ethanol.

A stock titanium solution was prepared by dissolving high purity titanium dioxide in hydrofluoric acid, and, after evaporation nearly to dryness, the residue was fumed with 10 ml of concentrated sulphuric acid and then diluted to 500 ml with a 4% sodium oxalate solution. The standard contained 0.479 mg of titanium per ml as determined by precipitation with neocupferron and ignition to the oxide.

All other reagents were of analytical reagent grade quality.

Effect of acid on absorbance

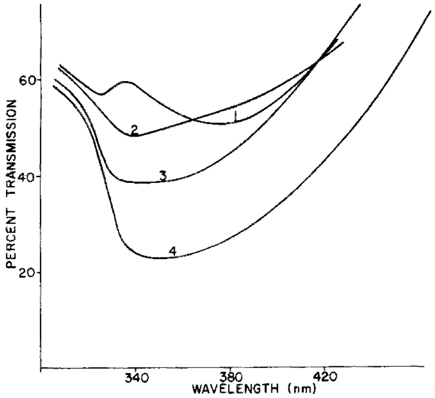
The titanium compound precipitated by BPHA from dilute acid is of varying composition and its solubility increases as the acid concentration increases[2]. In initial experiments to determine the effect of acid on absorptiometric measurements, varying amounts of hydrochloric, perchloric, or sulphuric acid were present in 25 ml of aqueous solution containing 75.7 μg of titanium. The solutions were extracted with two 10-ml aliquots of a 0.1% solution of the reagent in chloroform. The resulting organic phases, after careful phase separation, were collected in a 25-ml volumetric flask and diluted to the mark with chloroform. The results obtained, measured in a 1-cm cell against a reagent blank, are shown in Table I.

There was no noticeable color in the chloroform extract from 2–4 *N* acid but a yellow color developed at higher acidities and the intensity increased as the acid concentration was increased to 6 *N*; the absorbance leveled off in 10–12 *N* acid.

TABLE I

VARIATION IN ABSORBANCE WITH ACIDITY

Concentration (N)	*Hydrochloric acid*		*Sulphuric acid*		*Perchloric acid*	
	λ max. (nm)	*abs.*	*λ max. (nm)*	*abs.*	*λ max. (nm)*	*abs.*
6	370	0.0861	—	—	345	0.105
8	374	0.398	340	0.469	345	0.509
10	380	0.482	345	0.553	350	0.678
12	380	0.488	345	0.545	355	0.699



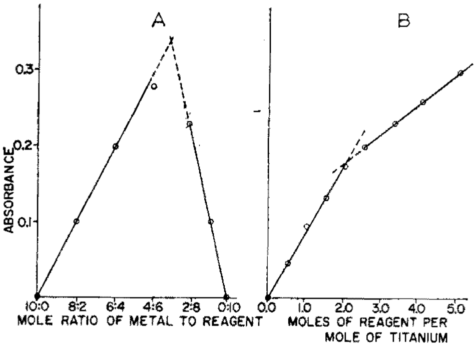


Fig. 1. Transmittance spectra of Ti^{4+}–BPHA complex extracted in chloroform from: (1) 10 *M* HCl; (2) 10 *M* H_2SO_4; (3) 10 *M* $HClO_4$; (4) 10 *M* HCl containing SCN^-.

Fig. 2. (A) Continuous variation plot of Ti^{4+}–BPHA extracted in chloroform from 10 *M* HCl; (B) mole ratio plot.

Figure 1 shows absorption spectra obtained from 10 N acids. Addition of thiocyanate to acids before extraction resulted in increased absorbance; the molecular extinction coefficient increased from $7.1 \cdot 10^3$ to $15.4 \cdot 10^3$ in 10 N sulphuric acid solutions and from $6.7 \cdot 10^3$ to $12.0 \cdot 10^3$ in 10 N hydrochloric acid in the presence of thiocyanate. Addition of sodium chloride to perchloric and sulphuric acid samples before extraction resulted in spectra similar to those obtained from hydrochloric acid solutions alone.

These results suggest that the differences observed are due to the formation of various association species involving anions. Compounds were therefore precipitated from fairly concentrated titanium solutions and analyzed. Chloride, sulphate, and thiocyanate were found in compounds separated from 10 N hydrochloric, sulphuric, and sulphuric acid containing thiocyanate, respectively: the composition varied with acid concentration and anion present. From sulphuric acid the titanium dioxide content varied from 13.8% (10 N H_2SO_4) to 14.7% (10 N $H_2SO_4 + SCN^-$); no precipitate was formed in 18 N sulphuric acid until thiocyanate was added. From 10 N hydrochloric acid the titanium dioxide content was 14.9% (theoretical for $Ti(BPHA)_2Cl_2$ is 14.7%): the compound precipitated from 10 N hydrochloric acid with thiocyanate present contained 13.2% TiO_2 (theoretical for $Ti(BPHA)_2(SCN)_2$ is 13.6%). Although the conditions of precipitation are not the same as those used in color development (and high purity of compounds precipitated is doubtful), it is apparent that ternary complexes containing titanium, BPHA and anion are formed over a wide range of acidity; the anions present and their concentration determine the species formed and the molecular extinction coefficient observed.

Effect of other ions

The above procedure was used in 10 N hydrochloric acid to study the effect of diverse ions on the absorbance obtained for the titanium complex. In the presence of 100-fold molar excess, for a solution $5 \cdot 10^{-5}$ M in titanium, chromium, iron, molybdenum, nickel, niobium, tantalum, vanadium and zirconium interfere as a result of absorption in the region of maximum absorption for the titanium complex; however, in the presence of tin(II) chloride, only niobium can be considered a serious interference. Similarly, 100-fold excesses of common anions such as acetate, citrate, fluoride, nitrate, oxalate, phosphate and tartrate did not interfere.

Determination of titanium

In order to apply BPHA to the determination of titanium in steels and other materials, the masking efficiency of tin(II) chloride on large amounts of iron was fully investigated. One gram of electrolytic iron was dissolved in hydrochloric acid, the solution was evaporated nearly to dryness, and the residue redissolved in a minimum amount of hydrochloric acid. The solutions were salted with 1.0 ml of $5 \cdot 10^{-4}$ M titanium solution and varying amounts of 5 M tin(II) chloride (in concentrated hydrochloric acid) added; the solutions were made 10 N in hydrochloric acid before extraction with a 0.1% solution of the reagent in chloroform. Iron showed no interference in the presence of 1–5 ml of tin(II) chloride solution but there was some difficulty in phase separation when 10 ml of tin(II) chloride solution were added; a Beer's law plot gave a straight-line calibration curve through the origin for 1.0–6.0 p.p.m. of titanium. The lower limit for determination was 0.25 p.p.m.; chloroform extracts from 10, 25, 50 and 100 ml of aqueous phase gave the same absorbance and increased sensitivity could be obtained through this concentration effect. Eleven samples, each containing 1.0 p.p.m. of titanium in the presence of 1 g of iron, were analyzed by the above procedure; the percent standard deviation was 1.3.

Table II shows the results obtained for titanium in the presence of 0.1 g of iron and other ions that are interferences if tin(II) chloride is not present before extraction. Niobium is the only serious interference; results are 10% high for a 30-fold molar excess of zirconium and are less than 5% high for a 25-fold molar excess of tantalum.

TABLE II

ABSORBANCE OF KNOWN TITANIUM SAMPLES IN THE PRESENCE OF 0.1 g IRON AND OTHER IONS

Absorbance expected[a] *(according to calib. curve for* $6.33 \cdot 10^{-5}$ *M solution of Ti)*	*Absorbance found*	*Foreign ions present (molar ratio to Ti)*
0.476	0.476	25-fold excess of Cr, Mo, Ni, U and V
0.476	0.483	- do -
0.476	0.469	50-fold excess of Cr, Mo, Ni, U and V
0.476	0.478	- do -
0.476	0.483	100-fold excess of Cr, Mo, Ni, U and V
0.476	0.469	- do -
0.476	0.523	30-fold excess of Zr
0.476	0.491	25-fold excess of Ta
0.476	0.814	2-fold excess of Nb

[a] Absorbances measured at 380 nm.

Table III shows the results obtained for the analysis of titanium in different materials. A suitable weight (0.1–1 g) of sample was dissolved by an appropriate procedure (Table III) and the solution was then diluted to a known volume in a volumetric flask. A 1-ml aliquot, containing 10–50 μg of titanium, was transferred to a separatory funnel, 2.5 ml of 5 *M* tin(II) chloride (in concentrated hydrochloric acid) added, and the solution diluted to approximately 25 ml with 10 *N* hydrochloric acid. The aqueous phase was extracted with two 10-ml portions of a 0.1% BPHA solution in chloroform, the extracts diluted to 25 ml with chloroform, and the absorbance measured at 380 nm against a reagent blank. The results recorded for each analysis are on separate samples and are not repeats of a single sample.

Ligand-to-metal ratio

Analysis of compounds precipitated from 10 *N* hydrochloric acid suggests that the ligand-to-metal ratio is 2:1. Figure 2 shows continuous variations and mole ratio plots obtained from 10 *N* hydrochloric acid; the BPHA to titanium ratio corresponds to 2:1 from both these studies. In sulphuric acid complete formation of the colored complex is not attained unless there is a large excess of reagent and a Job's plot and a mole ratio study failed to give conclusive results; however, in slope ratio studies with excess of reagent, the slope was approximately 60° suggesting formation of a 2:1 species.

TABLE III

ANALYSIS OF BCS AND NBS STANDARD SAMPLES

Sample	*Type of material*	*Certified values (%)*	*Found (%)*	*Dissolution procedure*
BCS 321	Mild steel	0.13	0.134, 0.132, 0.136	Steel dissolved in 12 *N* HCl, oxidised with HNO_3 and evaporated to dryness. The residue redissolved in 12 *N* HCl.
BCS 322	- do -	0.042	0.041, 0.040	- do -
BCS 324	- do -	0.034	0.033, 0.036, 0.035	- do -
NBS 170A	Basic open-hearth steel	0.28	0.279, 0.283, 0.281	- do -
NBS 87A	Silicon–aluminium alloy	0.18	0.165, 0.176, 0.174	Dissolved in acid mixture (150 ml of 36 *N* H_2SO_4, 300 ml of 12 *N* HCl, 100 ml of 18 *N* HNO_3 and 450 ml of H_2O) evaporated to dryness and redissolved with 12 *N* H_2SO_4 solution.
NBS 77A	Burnt refractory	2.93	2.90, 2.87, 2.90, 2.95	Fused with $KHSO_4$ and dissolved in 12 *N* H_2SO_4. Residue fused with $NaHCO_3$, dissolved in the same medium and the insoluble material, after filtration, was redissolved in the acid mixture (see above) and evaporated to dryness. Redissolved and was diluted with 12 *N* H_2SO_4.

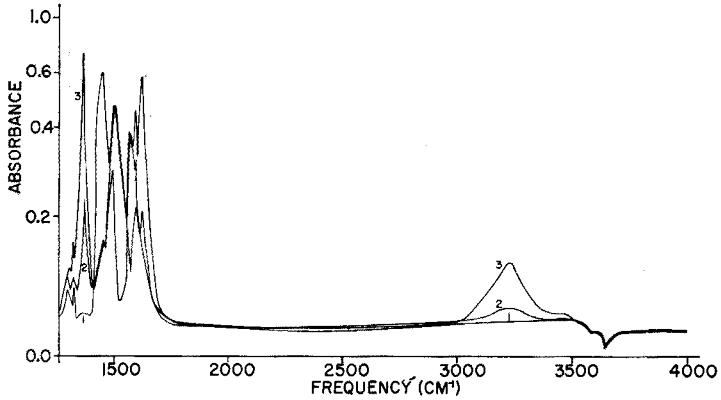


Fig. 3. Infrared spectra. (1) Ti^{4+}–BPHA complex extracted in chloroform when aqueous phase contained 4-fold molar excess of titanium to reagent; (2) Ti^{4+}–BPHA complex extracted in chloroform containing 2.5-fold molar excess of the reagent to titanium; (3) BPHA extracted in chloroform from 10 *N* HCl.

Figure 3 shows infrared spectra for chloroform solutions of BPHA and BPHA–titanium complexes extracted from 10 *N* hydrochloric acid solutions. BPHA shows a characteristic peak at 3225 cm^{-1} due to a hydrogen band stretching mode and a low frequency vibration at 1365 cm^{-1} (C=N?); these peaks are not present in BPHA–titanium complexes extracted from solutions containing excess titanium but they reappear after the ligand-to-metal ratio exceeds 2 to 1. A plot of absorbance measured at 1365 cm^{-1} against mole ratio of reagent is shown in Fig. 4.

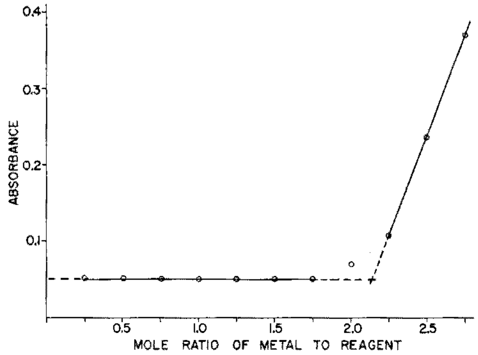


Fig. 4. Mole ratio plot at 1365 cm^{-1}.

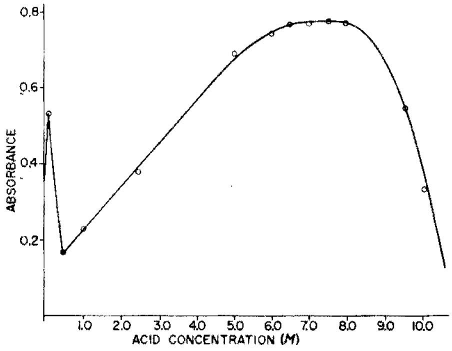


Fig. 5. Effect of variation of acid concentration on the extraction of Ti^{4+}–BPHA–SCN complex in chloroform.

Effect of thiocyanate

The use of thiocyanate to increase the color intensity of titanium–BPHA complexes has been reported[8,9]. Although the molecular extinction coefficient from sulphuric acid solutions containing thiocyanate was $15.4 \cdot 10^3$, this value decreases in the presence of tin(II) chloride to $11.1 \cdot 10^3$ (5 ml 5 *M* $SnCl_2$) which is comparable to that found from hydrochloric acid–thiocyanate solutions. Attempts to use tin(II) sulphate instead of the chloride to eliminate iron interference and retain the higher sensitivity of sulphuric–thiocyanate solutions were unsuccessful; the solubility of tin(II) sulphate in 10 *N* sulphuric acid is not large enough to be useful.

From hydrochloric acid solutions no appreciable increase in absorbance occurred up to a 25:1 molar excess of thiocyanate to titanium but the absorbance then increases as the concentration of thiocyanate is increased; consistent results were obtained if at least 2 ml of a 10% solution of potassium thiocyanate were present. The sensitivity obtained varies also with the amount of hydrochloric acid present. Figure 5 shows that maximum sensitivity in the presence of thiocyanate occurs between 6.5 and 8 *N* hydrochloric acid when 2 ml of a 10% potassium thiocyanate solution are added to the sample mixture before extraction; the high molecular extinction coefficient ($16.7 \cdot 10^3$) is attractive but 0.1 g of iron, in the presence of 2.5 ml of 5 *M* tin(II) chloride, interferes and the procedure with thiocyanate cannot be recommended for the analysis of steels.

The increase in color intensity of the titanium–BPHA complex extracted from hydrochloric or sulphuric acid solutions of titanium containing thiocyanate could be useful for the analysis of non-ferrous materials; in addition to iron, tantalum and zirconium interfere much more seriously in the presence of thiocyanate at the wavelength of maximum absorption (~350 nm). For general use, the extraction from 10 *N* hydrochloric acid solutions of titanium, with tin(II) chloride present, is to be recommended.

CONCLUSIONS

Various methods that have been used for the spectrophotometric determination of titanium are compared in Table IV. It is evident that non-selectivity of the reagent or the lack of suitable masking agents seriously limits the usefulness of most procedures. The commonly used hydrogen peroxide method, for example, requires careful control of experimental conditions for reproducible results; iron, molybdenum and vanadium must be removed if present in appreciable amounts, and the color is bleached by certain anions. Comparatively, the determination of titanium with BPHA in 10 *N* hydrochloric acid containing tin(II) chloride shows to advantage; the sensitivity is good (nearly 10 $>H_2O_2$), 100-fold molar excess of citrate, fluoride, oxalate, phosphate, and tartrate do not interfere, and the only serious cation interference, at 380 nm, is niobium.

TABLE IV

COMPARISON OF SPECTROPHOTOMETRIC METHODS FOR DETERMINATION OF TITANIUM

Reagent	*Extinction coefficient* ε^{nm}	*Interferences*
Gallic acid + sodium acetate	$\varepsilon^{400nm} = 15 \cdot 10^3$	Fe^{3+}, UO_2^{2+}, Ce^{4+}, Co^{2+}, CrO_4^{2-}, MoO_4^{2-}, VO_3^-, F^- and oxalate interfere. Al^{3+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Be^{2+}, Th^{4+}, etc. are precipitated in presence of excess of sodium acetate
Salicylic acid + sulphuric acid	$\varepsilon^{425nm} = 3.54 \cdot 10^3$	Fe^{3+}, Ce^{4+}, Cu^{2+}, Zr^{4+}, Th^{4+}, CrO_4^{2-}, MoO_4^{2-}, NbO_3^-, TaO_3^-, F^-, NO_3^- and NO_2^- interfere
Chromotropic acid, disodium salt	$\varepsilon^{410nm} = 11.5 \cdot 10^3$	Fe^{3+}, UO_2^{2+}, Hg^{2+}, Ag^+, CrO_4^{2-}, NbO_3^-, TaO_3^-, WO_4^{2-}, PO_4^{3-}, F^-, NO_2^-, and NO_3^- interfere. Zr^{4+} and Th^{4+} are precipitated
Tiron	$\varepsilon^{410nm} = 15.9 \cdot 10^3$	UO_2^{2+}, Fe^{3+}, VO^{2+}, MoO_4^{2-} and OsO_4^{2-}, interfere due to color formation. Ce^{4+} and CrO_4^{2-} absorb in the region of measurement. Al^{3+}, Ca^{2+}, Hg^{2+}, Pb^{2+}, Sn^{4+}, Th^{4+} and WO_4^{2-} consume the reagent. F^-, oxalate etc. form complexes with titanium
Salicylhydroxamic acid	$\varepsilon^{390nm} = 6.1 \cdot 10^3$	Fe^{3+}, Ce^{3+}, $Cr_2O_7^{2-}$, VO_3^-, WO_4^{2-} and PO_4^{3-} interfere
Hydrogen peroxide + sulphuric acid	$\varepsilon^{410nm} = 0.72 \cdot 10^3$	Fe^{3+}, Ce^{4+}, CrO_4^{2-}, VO_3^-, MoO_4^{2-}, and WO_4^{2-} interfere. F^-, oxalate, and citrate bleach the color
Benzoylphenylhydroxylamine + thiocyanate	$\varepsilon^{352} = 16.7 \cdot 10^3$	Fe^{3+}, Zr^{4+}, Nb^{5+}, Ta^{5+}
Benzoylphenylhydroxylamine	$\varepsilon^{380} = 6.7 \cdot 10^3$	Only Nb and slight interference due to Zr when present in more than 25-fold molar excess

Note. Above data was obtained from Ref. 11.

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

SUMMARY

Benzoylphenylhydroxylamine reacts with titanium in 10 *N* hydrochloric acid to give a ternary complex which, on extraction, permits the determination of 1–6 p.p.m. of titanium. Only niobium, in the presence of tin(II) chloride, is a serious interference. An enhanced sensitivity which is obtained if thiocyanate is present is advantageous if iron is absent. Titanium is accurately determined in steels, other alloys and refractories.

RÉSUMÉ

La benzoylphénylhydroxylamine réagit avec le titane en solution acide chlorhydrique 10 *N* pour donner un complexe ternaire qui, par extraction, permet le dosage de 1–6 p.p.m. de titane. Seul le niobium, en présence de chlorure d'étain(II) gêne sérieusement. Une addition de thiocyanate est avantageuse, en l'absence de fer; la sensibilité est ainsi améliorée. Le titane est dosé avec précision dans des aciers, autres alliages et matières réfractaires.

ZUSAMMENFASSUNG

Benzoylphenylhydroxylamin reagiert in 10 *N* HCl mit Titan zu einem ternären Komplex, der nach Extraktion die Bestimmung von 1–6 p.p.m. Titan erlaubt. Nur Niob führt in Gegenwart von Zinn(II)-Chlorid zu ernsthaften Störungen. Falls Eisen abwesend ist, lässt sich die Empfindlichkeit durch Thiocyanat verbessern. Titan wurde in Stählen, Legierungen und feuerfestem Material mit grosser Genauigkeit bestimmt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM IN ZIRCONIUM WITH 4-(2-PYRIDYLAZO)RESORCINOL

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(Received October 14th, 1967)

ELWELL AND WOOD[1] described the determination of 2–7% niobium in zirconium alloys, based on the formation of a yellow-coloured complex when niobium ions react with pyrogallol in an alkaline solution of ammonium oxalate; zirconium metal is dissolved by fusion with potassium hydrogen sulphate, for which finely divided samples are essential. WOOD AND ADAMS[2] determined niobium in zirconium–niobium alloys by measuring the intensity of the colour produced with hydrogen peroxide in concentrated sulphuric acid; the limit of determination is 0.1% niobium.

BELCHER *et al.*[3] reported a selective method for the determination of niobium with 4-(2-pyridylazo)resorcinol, disodium salt (PAR) in an acetate–tartrate medium at pH 5.8. In the present work, however, it was found that moderate amounts of zirconium and fluoride interfered. ELINSON *et al.*[4] showed that niobium can be determined with PAR in the presence of milligram amounts of fluoride, although the absorbance decreased with an increase in the fluoride concentration.

Since hydrofluoric acid must be used to dissolve zirconium metal, and mixtures of hydrofluoric acid and sulphuric acid to dissolve zirconium-based alloys, the PAR method was modified to permit the direct determination of niobium in the presence of fluoride. The PAR method has the additional advantage that small amounts of tungsten, vanadium, iron, molybdenum and titanium, which are usually present in zirconium metal and interfere seriously with the pyrogallol method, do not interfere. The method allows niobium contents as low as 0.005% to be determined in zirconium alloys.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer was used for all the experimental work.

Standard niobium(V) solutions, 100 μg/ml and 10 μg/ml. Prepare a stock solution containing 100 μg Nb/ml by fusing 0.1431 g of Nb_2O_5 with 3.5 g of potassium hydrogen sulphate. Extract the melt with 20 ml of 20% tartaric acid and add another 80 ml of tartaric acid solution. Dilute to 1 l with water. To obtain a 10-μg Nb/ml solution, take 25 ml of the 100 μg/ml solution, add 22.5 ml of 20% tartaric acid and dilute to 250 ml with water. Adjust the pH to 6.0 with sodium hydroxide or hydrochloric acid and dilute to 250 ml.

Buffer solution, pH 6.2. Dissolve 80 g of ammonium acetate in water, add 6.0

ml of glacial acetic acid and dilute to 1 l. Adjust the pH to 6.2 with either ammonia or acetic acid.

Standard zirconium solution, 1 mg/ml. Dissolve 3.538 g of $ZrOCl_2 \cdot 8H_2O$ in 1 l of water.

Recommended procedure

Weigh 1.0 g of sample (solid pieces or drillings) into a 250-ml Teflon beaker, add 10 ml of 18 *N* sulphuric acid and 2.0 ml of 40% hydrofluoric acid. Heat gently until action ceases, add 1 ml of nitric acid and boil until all the residue has dissolved. Cool, transfer the sample to a 500-ml volumetric flask containing 50 ml of 20% tartaric acid and dilute to volume.

Transfer an aliquot containing 1–100 µg of niobium and not more than 10 mg of zirconium to a 250-ml beaker and add 20% tartaric acid solution to increase the total amount of tartaric acid to 400 mg. Add 5 ml of saturated boric acid solution and dilute to 40 ml. Adjust the pH to 6.3–6.4 with ammonia or dilute hydrochloric acid using a pH meter. Add 5 ml of 0.04 *M* EDTA and 5 ml of buffer solution and transfer to a 100-ml volumetric flask. Add 5 ml of 0.002 *M* PAR solution (0.59 g of the disodium salt per l) and dilute to the mark with water. Measure the absorbance after 60±5 min at 550 nm against a blank. Use 1-cm cells for 75–100 µg Nb, 2-cm cells for 25–75 µg Nb and 4-cm cells in the 1–25 µg range.

The blank and standard solutions must each contain the same amount of zirconium and hydrofluoric acid as does the sample aliquot; 2.0 ml of 0.04% hydrofluoric acid should be added for each mg of zirconium.

DISCUSSION

Sensitivity and stability of the method

The niobium–PAR complex, when measured against a blank containing the same amounts of zirconium and fluoride, has maximum absorbance at 550 nm, *i.e.* the wavelength recommended by BELCHER *et al.*[3]. Beer's law is obeyed to 1.0 µg Nb/ml. The molar absorptivity of the niobium complex was found to vary with the amount of zirconium fluoride complex in solution. With 1 mg of zirconium (and corresponding fluoride) and 400 mg of tartaric acid, the molar absorptivity was $3.67 \cdot 10^4$, but this dropped to $3.0 \cdot 10^4$ at the 25-mg zirconium level. The solution reached its maximum absorbance in 1 h, the absorbance being stable for at least 24 h, as occurs in the absence of zirconium fluoride[3]. When niobium was determined in zirconium alloys containing interfering ions, the absorbance was read 60±5 min after mixing because of the increase in the absorbance caused by some metals (such as iron) present in these alloys.

The absorbance of the niobium-free blank decreased with time, but after 60 min reached a constant absorbance of 0.075 for 2 mg Zr, and 0.040 for 25 mg Zr, measured against water.

Maximum absorbance was obtained at pH 6.0, and the pH should be kept within the range 5.9–6.1, since the sensitivity decreases rapidly outside the limits[3].

Effect of varying reagent concentrations

In the presence of fluoride the addition of 5 ml of 0.04 *M* EDTA prevents the interference of up to 10 mg of zirconium. If more than 10 mg of zirconium is present the amount of EDTA must be increased proportionately. By selecting a sample aliquot containing 25 mg of zirconium it is possible to determine 0.005% niobium in zirconium alloys (Table I).

TABLE I

DETERMINATION OF NIOBIUM IN ZIRCONIUM

(25 mg Zr, 4-cm cells)

Nb added[a] *(%)*	*Nb found* *(%)*	*Relative error* *(%)*
None	None	–
0.0050	0.0048	4
0.0200	0.0210	5
0.0500	0.0520	4
0.100	0.102	2

[a] Nb added to 1 g Zr metal, dissolved in 2 ml 40% HF and 10 ml 18 *N* H_2SO_4.

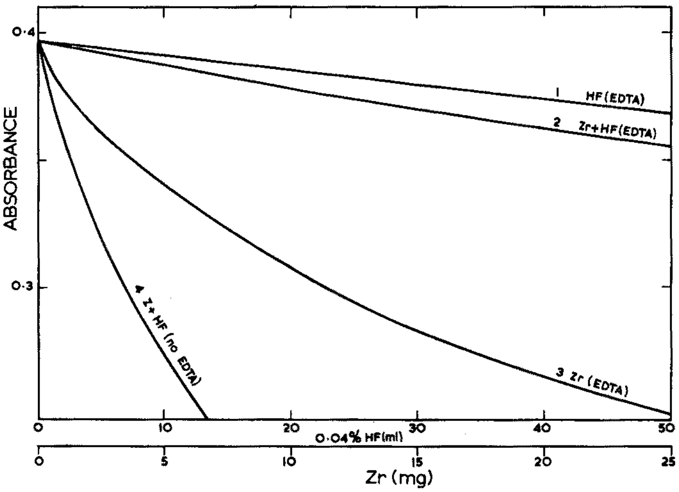


Fig. 1. The effect of zirconium and hydrofluoric acid on the absorbance (50 μg Nb/100 ml; 2-cm cells). Reagents added: (1) HF and EDTA; (2) Zr, HF and EDTA; (3) Zr and EDTA; (4) Zr and HF. All samples measured against blanks containing the same amount of Zr and/or HF, and H_3BO_3 and tartaric acid.

Niobium forms a Nb–PAR–tartrate complex on reaction with PAR in solutions containing tartaric acid[4]. A minimum amount of 50 mg of tartaric acid in 100 ml of final solution is required to produce maximum absorbance. The molar absorptivity of the Nb–PAR–fluoride complex is[4] $3.03 \cdot 10^4$ being lower than that for Nb–PAR–tartrate complex $(3.87 \cdot 10^4)$[3]. Therefore in solutions containing fluoride and tartrate, there is a competition between these two complex species and the Nb–PAR–tartrate complex is formed when at least 300 mg of tartaric acid is present in 100 ml (see Fig. 2).

The effect of zirconium, fluoride and EDTA on the absorbance of niobium–PAR complex is shown in Fig. 1. Zirconium in solutions containing fluoride but no

EDTA reacts with PAR to produce deep colours (5 mg Zr = 1.3 abs. units) and the absorbance of niobium–PAR complex is very low. Solutions containing zirconium and EDTA also produce colours with PAR (10 mg Zr = 0.193 abs. units) and therefore the absorbance of niobium–PAR complex is low. Increasing amounts of fluoride reduce the colour of niobium–PAR complex gradually. When fluoride and EDTA are added to niobium solutions containing zirconium, the blanks are low and the effect of zirconium on the niobium–PAR complex is only somewhat larger than that produced by the fluoride ion alone (Fig. 1).

Although BELCHER *et al.*[3] recommended a change in the order of addition in presence of zirconium, we found that in solutions containing a sufficient amount of fluoride to form the zirconium fluoride complex, the order of addition did not make any difference.

An amount of 2.0 ml of 40% hydrofluoric acid per 1.0 g of zirconium is necessary to dissolve zirconium alloys and this ratio must be maintained even when smaller or larger samples are taken for analysis. It is important that when blanks and standards are prepared 2.0 ml of 0.04% hydrofluoric acid is added per 1 mg of zirconium (Table II).

TABLE II

THE EFFECT OF THE RATIO OF HYDROFLUORIC ACID AND ZIRCONIUM ON THE ABSORBANCE

(50 μg Nb, 5 mg Zr, 2-cm cell)

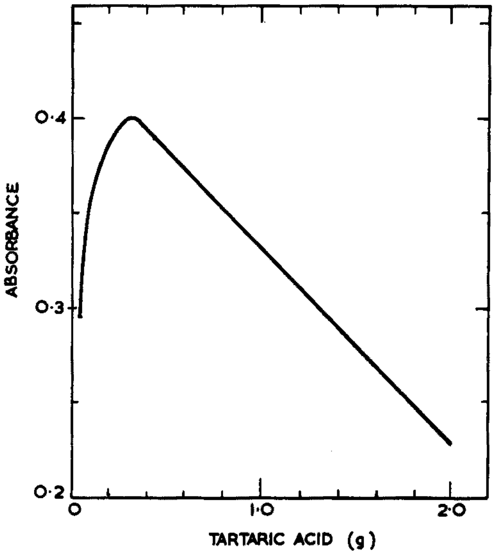
0.04% HF (ml)	*Absorbance*	*Error (%)*
8	0.388	0
10	0.388	0
10.5	0.388	0
10.75	0.385	−1
11.0	0.378	−3
12.0	0.368	−5

Boric acid has no effect on the development of the colour and does not mask the effect of fluoride on the formation of the niobium–PAR complex. There is a steady decrease in absorbance, when increasing amounts of hydrofluoric acid are added to niobium solutions containing 5 ml of saturated boric acid (Fig. 1). Boric acid was added as an additional precaution to protect the glass electrodes against a mistaken addition of excessive amounts of fluoride.

It is generally recommended that 20 mg of tartaric acid per ml should be present in the solution containing niobium, to prevent hydrolysis. A total amount of 400 mg of tartaric acid per determination was selected to give more flexibility with sample dilutions and the selection of aliquots for analysis. Any other level of tartaric acid above 300 mg may be selected. The effect of tartaric acid on the absorbance is given in Fig. 2.

Calibration procedure

It is evident from the previous discussion that the concentrations of zirconium, tartaric acid, fluoride and EDTA have an important effect on the absorbance of the niobium–PAR complex. Therefore blank and standard solution must contain the



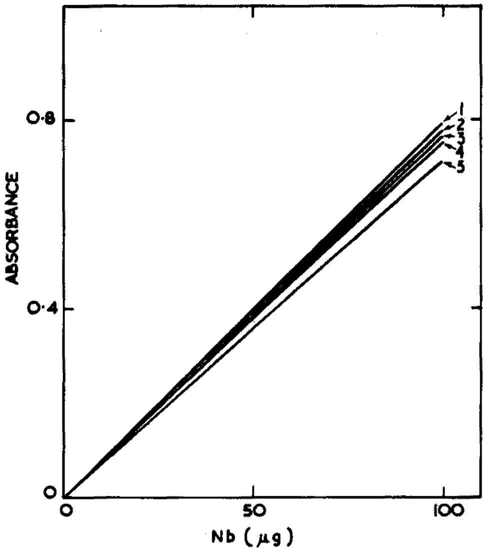


Fig. 2. The effect of tartaric acid on absorbance. 1 h after mixing, 50 μg Nb, 2 mg Zr, 4 ml of 0.04% HF.

Fig. 3. Calibration curve for niobium in zirconium. Zirconium added: (1) 1 mg; (2) 2 mg; (3) 5 mg; (4) 10 mg; (5) 25 mg. 550 nm, 2-cm cells, 400 mg tartaric acid.

TABLE III

EFFECT OF VARIOUS ELEMENTS

(50 μg of Nb)

Foreign ion added	*Amount taken (mg)*	*Niobium found (μg)*	*Relative error (%)*
Al^{3+}	0.5	52.4	5
Co^{2+}	0.05	51.7	3
Cr^{3+}	1.0	45.2	−10
Cr^{3+}	1.0	50.0	0[a]
Cr^{3+}	0.1	49.4	−1
Fe^{3+}	0.5	52.1	4
Sn^{2+}	1.0	52.1	4
Sn^{4+}	1.0	51.4	3
Ta^{5+}	0.05	58.7	17
Ta^{5+}	0.05	52.0	4[b]
V^{5+}	0.05	51.0	2
SO_4^{2-}	100	50.0	0
NO_3^-	100	50.0	0

[a] Sample brought to boiling and cooled after EDTA addition.
[b] Tartaric acid increased to 2 g.

same concentrations of all 4 reagents as found in the sample solution. Calibration curves for niobium containing varying amounts of zirconium are shown in Fig. 3.

Interference by various elements

Some elements form strong colours with PAR even in solutions containing tartaric acid, fluoride and EDTA, for example Co^{2+}, V^{5+}, and Ta^{5+}, while other elements such as iron(III) increase the absorbance on standing (Table III). In agreement with previous work[3], no interference was found with 1-mg amounts of Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Ti^{4+}, Mo(VI) or W(VI).

Chromium(III) reacts slowly with EDTA, and amounts in excess of 0.1 g interfere by reducing the absorbance of the niobium complex. The interference of chromium can be overcome after EDTA addition by bringing the sample aliquot to boil, cooling and continuing as in the recommended procedure.

Tantalum(V) forms a PAR complex which is one-sixth as sensitive as the niobium–PAR complex. It has been shown that tantalum interference can be overcome by increasing the tartaric acid concentration to 5 g per 100 ml[3]. We found that by increasing the tartaric acid to 2 g, the error caused by an equal amount of tantalum was reduced to 4% and the sensitivity was decreased by only 34%.

Cobalt and vanadium form strong colours with PAR, but their interference can be masked with potassium cyanide[3] and hydroxylamine hydrochloride, respectively. However, these reagents interfere when other metallic impurities, such as iron and copper, are present.

Reproducibility of the method

Ten repeat determinations were made at the 50-μg of niobium level using 2-cm cells; the relative standard deviation was ±0.6%.

A niobium–zirconium alloy was analysed by taking two separate samples in duplicate; the results were found to be 2.70±0.04% niobium.

SUMMARY

The direct spectrophotometric determination of niobium in zirconium alloys with 4-(2-pyridylazo)resorcinol is described. Samples are dissolved in hydrofluoric–sulphuric acid mixture and the colour developed without the removal of fluoride. In the presence of EDTA only Co^{2+}, Ta^{5+}, and V^{5+} cause serious interference. The molar absorptivity is $3.67 \cdot 10^4$ in the presence of 1 mg of zirconium, and Beer's law is obeyed up to 1.0 μg Nb/ml. The method can be applied to zirconium alloys containing as little as 0.005% niobium.

RÉSUMÉ

Le dosage spectrophotométrique direct du niobium dans des alliages au zirconium à l'aide de 4-(2-pyridylazo)résorcinol est décrit. Les échantillons sont dissous dans un mélange acide fluorhydrique–acide sulfurique; la couleur est développée sans élimination du fluorure. En présence d'EDTA, seul Co^{2+}, Ta^{5+} et V^{5+} causent une sérieuse interférence. L'absorption molaire est de 3.67×10^4 en présence d' 1 mg de zirconium; la loi de Beer peut s'appliquer à partir de 1.0 μg Nb/ml. Ce procédé peut s'appliquer aux alliages de zirconium renfermant jusqu'à 0.005% de niobium.

ZUSAMMENFASSUNG

Die direkte spektralphotometrische Bestimmung von Niob in Zirkoniumlegierungen mit 4-(2-Pyridylazo)-resorcinol wird beschrieben. Die Proben werden in einer Mischung von Fluss- und Schwefelsäure gelöst und die Farbe ohne Beseitigung des Fluorids entwickelt. In Gegenwart von AeDTE verursachen nur Co^{2+}, Ta^{5+} und V^{5+} ernsthafte Störungen. Die molare Absorption beträgt $3.67 \cdot 10^4$ in Gegenwart von 1 mg Zirkonium. Das Beersche Gesetz wird hinauf bis zu 1.0 µg Nb/ml befolgt. Die Methode eignet sich für Zirkoniumlegierungen mit 0.005% Niob.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

NEUTRON ACTIVATION ANALYSIS OF HIGH-PURITY SELENIUM

PART II. DETERMINATION OF TELLURIUM

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(Received September 25th, 1967)

In a previous paper[1], the determination of bromine in selenium was described. Another important impurity to be expected in selenium, is tellurium which has a chemical behaviour very similar to selenium. Several tellurium determinations in selenium by neutron activation have already been published[2–10]. Generally the pure β^--emitter ^{127}Te ($T_{\frac{1}{2}}=9.3$ h) is separated in the elementary state and counted with a G.M. tube.

Nuclear properties and interferences

Neutron activation of tellurium gives rise to the isotopes listed in Table I. It is obvious that the highest sensitivity would be obtained with the isotope ^{131}Te ($T_{\frac{1}{2}}=24.8$ m), but it is difficult to decontaminate tellurium from selenium efficiently in a time compatible with a half-life of 24.8 min.

The daughter isotope ^{131}I ($T_{\frac{1}{2}}=8.08$ d) was therefore preferred as a separation of iodine from selenium is easier. From the nuclear data it can be seen that the ^{131}I is mainly formed as the daughter of the isotope ^{131}Te. If the separation is started about 30 h after the end of irradiation, one can consider that ^{131}I has been formed almost quantitatively. A possible nuclear interference due to the reactions ^{131}Xe (n,p) ^{131}I ($\sigma=0.09$ mb)[14] can be neglected. Another possible interference is fission of uranium (% yield of ^{131}I: 3.1%)[15]. Fortunately, the uranium content of the samples under investigation is very low: after distillation of the selenium from sulfuric–hydrobromic acid, no ^{239}Np ($T_{\frac{1}{2}}=2.33$ d) could be detected with a Ge(Li) diode, measuring 3 days after the end of irradiation.

Chemical separation of iodine

It appeared that complete isotopic exchange between the ^{131}I formed and the added iodide carrier is rather difficult to obtain[16]. Precipitation as silver iodide, after the dissolution of the selenium in hot concentrated nitric acid in the presence of 10 mg of iodide and 1 ml of 0.1 *N* silver nitrate, did not result in a quantitative separation of ^{131}I, nor did a percolation of the filtrate on silver sponge.

To obtain exchange, oxidation with hypochlorite in alkaline solution can be applied; the iodate is then reduced with hydroxylamine to elementary iodine which can easily be extracted into carbon tetrachloride[17]. However, hydroxylamine

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TABLE I

NUCLEAR DATA OF TELLURIUM[11-13]

Stable isotope	*Abundance (%)*	*Cross-section (b)*	*Isotope formed*	$T_{\frac{1}{2}}$	*Radiation energy (keV)*		*d.p.s./g ($t = 1$ sec, $\varnothing = 10^{12}$ n/cm²/sec)*
					β	γ	
^{120}Te	0.089	20	^{121m}Te	150 d		70–81.8–*213.6*–1130	hour
		0.3	^{121}Te	17 d		70–506–*575*	
^{122}Te	2.46	1.1	^{123m}Te	104 d		88.6–*159*	9
^{124}Te	4.61	5	^{125m}Te	58 d		*35.5*–110	$2 \cdot 10^2$
^{126}Te	18.71	0.1	^{127m}Te	105 d	119–726	*58.5*–88.5–665	4
		0.9	^{127}Te	9.3 h	277–325–492–*695*	58.5–145–203–215–360 *418*	$2 \cdot 10^4$
^{128}Te	31.79	0.015	^{129m}Te	33.5 d		106.3	5
		0.13	^{129}Te	72 min	290–690–989–1453 1453	26.8–211–*475*–720–1120	$3.1 \cdot 10^4$
^{130}Te	34.49	<0.008	^{131m}Te	30 h	420–570–980–2460	99–147–181–239–275–331 446–575–773–842–925	80
		0.22	^{131}Te ↓	24.8 min	1350–1690–2140	99–*147*–181.7–239–275–331– 446–575–*773–842–925–1140–1220*– *1500*–1850–2200	$1.6 \cdot 10^5$
		daughter	^{131}I	8.08 d	250–340–430 *610*–812	80.164–177.1–284.3–*364.47*– 514–638–723.8	

also partially reduces the selenious acid to elementary colloidal selenium, resulting in an important selenium contamination of the organic phase.

From tracer experiments, it appeared that complete exchange also occurs in hot concentrated nitric acid by oxidation with potassium permanganate to iodate, followed by reduction with sodium bisulfite to iodide and oxidation with hydrogen peroxide to elementary iodine[13], which can be volatilized quantitatively together with bromine and chlorine. For further purification, the iodine is extracted into carbon tetrachloride after the addition of nitric acid, sodium nitrite and hydrogen peroxide to the alkaline sodium iodide distillate, and back-extracted into sodium bisulfite. The bromine remains in the organic layer. This extraction cycle is repeated three times. Finally the iodide is precipitated as silver iodide for counting and yield determination. Tracer experiments showed that an excellent decontamination from the isotopes ^{22}Na, ^{54}Mn, ^{64}Cu, ^{65}Zn, ^{76}As, ^{82}Br and ^{122}Sb is achieved and an almost quantitative yield ($\pm 95\%$) is obtained by this separation technique. Although a decontamination factor of more than 10^8 from ^{75}Se was obtained, this did not appear to be sufficient for direct γ-spectrometric counting (Fig. 1).

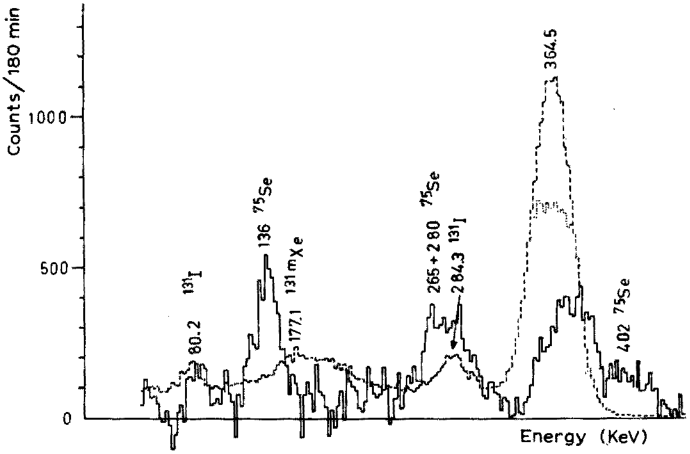

Fig. 1. γ-Spectrum of ^{131}I fraction separated from selenium.——— ^{131}I separated from 100 mg irradiated Se. ------ pure ^{131}I. ...... background.

Counting

Figure 1 shows the γ-spectrum of the ^{131}I fraction, separated from 100 mg of selenium, irradiated during 100 h at $6 \cdot 10^{12}$ n.cm^{-2}.sec^{-1}; it can also be seen that the background count rate is higher than the net count rate of the sample. The measurement of the samples thus requires the use of a more sensitive and selective counting technique.

From the decay scheme[12] of the isotope ^{131}I (Fig. 2), it can be seen that this isotope decays to the extent of 87% by emission of a β^--particle with an energy of 606.5 keV mainly followed by a 364.5-keV γ-ray, whereas ^{75}Se decays exclusively by electron capture. Thus, an important decrease of the count rate caused by ^{75}Se and by the background can be expected by applying β,γ-coincidence counting. In the applied technique, the β-particles were detected by means of a plastic scintillator 44 mm in diameter and 5 mm thick. After discrimination of the low-energy noise pulses, this signal was used as gate pulse for the coincidence circuit of the 400-channel analyzer. The coincident γ-spectrum was detected with a 3 × 3″ NaI(Tl) crystal. The activity under the photopeak at 364.5 keV was then summed and used for the determination of tellurium, after subtraction in this region of the ^{75}Se activity, which never exceeded 4% of the total activity.

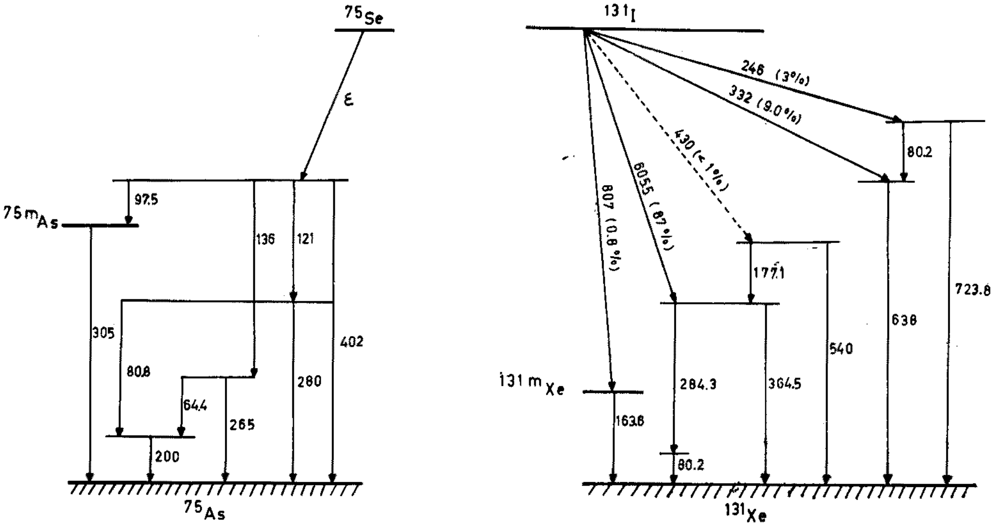

Fig. 2. Decay schemes of ^{131}I and ^{75}Se.

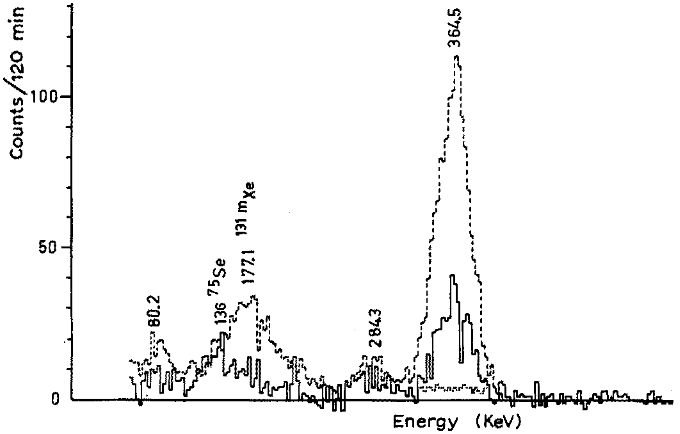

Fig. 3. Coincident γ-spectrum. ——— ^{131}I separated from 100 mg irradiated Se. – – – – pure ^{131}I ...... background.

In Fig. 3 the coincident γ-spectrum obtained from the above-mentioned iodine fraction is compared with that of the pure ^{131}I-tracer. The background level is also shown in the same figure. It is obvious that the net coincident count rate, caused by ^{131}I, is several times higher than the coincident count rate caused by the ^{75}Se contamination and by the background. Table II gives the count rate ratios of β, γ-coincidence

TABLE II

COUNT RATE RATIOS β,γ-COINCIDENCE/γ-SPECTROMETRY IN THE 347–382 keV REGION

Sample	*γ-Spectrometry (counts/min)*	*β,γ-coincidence counting (counts/min)*	*Ratio (%)*
Background	34	0.241	0.7
^{131}I	12,242	2,194	17.9
^{75}Se	2,872	64	2.2

counting to γ-spectrometry in the 347–382 keV energy region for the background activity and the isotopes ^{131}I and ^{75}Se. The count rates of the background and ^{75}Se are reduced respectively by factors of 141 and 45 while the count rate of ^{131}I is only reduced by a factor of 5.6.

EXPERIMENTAL

Apparatus

The block scheme of the β,γ-coincidence circuit, essentially the same as described by DAMS AND HOSTE[18], is presented in Fig. 4.

Preparation of samples and standards. Irradiation conditions

A block of selenium, weighing about 1 g, is etched twice with 4 *N* nitric acid, washed several times with tridistilled water, dried and powdered. Samples (100 mg) are sealed in quartz ampoules, packed in a standard aluminium capsule, irradiated for 4 days at a neutron flux of $6\cdot10^{12}$ n.cm^{-2}.sec^{-1} (BR-2 reactor) and cooled for 1 day. To avoid flux-depression, induced by the matrix[1] and self-shielding effects in the standards, a powdered selenium sample, spiked with 2.50 or 4.55 ng tellurium is used as a standard (100 μl of a solution of tellurium dioxide in high purity dilute nitric acid). This standard is treated in exactly the same way as the samples.

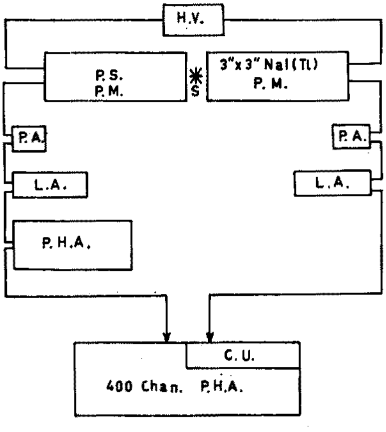

Fig. 4. Diagram of β,γ-coincidence circuit. S=Sample: ±18.4 mg AgI/4.9 cm^2. P.S.=Plastic scintillator: 44 mm diam., 6 mm thick. H.V.=High voltage. P.M.=Photomultiplier. P.A.=Preamplifier. L.A.=Linear amplifier. P.H.A.=Pulse height analyser. C.U.=Coincidence unit.

The flux-depression in the capsule was determined with a cobalt–aluminium wire, containing 1% cobalt, stretched in the center of the capsule over the whole length and half the width. After irradiation the wire was washed with concentrated nitric acid and water. The wire was cut in 8-mm sections and the length, weight and activity of each section determined. The specific activity of each section is shown in Fig. 5. It appears that no apparent flux gradient could be detected.

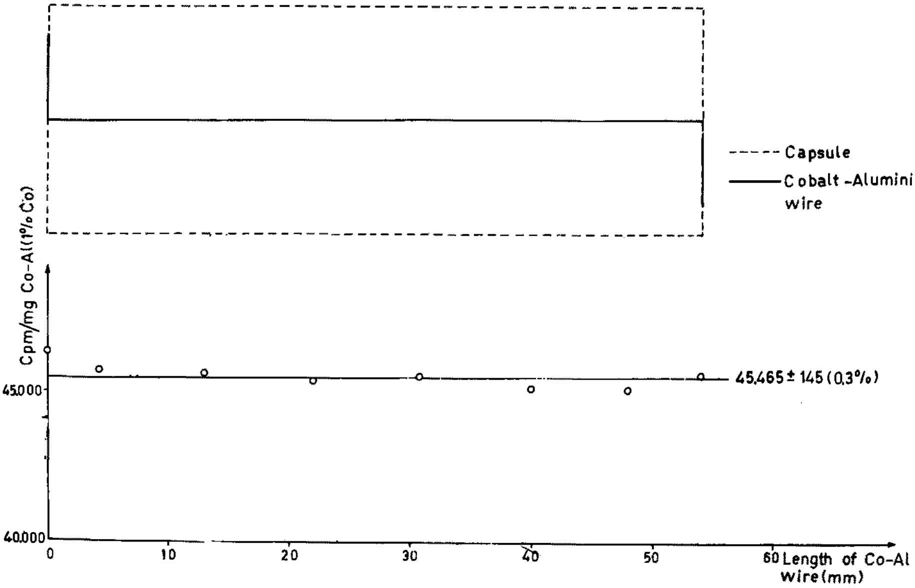

Fig. 5. Specific activity of each wire section.

Chemical procedure

At least one day after the end of irradiation, dissolve the selenium samples (3–6 mC ^{75}Se) in an all-glass distillation apparatus, together with 10 mg of iodide in 15 ml of 14 *N* nitric acid and heat to 100°. A moderate stream of carbon dioxide is bubbled through the solution. Through the separating funnel add saturated potassium permanganate until its color persists (*ca.* 2 ml) and continue heating for 15 min. Add 2 *N* sodium bisulfite until the disappearance of all manganese dioxide (*ca.* 4 ml). Distil for 30 min at 100–110° while adding 4 ml of 30% hydrogen peroxide. Heat the condenser with an infrared lamp to volatilize any condensed iodine. The receiving vessel was a large test-tube filled with 20 ml of 2 *N* sodium hydroxide containing 100 mg of selenium "hold-back" carrier. Transfer the distillate to a 200-ml separating funnel, acidify with 6 *N* nitric acid, add 1 ml of sodium nitrite and extract iodine into 10 ml of carbon tetrachloride. Add 1 ml of 14 *N* nitric acid and 1 ml of sodium nitrite and extract with 10 ml of carbon tetrachloride. Add 1 ml of 14 *N* nitric acid, 1 ml of 1 *N* sodium nitrite and 1 ml of 30% hydrogen peroxide, and extract with 5 ml of carbon tetrachloride. Repeat until a colorless organic layer is obtained. Discard the aqueous phase and extract the organic phase twice with 10 ml of water containing 1 ml of 2 *N* sodium bisulfite, and twice with 5 ml of water containing 1 ml of 2 *N* sodium bisulfite. Discard the organic phase, add 2 ml of 14 *N* nitric acid and 2 ml of 1 *N* sodium nitrite and extract with 10 ml of carbon tetrachloride. Repeat. Add 1 ml of 14 *N* nitric acid, 1 ml of 1 *N* sodium nitrite, 1 ml of 30% hydrogen peroxide and extract with 5 ml of carbon tetrachloride. Repeat. Filter the carbon tetrachloride solution to remove any colloidal selenium coextracted. Reextract the iodine in water as described above and repeat the extraction cycle 3 times more.

Add 1 ml of 6 *N* nitric acid to the iodide solution in dilute sodium bisulfite, boil to evaporate the sulfur dioxide, add 1 ml of 0.1 *N* silver nitrate, cool, filter on a paper and wash the precipitate 4 times with 5-ml portions of water, once with 5 ml of alcohol and once with 5 ml of ether. Mount for counting.

RESULTS

To investigate the possibility of systematic errors in this procedure, an addition method of analysis was performed. Six samples of 100 mg of powdered selenium, treated as described above, were placed in quartz ampoules. Four samples were spiked with a solution of tellurium dioxide in ultra-pure dilute nitric acid. The quartz ampoules were dried and sealed and their content thoroughly mixed by shaking. After irradiation the iodine was separated and measured as described above. The activities due to ^{131}I induced in the samples were plotted as a function of the amount of tellurium added.

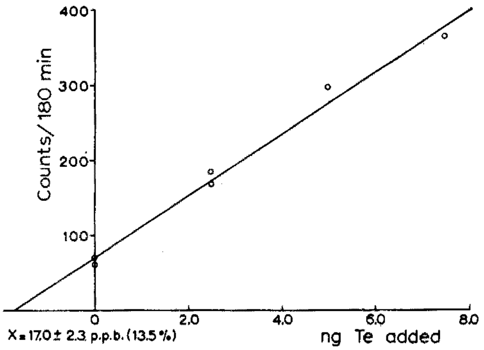

Fig. 6. Standard addition method. $b_0 = 70 \pm 9$ counts/180 min (12.9%); $b_1 = 412 \pm 22$ counts/100 p.p.b./180 min (5.4%); tellurium content: 17.0±2.3 p.p.b.

TABLE III

DETERMINATION OF TELLURIUM IN THE SELENIUM SAMPLES

Sample no.	*Te found (p.p.b.)*	*Mean value*
1	28.0, 22.1, 25.8	25.3±1.7 (6.7%)
2	22.4, 19.7, 19.2	20.4±1.0 (4.9%)
3	15.4, 14.4 —	14.9±0.5 (3.3%)

The slope of the straight line b_1, its intercept with the ordinate b_0 and the standard deviations were calculated as described by GUEST[19]. Figure 6 shows that no systematic error is perceptible for up to 7.5 ng tellurium added.

Finally the tellurium contents of 3 different selenium samples were determined. The results are listed in Table III. The standard deviations varied between 3 and 7%.

Thanks are due to the "Nationaal Fonds voor Wetenschappelijk Onderzoek" and the "Interuniversitair Instituut voor Kernwetenschappen" for financial support and to the "Metallurgie Hoboken" for providing the selenium samples.

SUMMARY

Neutron activation determination of 15–25 p.p.b. of tellurium in selenium can be done by irradiating 100-mg samples for 4 days at a neutron flux of $6 \cdot 10^{12}$ n. cm^{-2}.sec^{-1}. The daughter isotope of ^{131}Te, ^{131}I, is separated by distillation and extracted into carbon tetrachloride. Finally the silver iodide precipitate is measured by β,γ-coincidence counting. The standard deviation is 3–7%.

RÉSUMÉ

L'analyse par activation de 15–25 p.p.b. de tellure dans un sélénium peut être effectué en irradiant un échantillon de 100 mg pendant 4 jours avec un flux de neutrons de $6 \cdot 10^{12}$ n cm^{-2} sec^{-1}. L'isotope fille de ^{131}Te, ^{131}I est séparé par distillation et extrait dans le tétrachlorure de carbone. Finalement, le précipité d'iodure d'argent est mesuré par comptage en coincidence β,γ. La déviation standard est 3–7%.

ZUSAMMENFASSUNG

Mittels der Neutronenaktivierungsanalyse werden 15–25 p.p.b. Tellur in Selen bestimmt. Dazu werden Proben von 100 mg vier Tage lang bei einem Neutronenfluss von $6 \cdot 10^{12}$ n cm^{-2} sec^{-1} bestrahlt. Das Folgeprodukt vom ^{131}Te, ^{131}I, wird durch Destillation abgetrennt und mit Tetrachlorkohlenstoff extrahiert. Anschliessend werden im Silberjodidniederschlag die β-Strahlung und γ-Koinzidenzen gemessen. Die Standardabweichung beträgt 3–7 %.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

The determination of phosphorus in rocks by neutron activation

Determinations of phosphorus in geological materials have so far been carried out almost exclusively by standard gravimetric or spectrophotometric techniques. Although these methods are usually considered to be quite satisfactory, different investigators have obtained seriously different results when analysing the same rock; surveys of the results obtained for the content of P_2O_5 in the granite G-1 and diabase W-1 have been published by AHRENS AND FLEISCHER[1], FLEISCHER AND STEVENS[2] and FLEISCHER[3] (see Table I). The rather poor agreement with the use of purely chemical methods indicated that efforts to introduce new analytical techniques for the determination of phosphorus might be worthwhile for geological materials. Recently, BROWN AND WOLSTENHOLME[4] have used spark-source mass spectrometry, but their results for G-1 and W-1 are significantly low.

TABLE I

SUMMARY OF PREVIOUS RESULTS FOR THE P_2O_5 CONTENT OF G-1 AND W-1

Rock	*Reference*	*Number of analyses*	*Range of results (%)*	*Relative standard deviation (%)*
G-1	1	54	0.04–0.16	55.1
	2	4	0.022–0.10	
	3	7	0.06–0.19	
W-1	1	58	0.09–0.21	40.5
	2	5	0.10–0.17	
	3	8	0.13–0.22	

Neutron activation analysis has proved very useful for the determination of phosphorus in many materials. Application of the technique for the determination of phosphorus in geological samples seems to be very limited. VINCENT[5], however, has obtained results for G-1 and W-1 by a neutron activation method which are in close agreement with the recommended values for phosphorus in these rocks[3]. This indicated that activation analysis could advantageously be used for determination of phosphorus in rocks and minerals.

The neutron activation method described in this paper for the determination of phosphorus has, in addition to G-1 and W-1, been applied to some recent primary standard rock samples from the U.S. Geological Survey (see Table II) and to tonalite T-1 from the Geological Survey of Tanganyika.

Experimental

Accurately weighed samples of about 100 mg were wrapped in a double layer of aluminium foil and irradiated for 7 days in the reactor JEEP-1 (Kjeller, Norway) at a thermal neutron flux of about $1.5 \cdot 10^{12}$ n/cm²/sec. About 50 mg of potassium dihydrogen phosphate, also wrapped in aluminium foil, was used as phosphorus standard. After one week's delay, for the decay of short-lived activities, each sample was treated according to the following procedure.

TABLE II

CONTENT OF P_2O_5 IN SOME STANDARD ROCKS

Standard rock	*Irradiation A* (%)	*Irradiation B* (%)	*Mean value* (%)	*Literature values* (%)
Andesite AGV-1	0.540 0.556	0.535 0.549	0.545	0.49–0.53[a]
Basalt BCR-1	0.384 0.391	0.432 0.398	0.401	0.35–0.47[a]
Diabase W-1	0.145 0.142 0.149	0.148 0.140	0.145	0.14[b]
Dunite DTS-1	0.0019 0.0017	0.0022 0.0016	0.0019	0.00–0.04[a]
Granite G-1	0.081 0.089		0.085	0.09[c]
Granite G-2	0.129 0.149	0.136 0.148	0.141	0.13–0.16[a]
Granodiorite GSP-1	0.316 0.318	0.298 0.318	0.313	0.28–0.32[a]
Nepheline Syenite STM-1	0.178 0.180	0.194 0.176	0.182	
Peridotite PCC-1	0.0017 0.0013	0.0023	0.0016[d]	0.00–0.05[a]
Tonalite T-1	0.173 0.172	0.168 0.170 0.176 0.183	0.174	0.14[e]

[a] FLANAGAN[7].
[b] Value recommended by FLEISCHER[3]; a value of 0.145 was obtained by VINCENT[5].
[c] Value recommended by FLEISCHER[3]; a value of 0.079 was obtained by VINCENT[5].
[d] Corrected for contribution from the reaction $^{32}S(n, p)^{32}P$.
[e] Median value obtained by THOMAS[9].

The sample was transferred to a nickel crucible containing 1 ml of phosphorus carrier (4 mg/ml), evaporated to dryness, and fused with 2 g of sodium hydroxide. The fusion "cake" was released from the crucible with water and transferred to a 250-ml beaker, and the mixture was acidified with nitric acid. After the acidity had been adjusted to about 1 *N*, 1 g of ammonium nitrate was added, and the phosphorus was precipitated with 10 ml of ammonium molybdate solution (25 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$/l of water) at a temperature of 40–50°. After centrifuging, the supernatant liquid was discarded. The precipitate was washed once with dilute nitric acid and subsequently dissolved in a few ml of ammonium hydroxide. Phosphorus was then re-precipitated by acidifying with nitric acid. The precipitate was filtered onto a tared membrane filter, washed with ammonium nitrate solution, dried for 20 min at 110°, and then weighed as ammonium phosphomolybdate. After weighing, the filter was mounted on a cardboard sample holder for β-counting.

The standard was dissolved in dilute nitric acid and made up to 25 ml with water. Aliquots of 100 μl were transferred to beakers containing 1 ml of phosphorus carrier solution, 1 ml of 100-vol hydrogen peroxide and 2.5 ml of concentrated hydrochloric acid, and heated for 10 min on a hot plate, to ensure exchange between active and carrier phosphorus (according to ARCHER *et al.*[6]). The solution was then diluted to 100 ml with 1 N nitric acid, 1 g of ammonium nitrate was added, and ammonium phosphomolybdate was precipitated as described above. After filtering and weighing, the standard was prepared for counting.

The β-activity of each sample was counted with a Geiger–Mueller counter. An aluminium absorber of 50 mg/cm^2 was used to eliminate possible contamination from low-energy β-emitters, *i.e.* ^{35}S and ^{45}Ca. No γ-emitting impurities were detectable from spectra of the samples recorded with a 400-channel γ-spectrometer. The half-life of the β-activity was checked by repeated measurements, and none of the samples showed appreciable deviation from a pure ^{32}P-decay. Before calculating the results, proper corrections were introduced for the influence of sample phosphorus in the chemical yield determination of the carrier. Errors due to self-scattering and self-absorption of the β-particles were found to be insignificant.

Results and discussion

Results obtained for the phosphorus content of the standard rocks in two different irradiations numbered A and B are presented in Table II as % P_2O_5. As the supply of G-1 was almost exhausted, only a duplicate determination was carried out for this rock. Previously published values are also shown in Table II. The results for G-1 and W-1 are seen to be in good agreement with the values recommended by FLEISCHER[3]. The agreement with the neutron activation results by VINCENT[5] is also very satisfactory. For the new series from the U.S.G.S., the results from the present work are compared with the values recently published by FLANAGAN[7], obtained by chemical methods. The agreement at P_2O_5-concentrations exceeding 0.1% appears to be good. The phosphorus content of the ultrabasic rocks DTS-1 and PCC-1, however, is most probably below the limit of detection for the chemical methods. It is to be noted that the present values for P_2O_5 in DTS-1 and PCC-1 are far lower than the average composition values for dunite and peridotite given by NOCKOLDS[8]. The present result for the content of P_2O_5 in tonalite is significantly higher than the mean value cited by THOMAS[9].

The precision of the method appears to be of the order ±5% for P_2O_5 contents above 0.1%. The accuracy of the presented mean values in the same concentration region seems to be quite satisfactory, perhaps as good as ±5%.

Possible interference from nuclear reactions due to fast neutrons in the reactor might be serious, because ^{32}P can also be produced from sulfur and chlorine by an (n, p) and an (n, α) reaction respectively. In order to study these interference effects in the actual irradiation position, where the fast neutron flux is about 5% of the thermal flux, a simultaneous irradiation of inorganic compounds of phosphorus, sulfur and chlorine was carried out. Subsequent β-activity measurements showed that the specific activity of ^{32}P induced in sulfur and chlorine, compared to the corresponding figure for phosphorus, was 1.8% and 0.4% respectively. This means that if the ratio of sulfur to phosphorus is less than 1, the error introduced is below 2%.

The interference from chlorine in the U.S.G.S. standard rocks could be calculated from the chlorine data of JOHANSEN AND STEINNES[10]. Except in the case of DTS-1 and PCC-1, the correction was negligible. No data seem to be available for the chlorine content of T-1.

Unfortunately, no data are available for the sulfur content of the rocks. It was therefore necessary to perform an extra irradiation of a set of samples covered by a 0.03-in. cadmium foil. By this means the production rate of ^{32}P from the (n, γ) reaction in phosphorus is strongly depressed, while the fast neutron reactions in sulfur and chlorine occur at the same rate. Together with the samples, weighed amounts of potassium dihydrogen phosphate and potassium sulfate placed within the same cadmium foil were irradiated for use as standards. After the irradiation, samples and standards were processed as described before. The results of this investigation showed that the sulfur interference in the ordinary irradiations was less than 1% for all samples except PCC-1, where the contribution corresponded to a correction of about 10%.

The present method should be especially useful for analyses of geochemical materials with low phosphorus content. Application to samples with higher concentration of phosphorus might also be favourable, as the method appears to yield good accuracy, and the simplicity is of the same order as for the conventional gravimetric methods.

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(Received September 25th, 1967)

A method for the determination of interferences in automatic colorimetric analysis

With any colorimetric method of analysis it is important to know the limiting concentration of interfering substances. The usual procedure is to add known quantities of an interfering substance and determine by separate absorbance measurements the concentration at which the interference becomes significant. This note describes a technique that can be used for studying interfering substances on the Technicon Autoanalyser. The method is based on established procedures employed in gradient elution chromatography, in which the concentration of the eluant is continuously increased with time. In principle it can be used generally, not only for determining interferences, but also for establishing optimum concentrations of reagents.

Experimental

An open vessel (A), containing the interfering substance at a known high concentration in a solution of the substance to be determined is connected by a capillary syphon to a second open vessel (B). Vessel B contains initially only the substance to be determined and the same concentration as in A. Vessel B is connected directly to the Autoanalyser pump manifold. The rate of mixing in this vessel is controlled by a variable-speed magnetic stirrer. It is important to avoid a vortex at the surface as this will lead to a variable syphon flow. For two vessels of identical cross-sectional area, assuming no volume change on mixing, the proportion by volume of the interfering substance in B at any time is given by the formula[1]

$$F_B = kt/2V$$

where k is the measured pumping rate of the sample tube, t is the elapsed time from beginning of syphoning, and V is the initial volume in each vessel.

The linear relationship between concentration and time was verified experimentally by introducing calcium chloride in vessel A and withdrawing small aliquots from vessel B at specified times. A plot of the calculated concentrations of calcium against the actual concentrations of calcium found by atomic absorption spectroscopy, proved to be linear with a slope of 1.

Results and discussion

The gradient mixing device was used to determine the concentration at which calcium interfered with nitrate determinations on soil extracts, and the removal of this interference by sequestering calcium with disodium pyrophosphate. The method used for nitrate determination is a modification of the Griess–Ilosvay method[2,3].

The device was set up as outlined and vessel B filled with 40 ml of a 4-p.p.m.

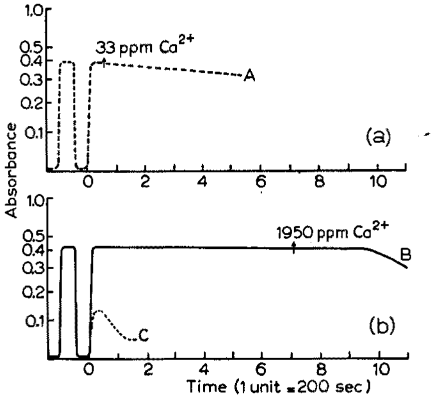

Fig. 1. Interference curves of calcium on 4 p.p.m. nitrate. (a) with an initial concentration of 500 p.p.m. calcium in vessel A (-----A) without disodium pyrophosphate. (b) with an initial concentration of 5,000 p.p.m. calcium in vessel A: (———B) with disodium pyrophosphate, (-----C) without disodium pyrophosphate.

standard solution of nitrate. This standard gave an absorbance of approximately 0.40. Vessel A was filled with the same volume of the nitrate standard solution containing 500 p.p.m. of calcium added as calcium chloride. The syphon was also filled with this solution.

After a constant base-line on the pen recorder had been established, a test-tube containing a 4-p.p.m. nitrate standard was placed in the sample wheel and sampled continuously. This produced a flat-topped peak which indicates a constant degree of colour formation; and the height of the peak serves as a standard of comparison during the gradient mixing of the interfering substance. Sampling was stopped after 5 min and the pump connected to vessel B at time "0" (Fig. 1).

Initially the concentration of calcium was low and had little effect on absorbance (*cf.* the reference peak in Fig. 1(a)). Interference became serious at about 33 p.p.m. and absorbance fell steadily as the concentration increased. Serious interference was judged to occur when a change of 0.01 absorbance was indicated on the recorder.

The method was also used to test the efficacy of disodium pyrophosphate in removing the interference caused by calcium ions. The same procedure was used except that disodium pyrophosphate was included with one of the reagents which entered the system before reduction. The standard solutions now gave a higher absorbance owing to the presence of this electrolyte. Absorbance was constant up to 425 p.p.m. Serious interference, *i.e.* a change of 0.01 absorbance, occurred at about 1,950 p.p.m. of calcium when vessel A contained 5,000 p.p.m. initially (Fig. 1). The absence of disodium pyrophosphate at this working concentration produced severe interference.

Another application of the method is in the determination of the optimum concentrations of reagents used in colorimetric measurements. The technique works well with dilute solutions, but a problem arises when the ionic strengths of the solutions in vessels A and B differ markedly, because reverse osmosis prevents the desirable syphon action. This may be corrected by incorporating a non-interfering electrolyte in vessel B. This technique has been used in developing methods for nitrogen and phosphate analysis in soil digests.

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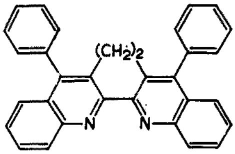
(Received September 8th, 1967)

Zur Komplexchemie der Cuproine. V[1]. Spektrophotometrische Kupferbestimmung mit 3,3'-Dimethylen-4,4'-diphenyl-2,2'-dichinolyl

Einige neue Verbindungen des Cuproin-Typs sind durch zweiseitige Friedländer-Synthese aus *o*-Aminoarylketonen und cyclischen 1,2-Diketonen präparativ leicht zugänglich geworden[2]. Ihre analytische Testung lieferte recht günstige Resultate[3]. Als weiterer Vertreter aus der Reihe dieser überbrückten 2,2'-Dichinolyle wurde deshalb 3,3'-Dimethylen-4,4'-diphenyl-2,2'-dichinolyl (I) auf seine Verwendung zur Kupferbestimmung geprüft. Der Kupfer(I)-Komplex von I weist eine starke charge-transfer-Bande bei 555 nm (ε=9800) auf, die für die photometrische Kupferbestimmung genutzt werden kann. In der Intensität dieser Bande wird I nur noch durch Bathocuproin und seine Derivate übertroffen.



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Reagenzien und Apparate

Zur Kupferbestimmung wurde eine 2.5 · 10^{-4} *M* Lösung von 3,3'-Dimethylen-4,4'-diphenyl-2,2'-dichinolyl in Isoamylalkohol verwendet, als Standardlösung kam eine 10^{-4} *M* Kupfersulfatlösung zum Einsatz. Das überbrückte Dichinolyl wurde nach den Angaben der Literatur[2] dargestellt und zur Reinigung je zweimal aus Dioxan und Chloroform umkristallisiert. Die Substanz bildet weisse Nadeln, die bei 365° unter Zersetzung schmelzen. Die Ausbeute erreichte 53% der Theorie.

Zur Messung der Extinktionen wurde das Kolorimeter nach HAVEMANN benutzt; alle Messungen wurden mit einer 1 cm-Küvette durchgeführt.

Ergebnisse und Diskussionen

Die analytische Bestimmung des Kupfers beruht auf der Extraktion seines Kupfer(I)-Komplexes aus wässrigem Medium mit einer geeigneten organischen Lösung des Liganden.

Als Lösungsmittel wurden Chloroform, Cyclohexanon, Methyläthylketon, Methylisobutylketon, Isobutylalkohol, Isoamylalkohol und Essigsäureäthylester geprüft. Die Löslichkeit des Dichinolyls I beträgt in Chloroform 24.8 Gew.%, bei den anderen Lösungsmitteln liegt sie in der Grössenordnung von 0.1–0.2 Gew.%. Trotz der günstigen Löslichkeit von I in Chloroform erwies sich dieses wegen unvollständiger Kupferextraktion und schneller Abnahme der Extinktion für die Kupferbestimmung als wenig geeignet. Dagegen bewährten sich höhere Alkohole, namentlich Isoamylalkohol, für die Extraktion. Auch bei Isoamylalkohol wurde eine geringe Abnahme der Extinktion beobachtet, die auf langsame Oxydation des Kupfer(I)-Chelates zurückzuführen ist. Diese Reaktion kann aber vermieden werden, wenn der verwendete Isoamylalkohol vor Gebrauch mit einer verdünnten Lösung von Hydroxylammoniumchlorid durchgeschüttelt wird; dann bleiben die Extinktionswerte mindestens 8 Tage konstant.

Die Extraktion kann im pH-Bereich von 5–10 erfolgreich durchgeführt werden. Aus stärker saurem Milieu wird sie stark zeitabhängig, so erfolgt bei pH 3 erst nach 8 Min eine 100 %ige Kupferextraktion. Als günstigster pH-Wert erwies sich pH 6, bei dem eine Extraktionszeit von 30 Sek bereits zur vollständigen Extraktion ausreicht.

In Abhängigkeit von der Menge des zugefügten Komplexbildners wurde bereits bei einem Verhältnis von Kupfer : Ligand = 1 : 2.3 konstante Extinktion erreicht. Dies bedeutet, dass für die quantitative Extraktion des Kupfers bereits ein sehr geringer Überschuss an Komplexbildner genügt.

Einfluss von Fremdionen

Zur Prüfung der Störwirkung anderer Metalle auf die Extraktion und spektrophotometrische Bestimmung von Kupfer wurden jeweils 6.35 μg Cu/ml mit einem tausendfachen Überschuss des Fremdions versetzt und im pH-Bereich 6–7 bestimmt.

Bei allen untersuchten Kationen—Ag(I), Pb(II), Bi(III), Cd(II), Sn(II), Co(II), Ni(II), Zn(II), Mn(II), Fe(III), Cr(III), Al(III), Be(II), Mg(II), Ca(II)—konnte keine Störung der Kupferbestimmung beobachtet werden. Im Einklang dazu steht der Befund, dass es nicht gelang, Komplexverbindungen des Dichinolyls I mit Ni(II) und Co(II) darzustellen. Als Ursache dafür ist die geringe Basenstärke des Dichinolyls anzusehen.

Bei Anwesenheit von Silber ist es zweckmässig, Sulfit als Reduktionsmittel zu verwenden, da durch Hydroxylammoniumchlorid Silberchlorid ausgefällt wird, und es damit zu schlechter Phasentrennung kommt. In diesem Fall ist dann aber eine längere Schüttelzeit erforderlich. Kationen, die im pH-Bereich 6–7 als Hydroxide ausfallen, können in den meisten Fällen durch Zusatz ammoniakalischer Tartratlösung komplex in Lösung gehalten werden.

Die Kupferbestimmung wird durch Anionen gestört, die selbst stabile Kupferkomplexe bilden. Während Tartrat auch bei tausendfachem Überschuss nicht stört, darf Citrat nur noch in hundertfachem Überschuss vorhanden sein. Aber auch dann erfordert eine vollständige Kupferextraktion mit dem Reagenz bereits eine Schüttelzeit von 10 Minuten und einen grösseren Reagenzüberschuss. Bei Thiosulfat ist die Störwirkung noch stärker ausgeprägt, und in Anwesenheit von Cyanid oder Amino-N-polyessigsäuren wird überhaupt keine Kupferextraktion mehr beobachtet. Cyanid kann sogar zur Rückgewinnung des Komplexbildners aus dem Kupferkomplex verwendet werden, da es das Kupfer aus diesem Komplex freisetzt und zur Tetracyanokupfer-Verbindung weiterreagiert.

Analyse von Hüttenprodukten

Zur Überprüfung der Genauigkeit der Methode wurde in 6 Hüttenprodukten nach dem angegebenen Verfahren der Kupfergehalt bestimmt. Der Aufschluss der Proben erfolgte durch Abrauchen mit Königswasser. Danach wurde der Rückstand mit Wasser ausgelaugt und die wässrige Lösung unter Zusatz von Tartrat mit Ammoniak auf pH 6–7 gebracht. Noch vorhandene Niederschläge wurden abgetrennt und sorgfältig ausgewaschen.

Als durchschnittlicher Fehler der Methode kann ein Wert von 2% angenommen werden (vgl. Tabelle I).

Arbeitsvorschrift zur spektrophotometrischen Kupferbestimmung

Als Reagenzlösung dient eine $2.5 \cdot 10^{-3}$ *M* Lösung von 3,3′-Dimethylen-4,4′-

diphenyl-2,2'-dichinolyl in Isoamylalkohol. Zur Durchführung der Kupferbestimmung werden 10 ml der Analysenlösung in einen 50-ml Schütteltrichter gegeben und die Lösung auf pH 6 gebracht. Durch Zusatz einiger Kristalle Hydroxylammoniumchlorid wird das Kupfer zur einwertigen Stufe reduziert und dann 5 ml Reagenzlösung zugegeben. Man verdünnt noch mit 10 ml Isoamylalkohol und schüttelt im Scheidetrichter zwei Minuten kräftig durch. Die wässrige Phase wird abgetrennt, die organische Schicht mit wenig wasserfreiem Natriumsulfat getrocknet und in einen 25-ml Messkolben filtriert. Die Extinktionsmessungen erfolgen bei 550 nm (HAVEMANN-Kolorimeter) oder 555 nm (Spektralphotometer). Die Extinktionen bleiben über einen Zeitraum von 8 Tagen konstant. Die Berechnung der Analysenwerte erfolgt nach dem Eichkurvenverfahren. Es sind Kupferkonzentrationen von 0.5–11 μg Cu/ml bestimmbar. Das Lambert–Beersche Gesetz ist in diesem Konzentrationsbereich streng gültig.

TABELLE I

ANALYSEN VON HÜTTENPRODUKTEN

Probe	*Bezugsanalyse Cu (%)*	*Gefunden Cu (%)*	*Fehler (%)*
Rohhüttenschlacke	0.194	0.198	2
Kupferschiefer	1.33	1.32	1
Vanadinschlacke	2.57	2.55	1
Kupferschlacke	2.37	2.34	1.4
Pyrit	0.307	0.301	2
Rohhüttenflugstaub	1.48	1.50	1

Kombination mit der Carbamat-Methode

Durch Kombination der Neocuproin- und der Carbamat-Methode der spektrophotometrischen Kupferbestimmung gelang es, die Empfindlichkeit der Neocuproinmethode unter Beibehaltung der hohen Selektivität fast zu verdoppeln[4]. Auch bei dem in dieser Arbeit vorgeschlagenen Verfahren ist eine solche Kombination möglich. Nach der Extraktion des Kupfers in Form seines Dichinolylkomplexes wurde die Messlösung mit 0.1 g Natriumdiäthyldithiocarbamat versetzt, kräftig durchgeschüttelt und bei 435 nm vermessen. Es gelang dadurch, die Nachweisgrenze für Kupfer von 0.5 μg/ml auf 0.1 μg/ml herabzusetzen. Gleichzeitig wurde der Fehler der Methode auf 1% reduziert.

Herrn Professor Dr. H. HOLZAPFEL danken wir für die Möglichkeit zur Durchführung dieser Arbeit, dem VEB Laborchemie Apolda für gute Zusammenarbeit und grosszügige Unterstützung. Dem VEB Mansfeld Kombinat "Wilhelm Pieck" gilt unser Dank für die freundliche Überlassung von Testproben.

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(Eingegangen den 24. August, 1967)

A study of interferences in the spectrophotometric determination of titanium with sulfosalicylic acid

Very few spectrophotometric methods are available for the determination of titanium which are sensitive and free from interferences. Ziegler and Glemser[1] used the yellow color with sulfosalicylic acid for the determination of titanium. According to Sandell[2]: "An attractive feature of this method is the noninterference of common metals: aluminum, manganese, calcium, magnesium, and iron. The effect of less common elements requires investigations." The sulfosalicylic acid method was therefore investigated in detail with regard to the proper wavelength, the interferences of common anions, less common cations, and effect of temperature. The possible masking of interfering ions was also studied. The results are summarized in the present report.

Apparatus

A Bausch and Lomb Spectronic-20 spectrophotometer and a pH meter model LI-10 (ELICO, Pvt. Ltd., Hyderabad, India) were used.

Reagents

Standard titanium solution was prepared by dissolving 1.00 g of titanium dioxide in 100 ml of concentrated sulfuric acid containing 50 g of ammonium sulfate and diluted to a litre. The resulting solution contained 0.5995 mg titanium per ml. It was standardized with iron(III) alum. Ten ml of this titanium solution was diluted with sulfuric acid (10 ml), ammonium sulfate (5 g) and water to 100 ml.

Acetate buffer pH 4 was prepared by dissolving 6.5 g of sodium acetate and 10.5 ml of glacial acetic acid in water and diluting to one liter.

All the chemicals were of reagent grade.

Procedure

Place an aliquot (5–10 ml) of slightly acidic titanium solution (5–100 μg of Ti) in a 50-ml volumetric flask and add 5 ml of aqueous 20% sulfosalicylic acid followed by one drop of slightly acidic aqueous 5% iron(III) chloride solution. Then add ammonia until the color changes to yellow, followed by 20 ml of buffer solution. Mix, add 5 ml of fresh 4% mercaptoacetic acid solution and dilute to 50 ml with water. After 10 min measure the absorbance at 355 nm against a blank. The color is stable and is proportional to titanium concentration.

Absorption spectrum

Figure 1 shows the absorption spectrum for a solution containing 60 μg of titanium; the maximum occurs at 355 nm.

Effect of variables

Studies of the effect of time showed that no significant change in absorbance occurred up to 20 h. The effect of pH was studied over the range 0–10; the color intensity remained constant from pH 3–5.5. The absorbance was found to be essentially constant over the temperature range 0–100°.

The Beer–Lambert law was obeyed over the range 0–120 μg of titanium at 355 nm.

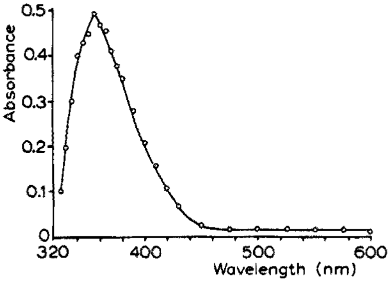

Fig. 1. Absorption spectrum.

TABLE I

EFFECT OF FOREIGN IONS ON TITANIUM DETERMINATION AT 355 nm
(100 μg of TiO_2 present; 6000 μg of interfering ion added)

Foreign ion	*TiO_2 found (μg)*	*% Error*	*Foreign ion*	*TiO_2 found (μg)*	*% Error*
Al	100	±0.00	AsO_4^{3-}	104	+4.0
Mn	98	−2.0	AsO_3^{3-}	103	+3.0
Ca	100	±0.0	S^{2-}	96	−4.0
Mg	98	−2.0	Formate	102	+2.0
Zn	98.5	−1.5			
Th	100	±0.00	I^-	98	−2.0
Zr	104	+4.0	Br^-	100	±0.00
La	100.5	+0.5	ClO_3^-	102	+2.0
			$C_2O_4^{2-}$	102	+2.0
Sn^{4+}	97	−3.0	IO_3^-	98	−2.0
Sn^{2+}	99	−1.0	SO_3^{2-}	94	−6.0
Ga^{3+}	93.5	−6.5	Cl^-	100	±0.00
Tl	96	−4	BrO_3^-	97	−3.0
In^{3+}	95	−5			
Ni	108	+8	SO_4^{2-}	100	±0.00
Cd	102.5	+2.5	Acetate	100	±0.00
Hg^{2+}	101	+1.0	NO_3^-	100	±0.00
			Co[a]	98	−2.0
Y^{3+}	99	−1.0	Pt[a]	100	±0.00
NH_4^+	105	+5.0	Pd[a]	101	+1.0
Ce^{3+}	101	+1.0	Cu[a]	100	±0.00
CN^-	101.5	+1.5			

[a] Ascorbic acid substituted for mercaptoacetic acid.

Effect of foreign ions

The influence of foreign ions on titanium was determined. The following ions did not interfere when present in hundred-fold excess: Al, Mn, Ca, Mg, Zn, Th, Zr, La, Sn, Ga, Tl^+, In, Ni, Cd, Hg^{2+}, Y^{3+}, NH_4^+, Ce^{3+}, S^{2-}, CN^-, Cl^-, I^-, Br^-, SO_4^{2-}, arsenite, formate, chlorate, oxalate, iodate, thiocyanate, nitrate. The results are summarized in Table I. Ions which interfered when present in 100-fold excess were Bi^{3+}, Ce^{4+}, Co, Cr, Cu, Mo, Pd, Pt, Te, U, V, W, citrate, tartrate, $S_2O_3^{2-}$, F^-.

Palladium could be masked by adding 10 drops of 10% potassium cyanide before adding sulfosalicylic acid in the above procedure. The interference of Co, Pt, Bi, Pd, and Cu was removed when 5% ascorbic acid was used in place of mercaptoacetic acid. The precipitate obtained in the case of Pt, Pd, Bi and Cu was removed by centrifuging before the solution was diluted to 50 ml.

Discussion

The present study shows that in the sulfosalicylic acid method even the less common ions like Th, Zr, La, Ga, Tl, In, Y, and Ce do not interfere in addition to the ions mentioned by ZIEGLER AND GLEMSER[1]. Interferences from metal ions such as Co(II), Pt(IV), Pd(II) and Cu(II) are completely removed when ascorbic acid is used in place of mercaptoacetic acid. Cyanide prevented the interference of palladium without separation. Of the various anions tested, only tartrate, citrate, fluoride and thiosulfate interfere. The method is therefore highly selective for the determination of titanium. When the absorbance is measured at 355 nm instead of 445 nm the method becomes 10 times more sensitive. It therefore appears that this is probably the best method for the determination of titanium.

The authors are grateful to Prof. A. R. KIDWAI for providing research facilities.

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(Received September 6th, 1967)

The spectrophotometric determination of nickel in sea water with pyridine-2-aldehyde-2-quinolylhydrazone

The accurate determination of the small amounts of nickel present in sea waters[1] is both difficult and time-consuming. Basic procedures involve combined separation and concentration of nickel from a relatively large volume of sea water before determination. Pyridine-2-aldehyde-2-quinolylhydrazone (PAQH) reacts with nickel to give a complex, readily extractable by benzene, with a molecular extinction coefficient of $67 \cdot 10^3$ l/mole cm; since the few metal ions that react to give colored species with PAQH[2] can be masked, a highly selective determination of nickel is possible[3]. The high sensitivity and selectivity of this procedure prompted investigation of its potential for the determination of nickel in sea water. A simple procedure, which involves solvent extraction for the concentration and simultaneous determination of nickel, has been developed; comparatively small volumes (250 ml) of sea water are required and the determination can be done in 3–4 h.

Apparatus, reagents and solutions

A Bausch and Lomb Spectronic 505 recording spectrophotometer was used.

PAQH was prepared as previously described[2]. Aqueous solutions (0.05 and 1%) of the reagent were prepared by dissolving the solid in a minimum amount of hydrochloric acid and, after dilution, adjusting to a pH of 3–4 with ammonia.

Spectrographically pure nickel sponge was used to prepare the stock solution; it contained 0.584 mg of nickel per ml as determined by a dimethylglyoxime precipitation. Diluted standards (10^{-4} and 10^{-5} M) were prepared daily from this solution.

Effect of different media

In the previously described procedure[3], solutions were made 20% in ethanol before extraction of the nickel complex by chloroform. In sea water, however, salt was precipitated on the addition of ethanol and phase separation was difficult. Although satisfactory results were obtained using a 1:5 butanol–chloroform extractant, different solvents were examined in order to eliminate the use of a binary mixture as extractant. An aqueous phase containing 1 ml of $10^{-4}M$ nickel solution, 5 ml of 0.05% reagent, 10 ml of 10% sodium citrate and 10 ml of ammonia–ammonium chloride buffer pH 10 (mixture A) was shaken with 25 ml of solvent. The absorbance of the resultant organic phase was measured in a 1-cm cell against a reagent blank prepared in the same manner.

Benzene proved the most satisfactory of the solvents investigated (benzene, butanol, chloroform, ethyl acetate, carbon tetrachloride, amyl alcohol); the nickel complex was readily extracted and the molecular extinction coefficient, at 515 nm, was $67 \cdot 10^3$. Figure 1 shows the spectrum for nickel–PAQH complex extracted into benzene.

Extraction from larger volumes

Since the abundance of nickel in sea water is low, concentration is necessary. This is usually done by precipitation with sodium carbonate[1] but chelating agents such as 8-quinolinol, tannic acid and thionalide[4] have been used. The high sensitivity of PAQH and the ready extractability of its nickel complex into benzene suggested that simultaneous concentration and determination of nickel in sea water might be possible. The efficiency of the extraction of the nickel–PAQH complex from larger volumes of aqueous phase, *viz.* 50, 100, 250 ml, into 25 ml of benzene was therefore investigated.

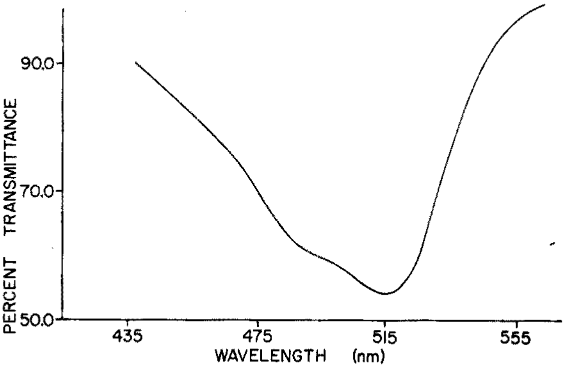

Fig. 1. Transmittance spectrum of $4 \cdot 10^{-6}M$ Ni^{2+}–PAQH complex extracted in benzene.

The aqueous phase contained 1 ml of $10^{-5}M$ nickel solution as well as the other reagents described above (mixture A); measurements were made against reagent blank in 10-cm cells. There was incomplete recovery of nickel from 100 ml and 250 ml volumes (absorbance was 0.226 and 0.204 respectively compared to 0.264 from 25 ml of aqueous phase). However, complete recovery of nickel was obtained if 2.5 ml of 1% reagent was added; the initial incomplete recovery was due to the low overall reagent concentration in the higher volumes of solution.

Salt effect

Absorbance measurements in aqueous solution often vary as the ionic strength changes and positive and negative errors, relative to results obtained in distilled water, have been reported in sea water[1,4]. To investigate this effect varying amounts of sodium chloride, covering the concentration range 1–10%, were added and the nickel–PAQH complex was extracted, from a 250-ml volume, into 25 ml of benzene. Identical results (A =0.264) were obtained for all solutions and no salt error is experienced with the nickel–PAQH reaction.

Interferences

Cadmium, cobalt, copper, iron, mercury and zinc form colored complexes with PAQH which are extracted by benzene. In the presence of thioglycollic acid, however, only nickel and iron form extractable complexes. Iron interference was previously removed by extracting the thiocyanate complex before determining nickel[3] but the method is unsatisfactory when a 250-ml aqueous phase is used. Iron (and other ions including nickel) can be masked at pH 10 with ascorbic acid and potassium cyanide[5]. Nickel (and other ions) but not iron can be demasked by formaldehyde and nickel was selectively determined by extracting the nickel–PAQH complex after addition of thioglycollic acid. The following procedure proved satisfactory to mask interfering ions and obtain 100% recovery of nickel.

Procedure

To 250 ml of aqueous solution containing nickel and other metal ions, add 10 ml of a 10% sodium citrate solution, 20 ml of ammonia/ammonium chloride buffer of pH 10, 2.5 ml of 5% potassium cyanide and 10 ml of 20% ascorbic acid; heat to 70° to 80°. Cool the solution to room temperature and add 2.5 ml of a freshly prepared 5% formaldehyde solution. Adjust the pH to 5.0 with 5 N hydrochloric acid, add 2.5 ml of 1% PAQH solution and 5 ml of thioglycollic acid, and make the pH of the resulting solution 10 with ammonia. Extract, after 30 min, with two 25-ml aliquots of benzene. Collect the extracts in a 50-ml volumetric flask, dilute to the mark with benzene and measure, in a 10-cm cell, against a reagent blank carried through the same procedure.

Calibration curves and results

Typical results are shown in Table I; each result is the average of 3 determinations.

Since different calibration curves are sometimes obtained in distilled water and sea water, 3 calibration curves for the nickel–PAQH system (2.5–10 p.p.b. Ni) were prepared, *viz.* from 25 ml of distilled water, from 250 ml of distilled water, and from 250 ml of sea water. Identical straight-line calibration curves, passing through the origin, were obtained.

TABLE I

RECOVERY OF NICKEL FROM SPIKED SAMPLES IN THE PRESENCE OF INTERFERING IONS

Foreign ions present	*Nickel taken (p.p.b.)*	*Nickel found*[a] *(p.p.b.)*
25-fold excess of Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+} and Zn^{2+}	4.70	4.77 ± 0.09
50-fold excess of above metal ions	4.70	4.84 ± 0.09
100-fold excess of above metal ions	4.70	4.89 ± 0.08

[a] The increasingly high average with increased amount of metal ions added is probably due to minute traces of nickel in the spiking solutions.

TABLE II

ANALYSIS OF SEA WATER SPIKED WITH KNOWN AMOUNTS OF NICKEL AND SEA WATER ALONE

Composition of solution	*Absorbance expected*	*Absorbance found*	*Amount of nickel found (p.p.b.)*
Sea water + 0.587 mg of nickel (2.35 p.p.b.)	0.264	0.268	2.38
	0.264	0.271	2.42
	0.264	0.264	2.35
Sea water + 1.174 mg of nickel (4.70 p.p.b.)	0.527	0.523	4.66
	0.527	0.516	4.60
	0.527	0.509	4.54
Sea water against the reagent blank in distilled water	—	0.256	2.31
	—	0.276	2.45
	—	0.251	2.29
Sea water against the reagent blank in 3.5% sodium chloride	—	0.262	2.34
	—	0.244	2.18
	—	0.251	2.29

Eleven samples of sea water were spiked with a known amount of nickel (4.70 p.p.b.) and the solutions analyzed; the samples were measured against a reagent–sea water blank. The results obtained were 4.70 ± 0.22 p.p.b. Table II also shows results for nickel added to sea water and the nickel content found for the sea water alone. The procedure described above was used but the aqueous phase was extracted with 20-ml and 5-ml aliquots of benzene; the organic phase was diluted to 25 ml with benzene and measured against a reagent blank carried through the same procedure.

A sample of sea water was provided by Dr. P. WANGERSKY of the Dalhousie Institute of Oceanography. The water was taken from 5 m below the surface, using 30-l Nuskin bottles, in March, 1967, from the North Atlantic on a 100-mile transect out of Halifax toward Bermuda. The nickel content of this sea water was found to be 2.31 ± 0.06 p.p.b. (6 analyses).

This work was supported by grants from the Defence Research Board and National Research Council. The award of a Dalhousie Postdoctoral Fellowship to B. K. A. is hereby acknowledged.

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(Received September 26th, 1967)

Anal. Chim. Acta, 41 (1968) 167–170

Combined thermo-dilatometric and derivatographic examination of hydrargillite and barium chloride dihydrate*

Recently, a new complex thermoanalytical method was developed by combining derivatography and dilatometry[1,2]. In this method, the weight change (TG curve), rate of weight change (DTG), thermal dilation (TD) and rate of dilation (DTD), as well as the temperature (T) and rate of enthalpy change (DTA) of the sample compressed into an appropriate size are measured and recorded.

The results obtained by the application of this method to the thermal decomposition of hydrargillite are shown in Fig. 1. According to the literature[3–5], the thermal decomposition of hydrargillite proceeds in two overlapping partial processes. The scheme of the thermal decay[6] is also shown in Fig. 1. According to the TG and DTG curves, the substance loses about 0.5 molecule of water between 180 and 220°. In this temperature range probably only boehmite will be formed[7]. The TD and

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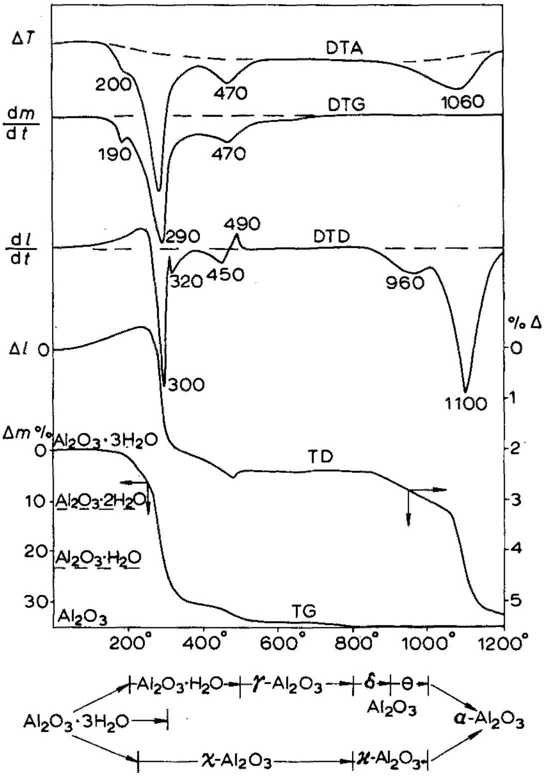
* Paper presented at the XXIst IUPAC Congress, Prague, 1967.



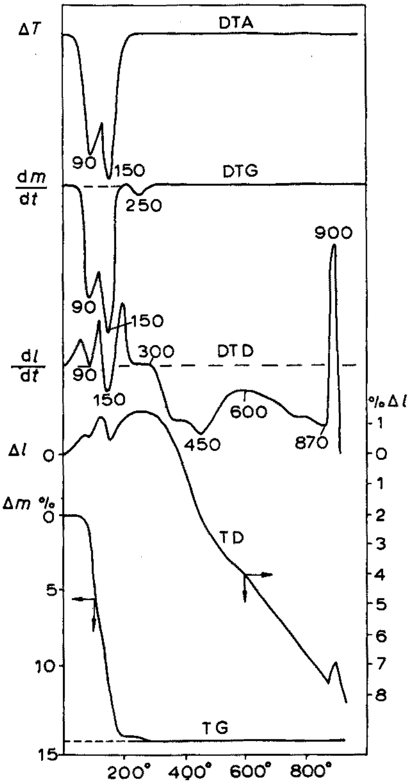


Fig. 1. Hydrargillite.

Fig. 2. Barium chloride dihydrate.

DTD curves indicate in this temperature interval a dilation of about 0.5% in the length of the test piece. Shrinkage only begins when the remaining undecomposed part of the hydrargillite transforms into χ-Al_2O_3. This process takes place between 220 and 310° while about 2 molecules of water escape. The temperature at 310° must be regarded as the critical point of the transformation. In this state of thermal decomposition the internal specific surface area reaches its maximum[7,8]; the substance loses its rehydration capacity at this stage and the X-ray lines specific for hydrargillite[6] also disappear. The peak of the DTD curve at 320° is probably also connected with this process. Subsequently, the temporarily formed boehmite will decompose with a maximum rate at 470°. The peak at 450° of the DTD curve showing contraction and the one at 490° showing expansion are probably connected with the collapse of the crystal structure of boehmite and the formation of the γ-Al_2O_3 lattice. The remaining amount of water (*ca.* 1%) will escape gradually up to 800°. According to the literature[6], at 800° a double transformation begins; first, γ-Al_2O_3 changes to δ-Al_2O_3 and then to θ-Al_2O_3, while χ-Al_2O_3 transforms to κ-Al_2O_3. This process takes place between 800 and 1000° and involves, according to the TD curve, a contraction of about 1% of the sample. According to the DTD curve, the contraction proceeds with maximum rate at 960°. About 1050° the formation of α-Al_2O_3 starts but is not completed even at 1200°.

Figure 2 shows the derivatogram of barium chloride dihydrate, the thermal expansion of which has been little studied[9]. According to the TD and DTD curves, the sample loses its water of crystallisation in two steps. First about 1 molecule and then another molecule of water escapes. The sample releases the last traces of the remaining small amount of water at about 250°. This process is remarkable from the point of view of dilation. In the course of the thermal decomposition of many other crystal hydrates it was observed that the release of the water of crystallisation is nearly always preceded by an expansion of the sample[1,10]. It seems likely that the water molecules, before escaping from the lattice, become highly excited and as a result of their augmented vibrational motion the lattice space increases. This probably happened in the present case but the effective release of water resulted in volume contraction. The part of the TD and DTD curves between 20 and 300° is the result of this double process. After the last traces of water have been released at about 300°, the monoclinic lattice of barium chloride dihydrate collapses. However, the rhombohedral lattice of the wholly inordinate crystal structure will be formed only later and then very slowly[11,12]. This process, consisting of several steps, is completed at 870°, while the compressed test piece decreases by about 8% in length. The very rapid dilation of about 0.5% at 900°, directly before the fusion of the substance, shows the transformation from the α- to the β-modification of the anhydride.

The authors wish to express their thanks to M. CSONKA and E. BORSAY for the technical assistance rendered.

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(Received September 28th, 1967)

Le dosage volumétrique du béryllium en présence de quantités importantes d'uranium

La méthode de dosage volumétrique du béryllium la plus fréquemment utilisée, consiste à ajouter un excès de fluorure de sodium à la solution contenant le béryllium en suspension sous la forme d'hydroxyde[1]. Les ions fluorures complexent le béryllium selon la réaction:

$$Be(OH)_2 + 4\ F^- \rightarrow [Be\ F_4]^{2-} + 2\ OH^-$$

On dose ensuite la quantité de soude libérée à l'aide d'une solution d'acide sulfurique de titre connu. La réaction n'étant pas toujours quantitative, il est nécessaire de tracer une courbe d'étalonnage avec des conditions opératoires rigoureusement définies.

En présence d'une quantité notable d'uranium, le dosage n'est plus possible car l'hydroxyde d'uranium précipité en même temps que celui du béryllium forme également un complexe avec les ions fluor avec libération d'ions hydroxyles. Pour éviter l'interférence de l'uranium, il est donc nécessaire de fixer cet élément dans un complexe dont le pK soit supérieur à celui du complexe fluoré susceptible de se former tout en restant stable dans l'intervalle de pH traversé au cours du dosage.

Les composés peroxouraniques formés avec le peroxyde d'hydrogène selon une réaction du type:

$$H_2UO_4 + 3\ H_2O_2 \rightarrow \text{``}H_4\ UO_8\text{''} + 2\ H_2O$$

remplissent ces conditions. Nous avons donc étudié l'influence de la présence de peroxyde d'hydrogène sur le dosage du béryllium seul ou en présence d'uranium.

Influence du peroxyde d'hydrogène

Afin d'étudier l'influence de la présence de peroxyde d'hydrogène, nous avons procédé au dosage de quantités croissantes de béryllium (0–18 mg) en présence d'un même volume de peroxyde d'hydrogène (2 ml à 110 vol.) et au dosage d'une même quantité de béryllium après addition de volumes croissants de peroxyde d'hydrogène. La courbe d'étalonnage obtenue dans le premier cas met en évidence l'existence d'un blanc. La valeur de ce blanc augmente avec la quantité de peroxyde d'hydrogène ajoutée ainsi que le montrent les résultats obtenus dans le deuxième cas (Tableau I). La valeur du blanc est donc uniquement fonction de la quantité de peroxyde d'hydrogène présente, cette quantité étant elle-même déterminée par la quantité d'uranium à complexer.

Pour que le dosage du béryllium en présence d'uranium reste encore possible, il est donc absolument nécessaire que la concentration variable en peroxyde d'hydrogène entraîne une variation du résultat ne dépassant pas les limites de la dispersion observée en l'absence d'uranium. Nous avons effectué deux séries de mesures, l'une pour du béryllium seul, l'autre en présence de quantités variables d'uranium (10–500 mg). Dans un cas comme dans l'autre, nous avons ajouté à la solution à doser 2 ml de peroxyde d'hydrogène à 110 volumes, c'est-à-dire la quantité théoriquement nécessaire pour complexer 1.5 g d'uranium. Le Tableau II rend compte de l'ensemble des résultats obtenus. Nous avons ensuite tracé à l'aide de la méthode des moindres carrés, la droite représentant la quantité de béryllium dosée en fonction de la quantité d'uranium présente. Cette droite a pour pente: $a = 8.62 \cdot 10^{-5}$ et pour ordonnée à l'origine: $b = 8.972 \cdot 10^{-3}$ g.

TABLEAU I

EFFET DU PEROXYDE D'HYDROGÈNE

Be théorique (mg)	*H_2O_2 110 volumes (ml)*	*N SO_4H_2 ajoutés (ml)*
4.5	0	0.985
4.5	2	1.005
4.5	5	1.100
4.5	10	1.260

TABLEAU II

LE DOSAGE DU BÉRYLLIUM EN PRÉSENCE D'URANIUM

Be théorique (mg)	*No. des essais*	*U ajouté (mg)*	*Be dosé (mg)*
9	10	0	8.99 ± 0.04
9	5	10	8.92 ± 0.02
9	4	100	8.99 ± 0.02
9	1	200	9.00
9	1	250	9.05
9	4	500	9.00 ± 0.04

Afin de vérifier si l'écart existant entre la droite obtenue et la droite théorique, dont la pente et l'ordonnée à l'origine sont respectivement $a_0 = 0$ et $b_0 = 9.00$ est significatif, nous avons appliqué la méthode décrite par NALIMOV[2]. Cette méthode permet de définir un domaine de certitude pour les couples $a_0 - a$ et $b_0 - b$ en dehors duquel on considère qu'il existe un écart significatif entre la droite théorique et la droite expérimentale. Le point représentatif du couple $a_0 - a = 8.62 \cdot 10^{-5}$ et $b_0 - b = 28 \cdot 10^{-3}$ g est à l'intérieur de l'ellipse limitant le domaine de certitude à 95%. On peut donc considérer qu'il n'y a pas d'écart significatif entre les deux droites. D'après ce test, la présence d'uranium jusqu'à 500 mg n'affecte pas le dosage du béryllium.

Conditions opératoires

Nous avons utilisé un potentiomètre enregistreur Metrohm. L'addition de la solution titrante s'effectue à l'aide d'une burette automatique.

On recueille dans un becher une partie aliquote de la solution à doser contenant au moins 5 mg de béryllium. On ajoute 2 ml de peroxyde d'hydrogène à 110 volumes, puis on ajuste le pH à la valeur 11 par addition d'une solution d'hydroxyde de sodium 10 *N*. On ramène ensuite le pH à une valeur légèrement supérieure à 8.5 par addition d'une solution d'acide sulfurique 4 *N*, l'ajustement final à la valeur 8.5 s'effectuant par addition d'une solution d'acide sulfurique 0.1 *N*. On ajoute ensuite 20 ml de fluorure de sodium (pH = 8.5). Après deux à trois minutes d'attente, on procède au dosage par addition lente de la solution titrée d'acide sulfurique. La vitesse d'addition du réactif est de $5 \cdot 10^{-2}$ ml/min. Le point équivalent correspond au point d'inflexion de la courbe enregistrée.

Conclusion

L'exploitation statistique des résultats obtenus, montre que le dosage volumétrique du béryllium reste possible même en présence d'uranium, l'influence de ce dernier élément ayant été préalablement éliminé par complexation au peroxyde d'hydrogène sous la forme d'un composé de type peroxouranique.

La présence de peroxyde d'hydrogène en léger excès entraîne des variations du résultat final qui ne dépassent pas les limites de la dispersion observée pour la mesure proprement dite.

En définitive, la méthode proposée permet donc le dosage du béryllium en présence de quantités d'uranium ne dépassant pas 500 mg, sans séparation et avec une précision acceptable. Celle-ci est de l'ordre de 1 à 3% pour des quantités de béryllium dosé comprises entre 2 et 20 mg.

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(Reçu le 30 septembre, 1967)

The use of chelating ion exchange in the determination of molybdenum and vanadium in sea water

Vanadium and molybdenum have been generally determined in sea water after concentration by coprecipitation[1–9] or co-crystallization[10,11]. Since the carrier or co-crystallizing agent must generally be removed before the elements can be determined spectrophotometrically, the analysis is time-consuming. The authors have recently described the use of chelating ion-exchange resins for the analytical concentration of trace metals from sea water[12*]. They observed that vanadium, molybdenum and tungsten were quantitatively adsorbed from sea water at pH 5 by a 6.0 × 1.0 cm bed of Chelex-100. These elements could be quantitatively eluted and separated from the other trace metals taken up by the resin with 20 ml of 2 *N* ammonia solution. This note describes the use of this technique in a simple and rapid photometric method for the determination of vanadium and molybdenum in sea water. The photometric procedures are based on those used by CHAN AND RILEY[8,9].

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[*] *Note added in press.* Further work has shown that with some batches of resin there is slight leakage of zinc in the first 150 ml of percolate, equivalent to a loss of 3–4% with a 1-l sample; the loss is negligible with 10-l samples. The loss can be prevented by converting the resin to the ammonium form by treating it with excess redistilled 4 *N* ammonium hydroxide and washing with water before packing into the exchange column.

Apparatus

A Unicam S.P. 500 spectrophotometer was used for all photometric measurements.

Reagents

Chelating resin. Digest Chelex-100 (50–100 mesh) with 2 *N* nitric acid and fill 1-cm diameter ion-exchange columns to a depth of 6 cm with it. Wash the columns with 20 ml of 2 *N* nitric acid and then with redistilled water until the pH of the washings is 4.5. The resin can be used many times, but should be removed from the glass column before regeneration with 2 *N* nitric acid.

For molybdenum determination. Reducing and complexing reagent. Dissolve 1 g of ascorbic acid, 5 g of citric acid and 5 g of thiourea in water and dilute to 100 ml.

Dithiol reagent. Dissolve 0.5 g of dithiol in 100 ml of 0.5% (w/v) potassium hydroxide solution. The reagent can be stored for up to 1 week at 0°.

Standard molybdenum solution (100 µg Mo/l). Dissolve 0.0750 g of A.R. molybdenum trioxide (dried at 250°) in 10 ml of 0.1 *N* sodium hydroxide solution, dilute to *ca.* 100 ml and add 20 ml of 0.1 *N* hydrochloric acid. Dilute to 1 l. Prepare a working standard solution from this solution, containing 1 µg Mo/l, by dilution with 0.1 *N* hydrochloric acid.

For vanadium determination. Diaminobenzidine reagent 0.4% (w/v) aqueous solution.

Standard vanadium solution (100 µg V/l). Dissolve 0.2296 g of A.R. ammonium vanadate in water and dilute to 1 l. Prepare a working standard solution from it containing 2 µg V/l.

Determination of molybdenum and vanadium in sea water

Take 3 l of the filtered (0.5-µ filter) sample and adjust it to pH 5.0±0.2 by cautious addition of 0.2 *N* nitric acid solution. Allow the sample to flow through the Chelex column at a rate not exceeding 5 ml/min. Wash the resin with 200 ml of redistilled water and elute molybdenum and vanadium with 24 ml of 2 *N* ammonia solution. Collect the eluate in a 25-ml graduated flask and dilute to volume.

Vanadium determination

Pipette out 12 ml of the solution and evaporate to dryness in a silica basin on the water bath. Dissolve the residue in 5 ml of 0.1 *N* ammonia solution, and transfer the solution quantitatively to a 10-ml graduated flask. Add 1 ml of 85% phosphoric acid, and after cooling add 1 ml of 3,3′-diaminobenzidine reagent. Dilute to volume, and after 30 min measure the optical density of the solution at 470 nm in a 4-cm cell relative to distilled water. Carry out a reagent blank in the same manner using 3 l of water which has been stripped of vanadium by passage through a Chelex column.

Calibrate the method by treating 2.5- and 5-ml aliquots of standard vanadium solution (5 and 10 µg V respectively) with 1 ml of 85% phosphoric acid and 1 ml of diaminobenzidine reagent and diluting to 10 ml. Measure the optical density of the solution at 470 nm in a 4-cm cell after 30 min. Carry out a corresponding reagent blank using distilled water.

Determination of molybdenum

Transfer 12 ml of the eluate solution to a 50-ml separating funnel. Add 10 ml of concentrated hydrochloric acid, 5 ml of the reducing and complexing reagent and 5 ml of 0.5% dithiol reagent. Mix well, and after 10 min extract the greenish molybdenum complex with 5 ml of *n*-butyl acetate. Measure the optical density of the organic extract at 670 nm in a 1-cm cell relative to *n*-butyl acetate. Determine the reagent blank by carrying a sample of sea water, which has been stripped of molybdenum by passage through a Chelex column, through the whole process.

Calibrate the method by treating 10-ml aliquots of the working standard molybdenum solution (10 μg Mo) with 10-ml of concentrated hydrochloric acid, 5 ml of the reducing and complexing reagent and 5 ml of 0.5% dithiol reagent. After 10 min extract the solution with 5 ml of *n*-butyl acetate. Measure the optical density of the extract at 670 nm in a 1-cm cell. Carry out a corresponding reagent blank using 10 ml of 0.1 *N* hydrochloric acid.

Results

Precision and accuracy of the methods. The reproducibility of the methods was evaluated by carrying out 5 replicate analyses on filtered Irish Sea coastal water (Cl = 18.34‰). These analyses showed that the water contained 3.12 ± 0.04 μg V/l and 8.40 ± 0.07 μg Mo/l. Since the water sample before filtration contained considerable amounts of suspended matter these concentrations should not be considered representative of ocean water.

TABLE I

RECOVERY OF VANADIUM AND MOLYBDENUM FROM SPIKED 3-l SAMPLES OF STRIPPED SEA WATER (μg/l)

Serial no.	*Vanadium*		*Molybdenum*	
	Added	*Found*	*Added*	*Found*
1	0.0	0.00	0.0	0.00
2	1.0	0.92	5.0	5.00
3	2.0	2.01	10.0	10.05
4	4.0	3.95	20.0	19.90
5	5.0	5.04		

In order to check the accuracy of the method a sample of sea water was brought to pH 5 and stripped of both vanadium and molybdenum by passage through a 30 × 2 cm column of Chelex-100. Aliquots (3 l) of the stripped sample were analysed both alone and after spiking with known amounts of vanadium and molybdenum. The results of these analyses (Table I) showed that the accuracy of the methods was satisfactory.

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(Received November 22nd, 1967)

Fluorimetric determination of glycine and other amino acids with 2,4-~~butanedione~~ pentanedione.

Many colorimetric methods have been developed for the analysis of amino acids. Some of these (*e.g.* ninhydrin[1]) have been applied to the analysis of complex mixtures of amino acids with automatic amino acid analyzers. Others have been applied to the quick analysis of one particular amino acid either directly or after a simple separation step. For example, these are some of the methods (and their properties) that have been used for the analysis of glycine: (*a*) reaction with ethyl chloroformate and pyridine (specific in presence of other amino acids, λ_{max} 420 nm, ε 2960)[2]; (*b*) formation of 3-phenyl-2-thiohydantoin and reaction with ammonia (only slight interference from serine and threonine, λ_{max} 520 nm, ε 9400)[3]; (*c*) reaction with *o*-phthalaldehyde in alkaline media (specific in absence of tryptophan and ammonium salts)[4,5]; condensation with 2,4-dinitrofluorobenzene[6]; nitrosation, followed by oxidation to formaldehyde and condensation with chromotropic acid (specific in presence of other amino acids, λ_{max} 580 nm and ε 15700)[6]; oxidation with ninhydrin to formaldehyde which is then reacted with chromotropic acid (non-specific, λ_{max} 580 nm and ε 15700)[7]; and reaction with 2,4-butanedione (primary amines react, λ_{max} 415 nm and ε 640)[8]. The most generally used colorimetric method for glycine and other amino acids depends on the reaction with ninhydrin to form a chromogen absorbing at 570 nm with ε 21000[9].

Although the sensitivity of the 2,4-pentanedione procedure was poor, it was

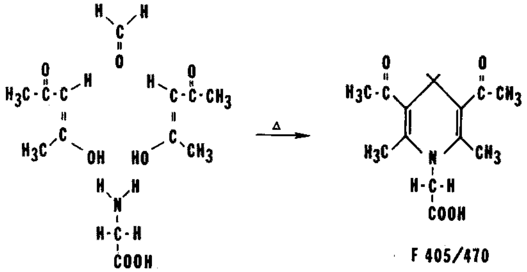

Fig. 1. Determination of glycine.

considered that it could be improved considerably by a radical change. Since fluorimetric methods are usually more sensitive than colorimetric methods and also have a greater potential for increases in sensitivity, it was decided to develop a fluorimetric method that could be useful in the analysis of primary aliphatic amines as well as of glycine and some of the other amino acids. The advantages and disadvantages of this procedure are discussed.

The method depends on the reaction of glycine (or some other primary amine) with 2,4-butanedione and formaldehyde to give 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine (Fig. 1). These compounds show vivid fluorescence in solution.

Reagents

All the reagents and amino acids are readily available from commercial sources in a pure form.

2,4-Butanedione solution. 25% sodium acetate, 0.4% acetic acid, and 0.5% 2,4-butanedione in water.

Apparatus

An Aminco-Bowman spectrophotofluorimeter with 0.1-ml and 1-ml cells was used with the following settings: sensitivity 50, slit arrangement No. 2, and phototube RCA type 1P21.

Procedure

Heat 1 ml of aqueous test solution with 2 ml of butanedione solution (in a test tube equipped with a cold finger) on the boiling water bath for 10 min. Cool under the tap. Add 1 ml of aqueous 4.1% formaldehyde solution and heat the mixture again on the boiling water bath for 10 min with the help of the cold finger. Cool under the tap. Read at F405/470 immediately. Fluorescence intensity holds for at least 1 h. One-tenth volumes can be used with no loss in sensitivity.

TABLE I

FLUORIMETRIC ASSAY OF GLYCINE AND OTHER PRIMARY AMINES AT F405/470

Compound	*Rel. fluor. intensity*	*Compound*	*Rel. fluor. intensity*
Ethanolamine	200	Ethylenediamine	15
i-Butylamine	120	Threonine	12
Allylamine	100	Guanine[b]	11
Glycine[a]	100	Cysteine	9.2
n-Butylamine[b,c]	78	Tryptophan[b,d]	6
Serine	54	3,4-Dihydroxyphenylalanine	5
Glutamine	41	Aniline[c]	2
Alanine	41	Histidine	1.5
Cysteine[b]	33	Proline	0.6
Arginine	30	Adenine[e]	0.3
Tyrosine[b,c]	21		

[a] MM · T = 0.68. Final concentrations for all compounds were $2.5 \cdot 10^{-5} M$.
[b] Dissolved in dilute aqueous hydrochloric acid.
[c] F405/510.
[d] F375/465.
[e] Dissolved in 5% aqueous acetic acid.

Results

The various volumes, concentrations, and heating times were adjusted to give optimum intensities with glycine. The fluorescence intensity was stable for at least 1 h. Conformance with Beer's law was observed with amounts of glycine from 0.5 to 60 μg for the macro procedure and from 0.05 to 6 μg for the micro procedure. The relative standard deviation for 11 determinations was ±2.9%. The blank gave an MMT value of 0.05 at F405/470, approximately equivalent to 0.5 μg of glycine in the macro procedure.

Since most pollutants are present in the atmosphere in trace amounts, sensitive methods of analysis are desirable. This method provides desirable sensitivity in the determination of glycine, aliphatic primary amines, and a few of the amino acids. The method is most sensitive for glycine and some of the aliphatic amines (see Table I). It can determine 50 ng of glycine and about 20 ng of ethanolamine. Ammonium acetate reacts also, giving a fluorescence intensity about 42% that of glycine. Thus, the method could be used for the analysis of ammonia and aliphatic amines and their precursors, as well as glycine and some of the amino acids.

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(Received September 21st, 1967)

Determination of lanthanum, holmium, and uranium in their tungsten bronzes by thermal neutron activation

The "tungsten bronzes" are nonstoichiometric compounds of the formula M_xWO_3, in which M is any one of a number of metals and $0<x<1$. The existence of the best known of these compounds, Na_xWO_3, was first reported by WÖHLER[1] in 1823, but its formula was not confirmed until 1935[2]. The bronzes were given this name because of the metallic luster and bronze color which many of them display. They are of considerable current interest in solid state science because of the remarkable changes in their properties which accompany changes in composition. In the sodium tungsten bronzes, for example, sodium is present as Na^+ ions in an expanded WO_3 lattice, with an equivalent number of electrons having many of the properties of conduction electrons in a metal. These non-localized electrons give the bronzes their metal-like properties, and since the value of x for sodium can be varied from about 0 to 1, the concentrations of these electrons can also be varied over this range.

Correlation of properties with electron concentration can be made if the x value is known, and the reliability of the correlation increases with the precision of the analysis. In addition to the sodium bronzes, which have received the most study, a number of other metals of the alkalis, alkaline earth and rare earth and other groups have been incorporated into the bronze structures, in some cases presenting a considerable task in synthesis.

The task of analysis is also considerable since the tungsten bronzes are chemically inert to most reagents and do not lend themselves well to most chemical analyses. Several analytical methods have been proposed[3-5], but because of the nature of these compounds, considerable time is required and destruction of the samples occurs in all cases. The method of activation analysis was first applied to the nondestructive analysis of the sodium tungsten bronzes[6], and more recently to those of potassium, rubidium, and barium[7]. The method is extremely rapid and has yielded excellent results.

Experimental

The concentrations of lanthanum, holmium, and uranium in their tungsten bronzes were determined by γ-scintillation spectrometry, following irradiation with thermal neutrons. In all cases ^{187}W, produced by the reaction $^{186}W(n,\gamma)^{187}W$, was the major interference. For all irradiations, standard samples were irradiated simultaneously with the bronze samples. Thus, the weight of metal present in the bronzes could be determined by the expression

$$\frac{\text{Activity of standard}}{\text{Weight of standard}} = \frac{\text{Activity of unknown}}{\text{Weight of unknown}} \qquad (1)$$

In all cases in which the oxygen to tungsten ratio in the bronzes has been determined[4], it has been found to be exactly 3. If this is assumed, the x values for the tungsten bronzes can be calculated by using the equation

$$x = \frac{F}{1-F} \cdot \frac{Mw}{My} \qquad (2)$$

In eqn. (2) F represents the weight fraction of metal present, My is the atomic weight of the metal and *Mw* the molecular weight of WO_3. For any other mixture of these elements and tungsten, determination of the metal content could be done equally easily.

The isotopes used and their important γ-radiations are shown in Table I.

TABLE I

NUCLEAR DATA USED IN ANALYSIS

Element	*Isotope produced*	*Half-life (h)*	*γ-radiation (MeV)*
La	^{140}La	40	1.597, 2.04[a]
Ho	^{166}Ho	27	1.38, 1.6
U	^{140}La, ^{135}I	40, 6.7	1.45, 2.75
W	^{187}W	24	0.69, 0.87

[a] Sum peak observed in well crystal.

Separation of the photoelectric peaks due to ^{140}La, ^{166}Ho, and ^{135}I from the lower energy peaks of ^{187}W was accomplished without interference. In the uranium analysis the measurement of the composite ^{140}La–^{135}I spectrum was made over the same time period for sample and standard.

Samples to be analyzed, together with suitable standards, were weighed on a microbalance and encapsulated in polyethylene tubing. They were then irradiated for 1 to 5 sec in a thermal flux of $1 \cdot 10^{13}$ neutrons/cm^2 sec in the 5 megawatt Ames Laboratory Research Reactor.

Following bombardment, samples were counted on one of two NaI(Tl) crystals. Lanthanum samples were counted in the well of a 4 × 4 in. Harshaw crystal which was optically coupled to an RCA 8055 photomultiplier tube. The ^{166}Ho activity and the ^{140}La–^{135}I activities used for the analysis for uranium were counted on a solid 3 × 3 in. Harshaw crystal which was optically coupled to an RCA 8054 photomultiplier tube. Spectral data were accumulated with an RIDL Model 24-1 multichannel analyzer with readout on a Friden adding machine. All activity measurements were corrected for background.

Results

The accuracy of the method devised was tested by analyzing known mixtures which were prepared by weighing together quantities of the metal oxides and WO_3. These mixtures were rotated on a ball mill for several days to insure homogeneity. Results of these analyses are given in Tables II and III.

Tables IV and V represent the analyses of several holmium and uranium bronzes obtained from Dr. WERNER OSTERTAG of the Wright-Patterson Air Force Base. The reported x values are based on the stoichiometric quantities of the compounds used to prepare these bronzes in a closed system by the method of thermal reaction[8]. A number of La_xWO_3 samples obtained from Mr. HOWARD SHANKS of this Laboratory were analyzed for their lanthanum concentrations. However, no other x values have been reported for these samples.

Results obtained for the analyses of known mixtures and for actual tungsten bronze samples indicate that the method of neutron activation analysis provides a rapid, accurate means for determining lanthanum, holmium, and uranium nonde-

TABLE II

THERMAL NEUTRON ACTIVATION ANALYSES OF KNOWN MIXTURES OF La_2O_3 OR U_3O_8 AND WO_3

Sample	*mg lanthanum*		*x*		*Sample*	*mg uranium*		*x*	
	Calc.	*Found*	*Calc.*	*Found*[a]		*Calc.*	*Found*	*Calc.*	*Found*[a]
La-IA	0.277	0.274	0.095	0.095±0.003	U-IA[b]	0.441	0.448	0.060	0.060±0.001
	0.303	0.316				0.403	0.421		
	0.267	0.272				0.313	0.317		
	0.333	0.326				0.339	0.335		
					U-2A	0.621	0.561	0.080	0.086±0.003
La-IB	0.426	0.400	0.142	0.137±0.004		0.598	0.553		
	0.535	0.525				0.481	0.469		
	0.433	0.422				0.523	0.469		
	0.410	0.411							
					U-3A	0.565	0.583	0.100	0.100±0.003
La-IC	0.564	0.545	0.190	0.185±0.005		0.599	0.614		
	0.591	0.596				0.516	0.517		
	0.592	0.597				0.635	0.619		
	0.538	0.524							
					U-4A	0.783	0.795	0.120	0.121±0.001
						0.397	0.403		
						0.545	0.544		
						0.561	0.567		

[a] Average of 4 determinations.

[b] In each case 4 separate samples and 3 standards were irradiated.

TABLE III

NEUTRON ACTIVATION ANALYSIS OF MIXTURES OF Ho_2O_3 AND WO_3

Sample	*Wt. ratio W/Ho*	*mg holmium*		*Sample*	*Wt. ratio W/Ho*	*mg holmium*	
		Calc.	*Found*			*Calc.*	*Found*
1	10	0.489	0.492	5	5	0.912	0.916
2	11	0.441	0.459	6	6	0.803	0.843
3	9	0.524	0.518	7	5	0.952	0.970
4	12	0.415	0.397				

TABLE IV

NONDESTRUCTIVE NEUTRON ACTIVATION ANALYSIS OF HOLMIUM TUNGSTEN BRONZES

Sample	*x*	
	Reported	*Observed*[a]
Ho-1	0.100	0.099±0.005
		0.102±0.003
Ho-2	0.140	0.138±0.003
		0.144±0.005
Ho-3	0.180	0.172±0.008
		0.174±0.007

[a] Results of 2 separate irradiations with 4 samples and 3 standards in each irradiation.

TABLE V

THERMAL NEUTRON ACTIVATION ANALYSIS OF URANIUM TUNGSTEN BRONZES

Sample	*x*	
	Reported	*Observed*[a]
U-1	0.078	0.077±0.002
U-2	0.080	0.080±0.001
U-3	0.083	0.087±0.002
U-4	0.090	0.096±0.002
U-5	0.100	0.100±0.002

[a] In each case 6 separate samples and 4 standards were irradiated.

structively in their tungsten bronzes, or in other mixtures with tungsten containing more than 5% of these elements. The sensitivity of the method is sufficient to permit accurate analyses to considerably lower levels, of the order of 0.1% for lanthanum and uranium and 0.5% for holmium.

Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission, Contribution No. 2112. The aid of Dr. WERNER OSTERTAG in providing samples of the bronzes and of the ALRR crew in performing the irradiations is gratefully acknowledged.

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1 F. WÖHLER, *Ann. Chim. Phys.*, Ser. 2, 29 (1823) 43; *Pogg. Ann.*, 2 (1824) 350.
2 G. HAGG, *Nature*, 135 (1935) 874; *Z. Physik. Chem.*, B29 (1935) 192.
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7 M. A. WECHTER AND A. F. VOIGT, *Anal. Chem.*, 38 (1966) 1681.
8 W. OSTERTAG, *Inorg. Chem.*, 5 (1966) 758.

(Received September 21st, 1967)

BOOK REVIEWS

G. PANNETIER AND P. SOUCHAY, *Chemical Kinetics*, Translated by H. D. GESSER AND H. H. EMOND, Elsevier Publishing Company, Amsterdam, 1967, xvi + 455 pp., price Dfl. 50,—.

The increased appreciation of the importance of reaction rates and mechanisms, as well as the application of kinetic methods of analysis, has made the study of reaction kinetics increasingly vital in the education of analytical chemists. The book under review is intended for undergraduate students, and the general approach is classical rather than modern. The aim is the establishment of reaction rate equations rather than the study of various factors, such as structure, ionic strength, solvent, etc., which affect the rate constants and allow the mechanisms to be deduced.

Methods used in the identification of intermediates and products, those used to follow fast reactions, and the use of isotopes, are barely mentioned. Some applications of dimensionless parameters are given, but the use of graphical methods in the determination of rate constants receives little attention and analogue computers are not mentioned at all. However, the text is useful as a source of preliminary information on the problems of formal kinetics.

P. ZUMAN (Prague)

Handbuch der Analytischen Chemie. 3. Teil. Band I bβ. Elemente der ersten Nebengruppe II. Silber. Gold, Herausgegeben von W. FRESENIUS UND G. JANDER, Springer-Verlag, Berlin, 1967, 271 S., geheftet DM 69,– ; gebunden DM 74,–.

Das Buch enthält eine Zusammenstellung der Verfahren zur Bestimmung und zur Abtrennung der Elemente Silber (137 Seiten) und Gold (81 Seiten) und ein besonderes Kapitel über dokimastische Verfahren (41 Seiten) zur Bestimmung dieser Elemente. In der gleichen Weise, wie sie sich bei früheren Bänden dieser Reihe bewährt hat, werden die in der Literatur beschriebenen Methoden hinsichtlich des ihnen zugrundeliegenden Prinzips, ihres Anwendungsbereiches, der zu beachtenden Störungsmöglichkeiten und der erreichbaren Genauigkeit charakterisiert. Die jeweils gegebenen Arbeitsvorschriften sind durchweg so vollständig, dass ein Arbeiten danach möglich ist. Die einschlägige Literatur ist mit bemerkenswerter Vollständigkeit erfasst worden. Die Gliederung und Gestaltung des Textes ist ausgesprochen übersichtlich, die Darstellungsweise des Sachverhaltes klar. Druck und Ausstattung lassen nichts zu wünschen übrig. Umfangreiche Übersichtstabellen erleichtern die Auswahl eines für einen bestimmten Zweck geeigneten Verfahrens ausserordentlich. Entsprechend dem allgemein referierenden Charakter der ganzen Reihe ist eine Wertung der verschiedenen Verfahren vom Bearbeiter nicht durchgeführt worden, soweit sie nicht in einer mehr oder weniger eingehenden Behandlung zum Ausdruck kommt.

Für alle, die sich mit der Analyse der hier behandelten Metalle zu befassen haben, wird das Buch ein zuverlässiger Ratgeber sein.

H. BODE (Hannover)

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Treatise on Analytical Chemistry. Part II. Analytical Chemistry of Inorganic and Organic Compounds. Vol. 13. Functional Groups, Edited by I. M. KOLTHOFF AND P. J. ELVING, Interscience – J. Wiley and Son, Inc., New York, 1966, xxi + 528 pp., prix 160 s.

Le tome 13 traite des méthodes de détermination des groupements fonctionnels dans les liaisons organiques: Hydrogène actif, C-méthyl, groupements carbonyles (inclusivement formales, acétales, cétales et éther-vinyliques), groupements carboxyliques (inclusivement les dérivés tels que des sels, anhydrides, halogénures, esters et acides aminés), groupes phosphorés et, dans un dernier chapitre; soufre dans les thiols, sulfures, disulfures, polysulfures et thiophènes.

Dans une introduction, la notion de groupements fonctionnels est expliquée et résumée en un tableau concis. Ensuite, des méthodes physiques telles que les UV, les IR, la spectroscopie NMR, ainsi que la diffraction des rayons X pour des substances solides, sont décrites brièvement et il est fait un parallèle entre ces méthodes et les méthodes chimiques.

Le chapitre suivant traite de la détermination de l'hydrogène actif. Outre la méthode classique de ZEREWITINOFF, des procédés avec d'autres réactifs tels que l' hydrure de Li–Al, l'hydrure de dialkyl–Al, le diéthylhydrure de Na–Al, la dispersion de Na, les diboranes, les échanges de deutérium sont décrits ou brièvement évoqués.

Puis nous avons une description détaillée de l'appareillage ainsi que de la détermination avec le réactif de Grignard, hydrure de Li–Al et échange de deutérium.

Le prochain chapitre traite, en 34 pages, de la détermination du groupement C-méthyl. Après la description des méthodes chimiques, la méthode au permanganate est évoquée et celle de Kuhn–Roth, au chromate, est discutée. Les auteurs attirent l'attention sur l'interprétation difficile des valeurs obtenues. Sur 18 pages de tableaux, les valeurs C-méthyl obtenues d'après Kuhn–Roth sont comparées aux valeurs calculées.

Le suivant traite en 82 pages, de la détermination du groupement carbonyle et de quelques dérivés tels que les formales, acétales, cétales etc. Après une brève description des propriétés physiques de la liaison carbonyle, des procédés pour la séparation et transformation des liaisons carbonyles sont décrits.

Sous le titre de carbonyle et fonctions dérivées, l'auteur donne les propriétés physiques des acides-COOH et de leurs dérivés tels que sels, anhydrides, halogénures, esters, orthoesters, acides aminés, puis il décrit les différents procédés de séparation, et quelques méthodes éprouvées de laboratoire.

Le chapitre suivant traite des composés organiques du phosphore. Il est probablement le premier où les procédés de dosage du groupement fonctionnel avec le phosphore sont présentés dans leur ensemble. Après une description des propriétés physiques, quelques méthodes physiques pour le dosage des groupements fonctionnels avec du phosphore sont données, ainsi qu'une énumération de méthodes chimiques de détermination des différentes fonctions phosphoriques, telles que les phosphines, phosphones, les P-halogénures et les composés contenant des liaisons P–S.

Le dernier chapitre traite sur 170 pages de la détermination du groupement fonctionnel avec du soufre bivalent: les thiols, les sulfures, les di- et polysulfures ainsi que les thiophènes.

Cet ouvrage est présenté de façon claire et concise, et les prescriptions de laboratoires données à la fin de chaque chapitre sont très précieuses pour le praticien. Ce tome, comme les autres de cette série, est, à mon avis, un document essentiel et précieux pour l'analyse des substances organiques.

D. MONNIER (Genève)

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Progress in Nuclear Magnetic Resonance Spectroscopy, Vol. 2, Edited by J. W. EMSLEY, J. FEENEY AND L. H. SUTCLIFFE, Pergamon Press, Oxford, 1967, vii + 269 pp., price 90 s.

Volume 2 of this series contains 5 chapters on topics of current interest to those specializing in the field of high resolution NMR. D. E. O'REILLY of the Argonne National Laboratory discusses the various methods of calculation of the chemical shift which are available and then surveys specific calculations which have performed for atoms, molecules and solids. A. D. BUCKINGHAM (Bristol University) and K. A. MCLAUCHLAN (Oxford University) develop the effective Hamiltonians for interpreting the NMR spectra of partially oriented molecules and show that such spectra can provide information on the orientation and structure of the molecules and on the anisotropy of the chemical shift. The chapter by E. DE BOER AND H. VAN WILLIGEN

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(University of Nijmegen) surveys the direct and the indirect methods of studying paramagnetic systems using NMR and reviews the numerous practical applications. R. M. LYNDEN–BELL (University of Sussex) shows how density matrix methods can be used to calculate line shapes in complicated spectra (ESR as well as NMR) for which the Bloch equations are not satisfactory. The chapter by R. F. ZÜRCHER (University of Basel) discusses the cause and calculation of proton chemical shifts in non-conjugated organic compounds. The σ-inductive effect causing proton chemical shifts is considered to be unimportant.

This volume represents an important contribution to the literature on NMR. It is excellently produced and is worthy of a place in the research worker's personal reference library.

B. D. FLOCKHART (Belfast)

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PUBLICATIONS RECEIVED

M. BECKE-GOEHRING, *Praktikum der qualitativen Analyse*, Bearbeitet von J. WEISS, Verlag T. Steinkopf, Dresden, 1967, ix+122 S., Preis Kld. 10.70 MDN.

Chapter headings: (A) Die wichtigsten Reaktionen der Metalle und ihrer Ionen: Übersicht über die Gruppeneinteilung der Kationen. (B) Die wichtigsten Reaktionen der Säuren. (C) Ausführung qualitativer Analysen. (D) Die wichtigsten Reaktionen einiger seltener Elemente.

W. J. YOUDEN, *Statistical Techniques for Collaborative Tests*, Association of Official Analytical Chemists, Washington, 1967, iv+60 pp., price $2.00 (domestic), $2.25 (foreign).

Chapter headings: Introduction; Collaborative Studies; Interpretation of Collaborative Test Data; Measurement of Precision and Accuracy; Planning the Collaborative Test; Problems connected with Collaborative Tests; Application of Collaborative Results.

C. DUVAL, *L'Oxygène*, "Que sais-je?" Le Point des Connaissances Actuelles No. 1273, Presses Universitaires de France, Paris, 1967, 125 pp., prix 3 F.

N. I. MILLER, *Index to Air Pollution Research*, Center for Air Environment Studies, Pennsylvania State University, Pa. 16801 (U.S.A.).

This is a guide to research projects and publications in the air pollution field and is available in six issues annually at a subscription of $ 15 per year.

ALVIN M. WEINBERG, *Reflections on Big Science*, Pergamon Press, Oxford, 1967, ix+182 pp., price 55 s.

This book is an amalgamation of various essays by the Director of the Oak Ridge National Laboratory.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ANNOUNCEMENTS

MEETINGS OF THE GESELLSCHAFT DEUTSCHER CHEMIKER, 1968

1–3 April 1968. *Polymers and Plastics Division, Bad Nauheim*: Chemical Reactions at High Polymers.

7–11 April 1968. *EUCHEM-Conference "Problems of Non-stoichiometry", Schloss Elmau/Mittenwald* (attendance is limited to 100 persons).

8–10 April 1968. *Food Working Party of the European Federation of Chemical Engineering and the Gesellschaft Deutscher Chemiker in conjunction with the Food Engineering Panel of the Society of Chemical Industry, Bristol (England)*: 3rd European Symposium Food–Recent Developments in Food Preservation.

April or May 1968. *Nuclear-, Radio- and Radiation Chemistry Division, Lindau (Bodensee)*: Preparative Radiochemistry.

29 April–2 May 1968. *Symposium "Biochemical Analysis", München*; joint meeting of the German Society of Clinical Chemistry, the Society of Biological Chemistry, the German Pharmaceutical Chemistry, and the Divisions "Analytical Chemistry" and "Food and Legal Chemistry" of the Gesellschaft Deutscher Chemiker; the meeting is combined with the exhibition "Analytica 1968".

13–17 May 1968. *2nd International High Pressure Conference, Schloss Elmau/Mittenwald* (attendance is limited to 100 persons).

21–22 May 1968. *Water Chemistry Division, Bad Ems.*

2 days in the week from 4–11 September 1968. *History of Chemistry Division, Deutsches Museum, München.*

8–11 September 1968. *IUPAC-Symposium Valenze Isomerisation, Karlsruhe.*

9–13 September 1968. *EUCHEM-Conference Non-Haem-Metal Proteins, Heligoland* (attendance is limited to 100 persons).

In the week from 16–20 September 1968. *Food and Legal Chemistry Division joint event with Danish Food Chemistry, Kiel*: Modern Food Analysis.

23–25 September 1968. *Semiconductor Chemistry Division joint event with Analytical Chemistry Division, Wiesbaden*: Analytical Problems in Production and Testing of Semiconductors.

3–4 October 1968. *Applied Electrochemistry Division, Lindau (Bodensee)*: Effects of Price Reductions for Electric Energy on Electrochemistry.

8 October 1968. *Chemistry Day of the Gesellschaft Deutscher Chemiker* during the 105th Assembly of the Gesellschaft Deutscher Naturforscher und Ärzte from 6–10 October 1968, Heidelberg.

In the week from 21–25 October 1968. *Joint meeting of the Austrian Society for Microchemistry and Analytical Chemistry in the Verein Österreichischer Chemiker, the Swiss Society for Analytical and Applied Chemistry and the Analytical Chemistry Division of the Gesellschaft Deutscher Chemiker, Wien (Austria)*: Automation in Analytical Chemistry

Autumn 1968. *Pigments and Dyes Division, Bad Meinberg*. Main theme: Macromolecular Basics in the Field of Surface Coating.

Details concerning the above mentioned events may be asked for at Gesellschaft Deutscher Chemiker, 6000 Frankfurt (Main), Postfach 9075, Deutschland.

FIRST CODATA CONFERENCE, 1968

The First International CODATA Conference on the critical evaluation of numerical property values in the physical sciences will be held at Arnoldshain in the Taunus Mountains near Frankfurt/Main, June 30–July 5, 1968. This Conference will be under the auspices of the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (ICSU). It will be run along the informal lines of the Gordon Conferences in the U.S.A. and the EUCHEM Conferences in Europe. The General Chairman of the Conference will be Prof. Dr. W. KLEMM, Vice President of CODATA and recently president of IUPAC.

CODATA is a committee of ICSU started in 1966 to stimulate and coordinate informally on a world-wide basis the rapidly growing effort to collect, evaluate, compile and publish the evaluated numerical data of science and technology. Six major countries (France, Germany, Japan, U.K., U.S.A., and U.S.S.R.) and eleven International Unions of ICSU are represented on the committee.

Information and application forms to attend the meeting may be obtained from Dr. GUY WADDINGTON, Executive Director, Central Office, CODATA, c/o National Academy of Sciences, 2101 Constitution Ave. N.W., Washington, D.C. 20418, U.S.A.

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PRINTED IN THE NETHERLANDS