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. 49, No. 3, 381–612, March 1970
Published monthly
Completing volume 49

ANALYTICA CHIMICA ACTA

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

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

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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 Edn., Elsevier, Amsterdam, 1966, p. 516.

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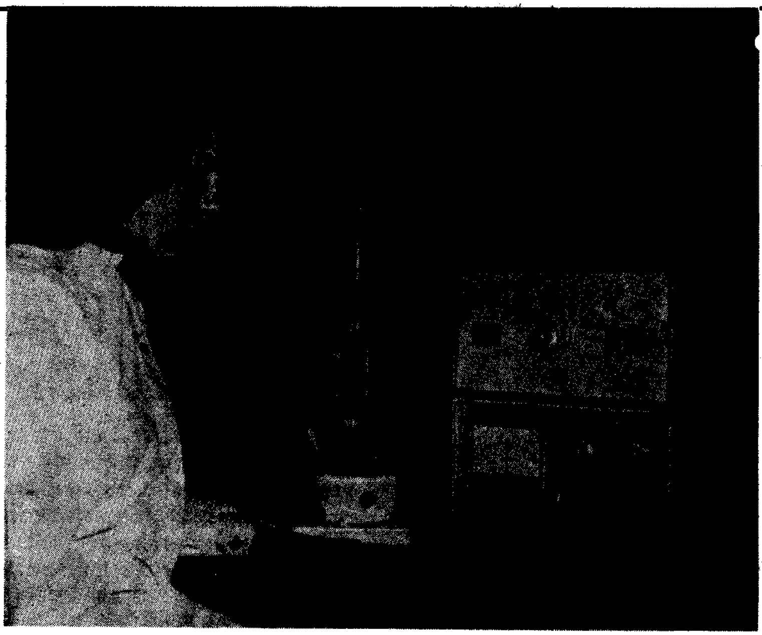

Coulomètre R. CONSTANT

On sait que la coulométrie consiste à effectuer des titrages en produisant un réactif par électrolyse quantitative au sein du milieu réactionnel. On déduit la quantité de réactif mise en jeu du nombre de coulombs consommés par l'électrolyse; d'où le nom de coulométrie. Dans le coulomètre R. CONSTANT, l'électrolyse est conduite à *intensité constante*, et le temps de passage du courant d'électrolyse est proportionnel au nombre de coulombs mis en jeu. Ce temps est enregistré sur un chronomètre électronique à lecture numérique.
L'intensité constante d'électrolyse peut être choisie à l'une des valeurs suivantes: 1 mA, 2 mA, 5 mA, 10 mA ou 25 mA. La tension d'électrolyse atteint 50V. Le chronomètre à lecture numérique est lu en dixièmes de seconde sur un cadran à 5 chiffres. Le déclenchement et l'arrêt du compteur de temps sont commandés électriquement par un contact extérieur, tel qu'un interrupteur manuel ou que le contact de sortie d'un relais; par exemple, le coulomètre peut être commandé automatiquement par un titrimètre. L'appareil effectue des dosages à des vitesses de réaction allant de 10^{-8} à $2,5 \times 10^{-7}$ équivalent par seconde. La précision du dosage est couramment meilleure que 0,5%.
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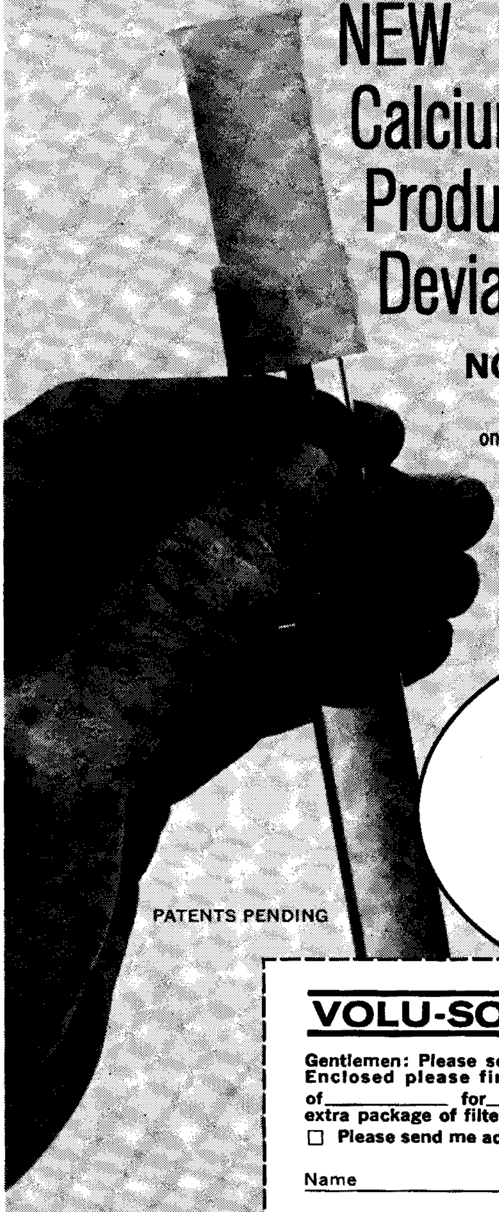

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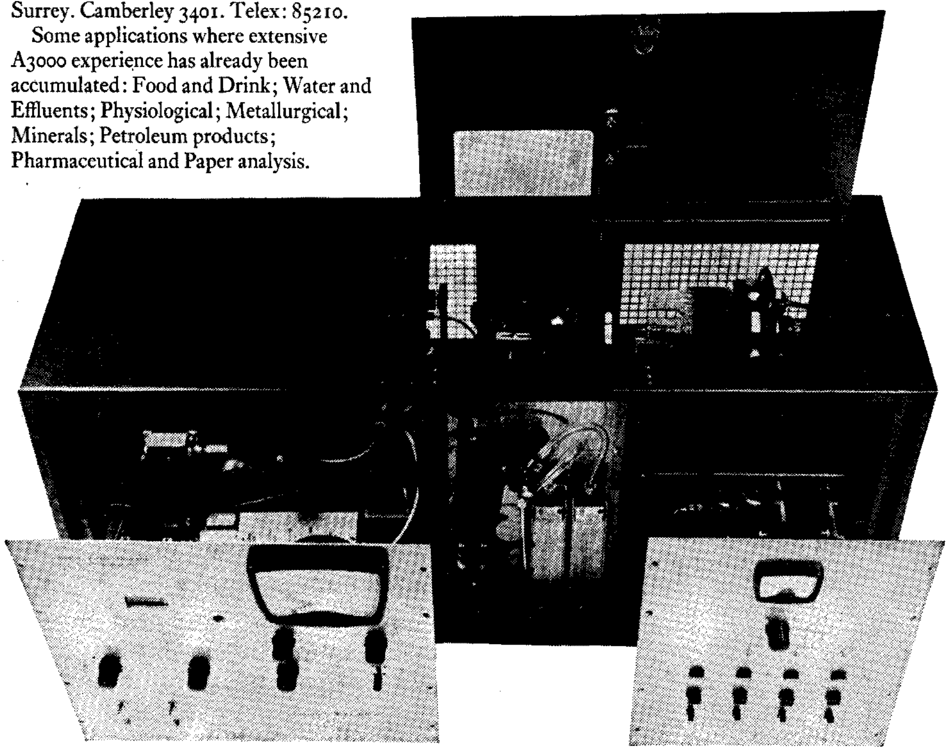

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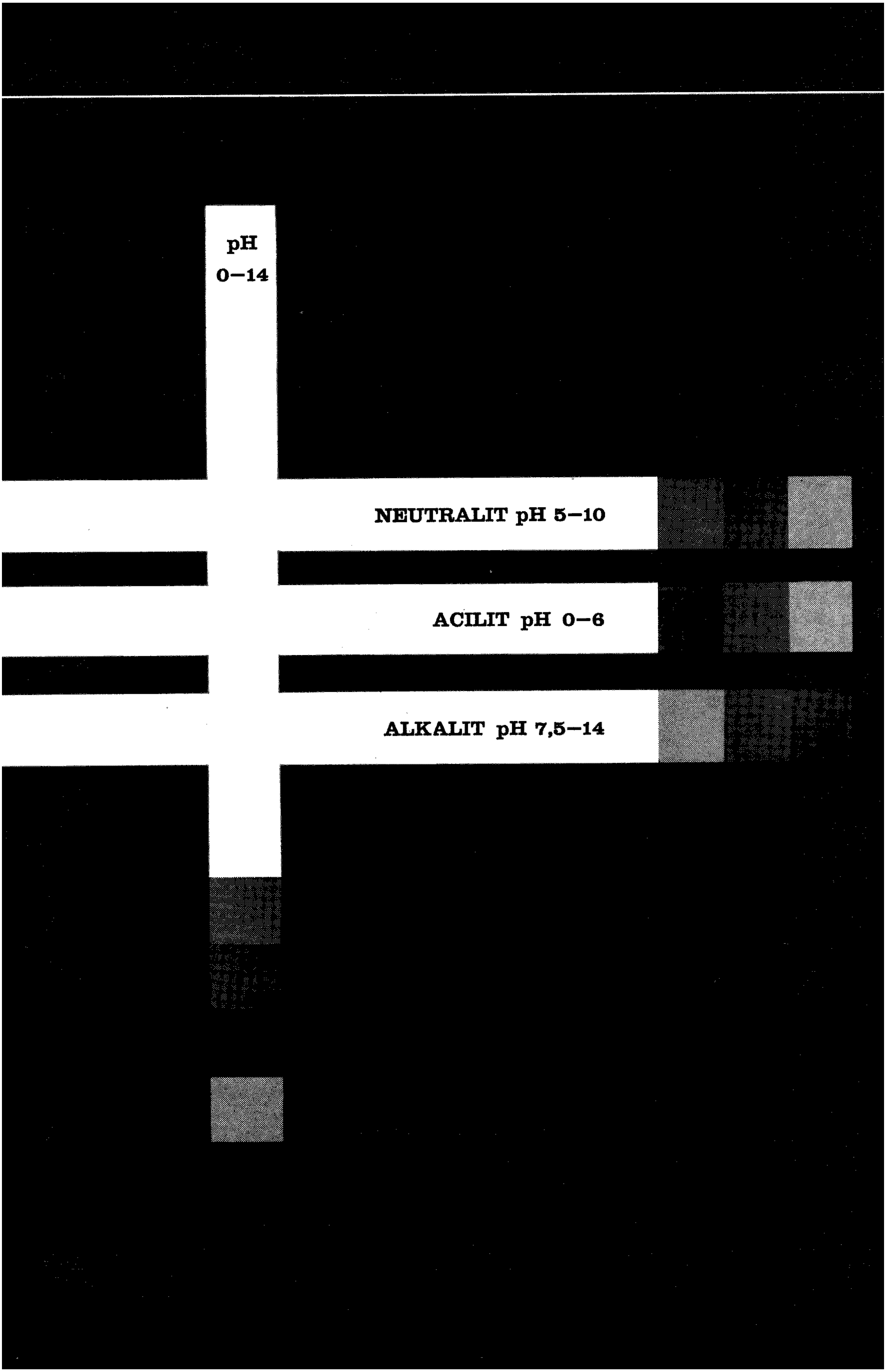
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ACILIT pH 0–6
ALKALIT pH 7,5–14

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 49, No. 3, March 1970

RADIOCHEMICAL SEPARATION OF GOLD BY AMALGAM EXCHANGE

A rapid and simple method for the radiochemical separation of gold after neutron activation. The technique is based on treatment with a dilute indium–gold amalgam, both chemical reduction and isotopic exchange being involved. The counting efficiency for ^{198}Au in small volumes of the amalgam is good. Few interferences occur and the method is applicable to clays, rocks, salts and metals. The possibility of determining silver, platinum and palladium by a similar method is mentioned.

R. R. Ruch,
Anal. Chim. Acta, 49 (1970) 381–389

THE PRECISE DETERMINATION OF URANIUM IN IMPURE URANYL NITRATE AND URANIUM OXIDES

A method is presented for the direct determination of uranium in uranium compounds containing up to several percent impurities with a precision of 0.04% at the 95% confidence interval. The method is simple and is a significant improvement over existing methods for analysis of this type of material. A sample containing about 2.5 g of uranium is dissolved in strong phosphoric acid and uranium(VI) is reduced with iron(II). After selective oxidation of the excess of iron(II) with nitrate in presence of molybdate catalyst, a small excess of potassium dichromate is added to oxidize uranium(IV) to uranium(VI). The excess of chromium(VI) is determined colorimetrically with diphenylcarbazide. The method requires some prior knowledge of the uranium content of the sample. It can be applied even in the presence of percent levels of impurities such as iron, nickel, and chromium. Copper, however, at concentrations of more than 1% of the uranium causes a low bias.

C. R. Walker and O. A. Vita,
Anal. Chim. Acta, 49 (1970) 391–400

SPECTROSCOPIC STUDIES OF RADIO-FREQUENCY INDUCED PLASMA

PART I. DEVELOPMENT AND CHARACTERIZATION OF EQUIPMENT

A highly stable and quiet induction-coupled radio-frequency plasma torch capable of continuous operation has been developed. The electronic spectra produced by various organic compounds when introduced into the plasma have been studied. Results indicate that the tendency is for the molecules to be shattered in the plasma and to emit electronic spectra typical of functional groups.

D. Truitt and J. W. Robinson,
Anal. Chim. Acta, 49 (1970) 401–415

Countercurrent Separation Processes

by H. R. C. Pratt

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

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

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

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

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

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

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

PART III. THE ABSORPTION OF RADIATION FROM HOLLOW CATHODES

Absorption produced at selected atomic-resonance wavelengths by species formed in oxyhydrogen flames from flame gases and organic solvents has been studied. Results indicate sources of spectral interferences in atomic absorption spectroscopy.

V. J. SMITH AND J. W. ROBINSON,
Anal. Chim. Acta, 49 (1970) 417–424

PHOTON SELF-ABSORPTION CORRECTIONS FOR THE MINIMIZATION OF SYSTEMATIC ERRORS IN 14-MeV NEUTRON ACTIVATION ANALYSIS

In comparative 14-MeV neutron activation analysis for oxygen, systematic errors are evidenced if attenuation of incident neutrons and induced γ-radioactivity by a thick sample is ignored. The present study pertains to the general case of measurement where photopeaks resulting from either direct nuclear transitions or from positron annihilation are counted. A quantitative evaluation of these attenuation processes is presented. The results show that the photon attenuation correction factor is related to the difference between the calculated linear absorption coefficients for sample and standard through a simple exponential expression. The slopes of the respective correction factor lines are compared with that for integral γ-counting in oxygen analysis. Differences in the magnitudes of the slopes are discussed. The results of this study are consistent with the removal cross-section theory describing 14-MeV neutron attenuation over a wide range of threshold energies. Typical analyses of Standard Reference Materials, with these correction factors, are given.

S. S. NARGOLWALLA, M. R. CRAMBES AND J. E. SUDDUETH,
Anal. Chim. Acta, 49 (1970) 425–436

DETERMINATION OF THE OXYGEN-TO-URANIUM RATIO IN HYPOSTOICHIOMETRIC URANIUM DIOXIDE

For the determination of the oxygen-to-uranium ratio in hypostoichiometric uranium dioxide, a method was developed in which the sample is dissolved in phosphoric acid. During dissolution, all uranium present is converted to uranium(IV) while an amount of hydrogen equivalent to the degree of hypostoichiometry is released. The O/U ratio is determined from the amount of released hydrogen. Satisfactory results, in accordance with those obtained gravimetrically on 1-g samples, can be obtained on 30–140 mg samples.

A. TOLK, W. A. LINGERAK AND D. BÖRGER,
Anal. Chim. Acta, 49 (1970) 437–442

Pigments

An Introduction to their Physical Chemistry

edited by David Patterson

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

$5\frac{1}{2} \times 8\frac{1}{2}''$, ix + 210 pages, 93 illus., 1967, Dfl. 32.50, 65s.

In this book the principles of physical chemistry are applied to the problems of making a using the insoluble organic and inorganic pigments manufactured for use in paints, printi 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 t use of such methods means that each case must be judged on its merits. On the other har 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 compoun and to emphasize this the purely preparative chemistry of pigments has been left outside t scope of this book. Instead, pigments are regarded as substances produced to exert particu 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. 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.

Contents

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

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CATALYTIC DETERMINATION OF SUBMICROGRAM AMOUNTS OF SELENIUM(IV) BY MEANS OF THE OXIDATIVE COUPLING REACTION OF PHENYLHYDRAZINE-*p*-SULFONIC ACID WITH 1-NAPHTHYLAMINE

In the presence of potassium chlorate, selenium catalyzes the oxidation of phenylhydrazine-*p*-sulfonic acid and the *p*-diazobenzenesulfonic acid formed is coupled with 1-naphthylamine to form an intensely colored azo dyestuff. By means of this catalytic reaction, submicrogram amounts of selenium(IV) can be easily determined. The method is simple and sensitive, and there are few interferences.

T. Kawashima, S. Nakano and M. Tanaka,
Anal. Chim. Acta, 49 (1970) 443–447

THE FORMATION CONSTANTS OF EUROPIUM(III)–SALICYLATE COMPLEXES AND THEIR EXTRACTION INTO ISOAMYL ALCOHOL

The distribution of salicylic acid (H_2Sal) between isoamyl alcohol and aqueous buffers of constant ionic strength ($\mu = 0.1$ *M* $NaClO_4$) was investigated over a range of pH values. The partition coefficient was found to be 109.3 and sodium salicylate was also found to be extracted to a small extent. The liquid–liquid extraction of europium(III) as its salicylate into isoamyl alcohol was investigated radiometrically. The partition coefficient log $p_c = 1.8(0)$ and the successive stability constants, $K_1 = 10^{2.59}$, $K_2 = 10^{1.62}$ and $K_3 = 10^{0.65}$, were evaluated.

H. M. N. H. Irving and S. P. Sinha,
Anal. Chim. Acta, 49 (1970) 449–454

COMPLEXES FORMED IN THE CHLOROFORM EXTRACTION OF NICKEL WITH OXINE

The equilibrium distribution ratios of nickel between aqueous 0.1 *M* perchlorate solutions and oxine solutions in chloroform (0.01–0.1 *M*) have been determined at 20°. The nickel–oxine complex extracted from acidic aqueous solutions and that from alkaline solutions have different absorbance spectra. A plot of $\log D_{Ni} - \log [HOx]_o$ *vs.* pOx gave a single curve for three different concentrations of oxine (D_{Ni} = distribution ratio of nickel, $[HOx]_o$ = equilibrium concentration of oxine in the organic phase, pOx = negative logarithmic concentration of oxinate anion) and it was concluded that nickel was extracted as $NiOx_2HOx$. The equilibrium constants describing the extraction of nickel with oxine were determined.

S. Ōki,
Anal. Chim. Acta, 49 (1970) 455–461

Molecular Vibrations and Mean Square Amplitudes

by SVEN J. CYVIN

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

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

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

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

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

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

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

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

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THE EXTRACTION OF ZIRCONIUM(IV) FROM HYDROCHLORIC ACID SOLUTIONS BY TRICAPRYLMETHYLAMMONIUM CHLORIDE

The partition of zirconium(IV) between hydrochloric acid solutions and organic solutions of a quaternary ammonium compound was investigated under different conditions. Infrared and high-resolution nuclear magnetic resonance spectroscopy were used to examine the composition of the extracted complex. The effect of organic solvent on the extraction was also examined. The mechanism of zirconium extraction is discussed.

T. SATO AND H. WATANABE,
Anal. Chim. Acta, 49 (1970) 463–471

ANION-EXCHANGE EQUILIBRIA IN ALKALINE MEDIA

The distribution ratios of a large number of species are reported for anion exchange from strongly alkaline solutions. The strongly basic macroreticular anion exchanger, Amberlyst A-29 was used. The elements in the oxidation states studied are classified by their ion-exchange behavior. The degree to which a species is absorbed by the resin depends on whether it exists in an anionic form and whether it is hydrated or forms hydrogen bonds with the water in the aqueous solution. While working with hydroxide solutions presents some practical problems, the sizeable differences in distribution coefficients for several groups of ions may be analytically useful.

R. F. HIRSCH AND J. D. PORTOCK,
Anal. Chim. Acta, 49 (1970) 473–479

STUDIES IN THE TETRAARYLBORATES

PART V. THE INFLUENCE OF SUBSTITUENTS ON THE STABILITY OF TETRAARYLBORATES

The stability of sodium tetraarylborates toward acid attack can be enhanced by placing electron-withdrawing substituents at the *m*- or *p*-positions of the phenyl rings, thus rendering them less susceptible to electrophilic attack. A series of tetraarylborates has been studied, and the following order of decreasing resistance toward acid attack has been established: *m*-fluorophenyl > *p*-trifluoromethylphenyl > *m*-trifluoromethylphenyl > *p*-fluorophenyl ⩾ *p* chlorophenyl ≈ phenyl > *p*-methylphenyl ≫ *p*-methoxyphenyl. Sodium tetrakis(*m*-fluorophenyl)borate does not undergo acid decomposition at pH 2.0 and 50.0°, but it is partially decomposed under these conditions via other pathways.

M. MEISTERS, J. T. VANDEBERG, F. P. CASSARETTO, H. POSVIC AND C. E. MOORE,
Anal. Chim. Acta, 49 (1970) 481–485

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

INVESTIGATION OF *n*-BUTYL PHOSPHATE AS A SOLVENT FOR VOLTAMMETRY

Controlled potential voltammetric investigations of several depolarizers and potentially useful carrier electrolytes have been carried out in *n*-butyl phosphate. Half-wave potentials have been measured and analytical calibration curves have been constructed. Most depolarizers gave well formed waves but adsorption behavior was present in some cases. The influence of water was very significant.

J. L. JONES, S. ADISESH, R. M. SMITH AND J. H. KARNES,
Anal. Chim. Acta, 49 (1970) 487–496

A SPECTROPOLARIMETRIC TITRIMETRIC METHOD FOR THE DETERMINATION OF CADMIUM, MERCURY, LEAD AND BISMUTH

Spectropolarimetric methods of analyses for cadmium(II), mercury(II), lead(II) and bismuth(III) were developed, based on the stereospecific ligand, D-(−)-1,2-propylenediaminetetraacetic acid (D(−)PDTA). The optical rotation of the solution was monitored with a photoelectric polarimeter to determine the end-point of the titration. The titrant and metal complexes formed are optically active and serve as self-indicators. Since D(−)PDTA is stereospecific in its reaction with these metals, maximum utilization of the optical rotation of these complexes is achieved. The observed optical rotation is linear with respect to concentration of the metal complexes, hence straight-line extrapolations to the end-point are possible. The effects of pH, wavelength, and dilution are discussed and the optimum conditions for the determination of each metal are established. The range of accurate spectropolarimetric analyses at 365 nm with the Perkin-Elmer 141 spectropolarimeter was 10^{-1}–10^{-3} *M* for cadmium(II), and 10^{-1}–10^{-4} *M* for lead(II), mercury(II) and bismuth(III). The range of the average deviations from visual chelometry for the four metals titrated was 0.05–0.29%.

R. J. PALMA, SR. AND K. H. PEARSON,
Anal. Chim. Acta, 49 (1970) 497–504

THE DIRECT SPECTROPOLARIMETRIC TITRATION OF ALUMINUM, INDIUM, AND THALLIUM WITH D-(−)-1,2-PROPYLENEDIAMINETETRAACETIC ACID

A direct spectropolarimetric titration method of analysis was developed for aluminum(III), indium(III) and thallium(III), with the stereospecific ligand, D-(−)-1,2-propylenediaminetetraacetic acid (D(−)PDTA). The optical rotation of the solution was monitored with a photoelectric polarimeter to determine the end-point of the titration. The metal complexes and titrant are optically active and serve as self-indicators. Since D(−)PDTA is stereospecific in its reaction with these metals, maximum utilization of the optical rotation of these complexes is achieved. The observed optical rotation is linear with respect to concentration of the metal complexes; consequently, it is possible to perform straight-line extrapolations to the end-point. The effects of some parameters were investigated and optimum conditions were established. The range of the average deviations from visual chelometry for the three metals determined was 0.11–0.18%.

D. L. CALDWELL, P. E. REINBOLD AND K. H. PEARSON,
Anal. Chim. Acta, 49 (1970) 505–509

COORDINATION CHEMISTRY REVIEWS

Editor: A.B.P. LEVER (Downsview, Ont., Canada)

This international journal offers rapid publication of relatively short review articles in the field of coordination chemistry. The term "coordination chemistry" is interpreted broadly, but does not include "organometallic chemistry". In general the reviews published fall into the following categories:

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CONTENTS Volume 4, No. 1, February 1969

Divalent transition metal β-keto-enolate complexes as Lewis acids - D.P. Graddon (Kensington, N.S.W., Australia)
Metal-halogen stretching vibrations in coordination complexes of gallium, indium and thallium - A.J. Carty (Waterloo, Ont., Canada)
Reactions involving metal complexes of sulphur ligands - L.F. Lindoy (Kensington, N.S.W., Australia)
Electronic spectra of quadrate chromium(III) complexes - J.R. Perumareddi (Pittsburgh, Pa., U.S.A.)
The effect of axial ligand fields on ground state properties of complexes with orbitally degenerate ground terms - G.A. Webb (Guildford, England)

CONTENTS Volume 4, No. 2, April 1969

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SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS IN ALLOY STEELS

A general method based on the extraction of phosphovanadomolybdate by isobutyl methyl ketone is presented for the spectrophotometric determination of 0–0.08% phosphorus in high-alloy steels. No interference is caused by less than 2% of chromium; larger amounts can be volatilized as chromyl chloride. The molar absorptivity is 1750 at 425 nm for the extracted phosphovanadomolybdate, with a standard deviation of ± 0.5%.

P. Pakalns,
Anal. Chim. Acta, 49 (1970) 511–517

RAPID COMBUSTION METHODS FOR DETERMINING SULFUR IN ROCKS, ORES AND STONY METEORITES

A COMPARATIVE STUDY OF THE USEFULNESS OF RESISTANCE-TYPE AND INDUCTION FURNACES

A satisfactory procedure for determining total sulfur in rocks, ores and stony meteorites with a Leco induction furnace is described. Suitable fluxes, time for complete evolution of sulfur dioxide, and suitable absorption solutions for sulfur dioxide are discussed. A comparative study of three different combustion methods for determining sulfur in a variety of geological materials has also been made. The results indicate that induction heating is superior to resistance heating for most samples containing up to 20% total sulfur.

J. G. Sen Gupta,
Anal. Chim. Acta, 49 (1970) 519–525

THE DETERMINATION OF NICOTINIC ACID AND NICOTINAMIDE BY THIN-LAYER CHROMATOGRAPHY AND *IN SITU* FLUORIMETRY

The specific determination of traces of nicotinamide and nicotinic acid by a combination of thin-layer chromatography and direct fluorescence spectroscopy is described. Two instruments are compared for performance. Instrumental detection limits of 0.001–0.002 μg/spot are reported. For an artificial mixture an average error of about 8% was found. The relative standard deviation for biological samples was between 8 and 14%. The method can be used for routine analysis and compares favourably with reflectance spectroscopic and fluorescence quenching techniques. The total time of analysis is 5–6 h with an actual working time of 2 h.

R. W. Frei,
Anal. Chim. Acta, 49 (1970) 527–534

THE COLORIMETRIC DETERMINATION OF TERTIARY ALCOHOLS WITH AN ALDEHYDE-ACID REAGENT

A colorimetric determination of several tertiary alcohols with a reagent consisting of an aromatic aldehyde and sulphuric acid is described. The nature of the coloured reaction product(s) is briefly discussed.

M. R. F. Ashworth and I. Venn,
Anal. Chim. Acta, 49 (1970) 535–540

Inorganic Macromolecules Reviews

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

Editors: F.G.R. Gimblett (London, Great Britain)
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K.A. Andrianov (Moscow, U.S.S.R.)

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SOME KINETIC DATA ON THE OXIDATION OF THE COBALT(II)–BIPYRIDYL COMPLEX BY COPPER(II) AND IRON(III) PERCHLORATES IN ANHYDROUS ACETONITRILE

On the basis of the polarographic behaviour of Co(II)–Co(III) bipyridyl complexes, Cu(II)–Cu(I) and Fe(III)–Fe(II) perchlorates in anhydrous acetonitrile at a rotating platinum electrode, kinetic data for the oxidation of the cobalt(II)–bipyridyl complex in acetonitrile were obtained. The rotating platinum electrode method was used to study the oxidation of the cobalt(II) complex by copper(II) and iron(III) in 0.1 *M* sodium perchlorate in anhydrous acetonitrile. The reactions follow the rate laws:

$$-\frac{\mathrm{d}[\mathrm{Co(II)}\ (\mathrm{bipy})_3]}{\mathrm{d}t} = k_1\, [\mathrm{Co(II)}\ (\mathrm{bipy})_3]\ [\mathrm{Cu(II)}]^{\frac{1}{2}},$$

$$-\frac{\mathrm{d}[\mathrm{Co(II)}\ (\mathrm{bipy})_3]}{\mathrm{d}t} = k_2\, [(\mathrm{Co(II)}\ (\mathrm{bipy})_3]\ [\mathrm{Fe(III)}]^2$$

where $k_1 = 4.9 \pm 0.37$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ sec^{-1}, $k_2 = (3.4 \pm 0.5) \cdot 10^3$ mole^{-1} l sec^{-1} at 20°. The oxidation of the cobalt(II) complex by iron(III) in the presence of an excess of bipyridyl follows the rate law:

$$-\frac{\mathrm{d}[\mathrm{Co(II)}\ (\mathrm{bipy})_3]}{\mathrm{d}t} = k\,\frac{[\mathrm{Co(II)}\ (\mathrm{bipy})_3]\ [\mathrm{Fe(III)}]^2}{[\mathrm{bipy}]^x}$$

where order x changes from 1.6 to 0.6 for the range $1.9 \cdot 10^{-2}$ *M*–$4.0 \cdot 10^{-1}$ *M* bipyridyl. The data for this oxidation are interpreted in terms of a reaction between a mononuclear cobalt(II) complex and a binuclear iron(III)–bipyridyl complex.

I. NĚMEC, H. L. KIES AND I. NĚMCOVÁ,
Anal. Chim. Acta, 49 (1970) 541–555

TITRATION CURVES OF COMPLEXIMETRIC BACK-TITRATIONS

PART III. CONDITIONS FOR SHARP END-POINTS WITH INDICATION BY MEANS OF AN INDICATOR ION

Conditions are derived for sharp end-points in compleximetric back-titrations of mixtures of metals, by means of potentiometric indication of one of the metals of the mixture. Some applications are given for the determination of Cu, Zn, Bi and Ni with EDTA as the ligand and thorium(IV) as the titrant.

U. HANNEMA, S. PRAKASH AND G. DEN BOEF,
Anal. Chim. Acta, 49 (1970) 557–566

INDIRECT ATOMIC ABSORPTION SPECTROMETRIC METHODS FOR THE DETERMINATION OF CYANIDE

(Short Communication)

R. S. DANCHIK AND D. F. BOLTZ,
Anal. Chim. Acta, 49 (1970) 567–569

TITRIMETRIC DETERMINATION OF IODIDE AFTER TWENTYFOUR-FOLD AMPLIFICATION

(Short Communication)

R. BELCHER, J. W. HAMYA AND A. TOWNSHEND,
Anal. Chim. Acta, 49 (1970) 570–572

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DETECTION OF THEOPHYLLINE AND THEOBROMINE BY REACTIONS WITH MECURY(II) CYANIDE

(Short Communication)

F. Feigl, D. Goldstein and E. Libergott,
Anal. Chim. Acta, 49 (1970) 573–574

REDOX REACTIONS ON THE RING-OVEN
PART I. MICRODETERMINATION OF MERCURY

(Short Communication)

S. K. Thabet, N. E. Salibi and P. W. West,
Anal. Chim. Acta, 49 (1970) 575–577

REDOX REACTIONS ON THE RING-OVEN
PART II. MICRODETERMINATION OF SILVER

(Short Communication)

S. K. Thabet and N. E. Salibi,
Anal. Chim. Acta, 49 (1970) 577–579

SEPARATION OF HIGH-BOILING CYCLIC DIOLEFINS BY AN IMPROVED SILVER NITRATE G.L.C. COLUMN

(Short Communication)

D. L. Schmitt and H. B. Jonassen,
Anal. Chim. Acta, 47 (1970) 580–584

VACUUM-FUSION DETERMINATION OF OXYGEN IN Al–Mg–Al_2O_3–MgO COMPOSITES

(Short Communication)

A. Colombo and E. Rodari,
Anal. Chim. Acta, 49 (1969) 584–587

A RAPID METHOD FOR THE DETERMINATION OF COBALT IN SEA WATER

(Short Communication)

E. Kentner and H. Zeitlin,
Anal. Chim. Acta, 49 (1970) 587–590

POTENTIOMETRIC DETERMINATION OF THE STABILITY CONSTANTS OF ZINC THIOCYANATE AND ZINC AZIDE COMPLEXES

(Short Communication)

E. F. de Almeida Neves, L. Sant'Agostino,
Anal. Chim. Acta, 49 (1970) 591–596

THE SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH ERIOCHROME BRILLIANT VIOLET B

(Short Communication)

K. Uesugi,
Anal. Chim. Acta, 49 (1970) 597–602

Inorganic Sulphur Chemistry

edited by GRAHAM NICKLESS, *Department of Inorganic Chemistry, University of Bristol, Great Britain*

7×10", xii+770 pages, 147 tables, 128 illus., over 4000 lit. refs., 1968
Dfl. 155.00, £18.5.0, SBN 444-40684-0

In recent years, the inorganic chemistry of sulphur has developed very rapidly. Although many specialized reviews on selected topics exist, a complete survey of this branch of chemistry was still lacking. The aim of the present book is to fill this gap, and to provide, for students and research workers alike, a complete reference book on inorganic sulphur chemistry.

The book is divided into two broad sections, the first discussing the various aspects of bonding and methods of investigation in sulphur chemistry, the second describing the latest developments in the inorganic chemistry of the element and its compounds.

CONTENTS: 1. The sulphur atom and its nucleus (G. Nickless). 2. Orbitals in sulphur and its compounds (D. W. J. Cruickshank and B. C. Webster). 3. Stereochemistry of sub-group VIB of the periodic table (W. J. Geary). 4. Mechanisms of sulfur reactions (R. E. Davis). 5. Structural studies on sulphur species (A. J. Banister, L. F. Moore, and J. S. Padley). 6. Analytical chemistry of sulphur compounds (E. Blasius, G. Horn, A. Knöchel, J. Münch, and H. Wagner). 7. Elemental sulphur (B. Meyer). 8. The sulphur cycle (J. R. Postgate). 9. The chemistry of the phosphorus-sulphur bond (D. E. Rogers and G. Nickless). 10. Sulphanes (K. W. C. Burton and P. Machmer). 11. Oxides of sulphur (P. W. Schenk and R. Steudel). 12. Compounds containing sulphur-halogen bonds (H. L. Roberts). 13. The nitrides, nitride-halides, imides and amides of sulphur (H. G. Heal). 14. The lower oxy-acids of sulphur (D. Lyons and G. Nickless). 15. Sulphuric acid: Physico-chemical aspects of manufacture (T .J. P. Pearce). 16. Sulphuric acid as a solvent system (R. J. Gillespie). 17. Fluorosulphuric acid (R. C. Thompson). 18. Amido- and imidosulphonic acids (K.W.C. Burton and G. Nickless). 19. Sulphides (F. Jellinek). Subject index.

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

RADIOCHEMICAL SEPARATION OF GOLD BY AMALGAM EXCHANGE

R. R. RUCH
Analytical Chemistry Section, Illinois State Geological Survey, Urbana, Ill. 61801 (U.S.A.)
(Received November 3rd, 1969)

Radioactive gold has been chemically separated by a variety of methods[1]; however, a one-step amalgam exchange and chemical reduction approach has not been reported. Such a rapid, simple procedure would be advantageous because the amalgam droplet could immediately be counted with minimal interference after complete exchange.

Amalgam exchange techniques have been reported previously for many elements[2–11] and generally effect high yields with good decontamination. A fast, simple, and general procedure has now been developed for separating radioactive gold from a variety of materials and chemical conditions.

The technique involves *both* isotopic exchange and chemical reduction of $^{198}Au(III)$ in acid solution by a dilute liquid indium–gold amalgam. The processes may be symbolically expressed as follows:

$$\text{excess } In^0(Hg) + {}^{198}Au^{3+} \rightarrow {}^{198}Au^0(Hg) + In^{3+}$$

$$\text{excess } Au^0(Hg) + {}^{198}Au^{3+} \rightleftarrows {}^{198}Au^0(Hg) + Au^{3+}$$

Indium, rather than mercury, preferentially reduces $^{198}Au(III)$ while the presence of inactive gold metal in the amalgam greatly enhances isotopic exchange of $Au^0(Hg)$–$^{198}Au^{3+}(H_2O)$ on the amalgam interface, significantly speeding up the process. High relative counting efficiency of ^{198}Au in small volumes of amalgam permits assay without any further separation.

EXPERIMENTAL

Apparatus, reagents and tracers

Separations were performed in 8-ml capped glass vials. All agitation was done with an Eberbach 6000 reciprocating laboratory shaker at the highest setting. Counting was performed with a 3 × 3″ NaI detector with a Nuclear Chicago 3427 multichannel analyzer.

Analytical reagent-grade chemicals were used throughout. Gold and indium metals were purchased from Johnson, Matthey and Company. Triple distilled mercury was washed with dilute nitric acid before use.

All tracers were prepared from reagent chemicals in the Argonne Juggernaut Reactor and were checked for radiochemical purity before use.

Amalgam preparation

A dilute 0.147% indium–0.074% gold amalgam was prepared by adding separately 20 mg of indium metal to 0.5 ml of mercury and then 10 mg of gold metal to another 0.5 ml of mercury. About 10 ml of 0.1 *M* citric acid was added to each. The mixtures were allowed to stand for *ca.* 1 h to achieve complete dissolution of indium and gold in the mercury and then were combined and thoroughly mixed. Anomalous results (low, irreproducible yields) were observed when both indium and gold were dissolved simultaneously and the resulting amalgam was used immediately. Amalgams used after several days storage also tended to break down and promote Hg_2Cl_2 formation.

Preliminary and evaluation studies

A series of experiments was conducted in order to determine an optimum procedure. The requirements of a radiochemical separation technique are high yield, good decontamination, favorable reproducibility, and rapid separation. In each series, a variable was introduced, such as the amount of indium or gold metal in the amalgam, amalgam volume, solution volume, amount of gold(III) in solution, time of agitation, concentration of different acids, kinds of cations and anions, and radioactive interferences. When the final procedure was established, different sample types were analyzed for gold to check the precision and accuracy.

Procedure

A 0.1-ml aliquot of the indium–gold amalgam (2 mg of indium and 1 mg of gold) was transferred to a small vial containing 5 ml of a 0.1–1 *M* hydrochloric acid solution of dissolved irradiated sample and 0.5 mg of *inactive* gold(III) carrier. The vial was capped and agitated for 15 min on a mechanical shaker. The amalgam, containing the radioactive $^{198}Au^{3+}$, was then physically removed from the solution by replicate transfers, with large separatory funnels filled with distilled water. The amalgam was counted at a suitable geometry for $^{198}Au^{3+}$ by integrating the area under the 0.411-MeV γ-peak. Counting efficiency and precision were checked by counting a 100% yield run for $^{198}Au^{3+}$ under similar conditions.

Analysis of samples

Various types of samples were spiked with trace amounts of gold and irradiated for 2 h at $2 \cdot 10^{11}$ n sec^{-1} cm^{-2}. Gold-198 was then separated by the general procedure. An irradiated diabase rock and a clay sample were dissolved by treatment with sulfuric and hydrofluoric acids and taken up in dilute hydrochloric acid. Samples of zinc metal and calcium carbonate were dissolved in dilute hydrochloric acid whereas ammonium bromide was dissolved in deionized water. In each case, 0.5 mg of gold(III) was added *after* irradiation and before dissolution. Ten ml of dissolved rock and clay samples, rather than 5 ml, was used and was agitated for 20 rather than 10 min. A standard addition technique was also used for these samples in order to compensate for any differences in yield caused by differences in sample-standard composition.

RESULTS

Effect of gold in amalgam

Figure 1 shows the effect of adding gold metal to the indium amalgam on recovery of $^{198}Au^{3+}$. An exchange experiment with 0.1 ml of amalgam, which contained

2 mg of indium with *no* gold, approached equilibrium in about 15 min, whereas the same amalgam volume with 2 mg of indium *and* 1 mg of gold approached equilibrium of quantitative yields of $^{198}Au^{3+}$ in 9–10 min. Such a beneficial effect is most probably due to isotopic exchange occurring on the amalgam–solution interface.

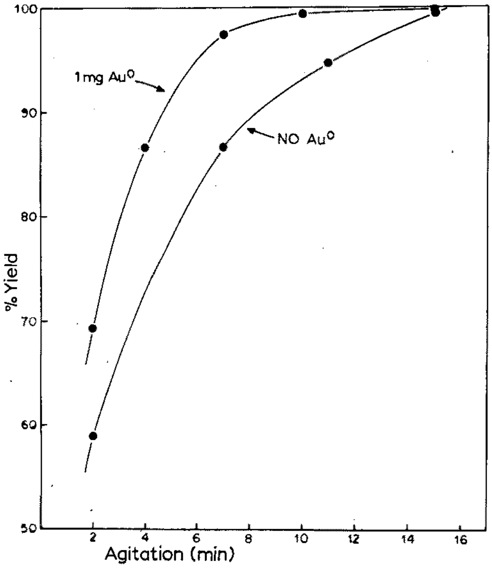

Fig. 1. Effect of gold dissolved in $In^0(Hg)$ upon ^{198}Au yield as a function of time. 0.1 ml $In^0(Hg)$ amalgam (2 mg In^0) and 5 ml of 0.6 *M* HCl containing 0.5 mg of gold(III).

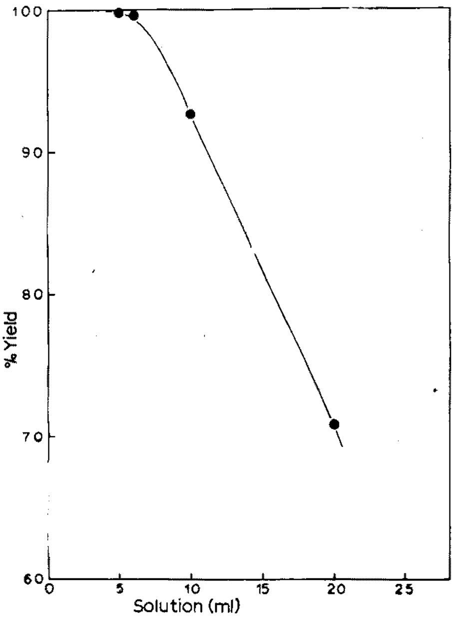

Fig. 2. Effect of solution volume upon ^{198}Au R–IE yields.

TABLE I

EFFECT OF INDIUM AND GOLD CONCENTRATION IN VARIOUS AMALGAM VOLUMES UPON REDUCTION–ISOTOPIC EXCHANGE YIELDS FOR $^{198}Au^{3+}$

Amalgam volume (ml)	*mg present in amalgam*		*% Yield*[a]
	In^0	*Au*^{0}	
0.025	2	1	88.6 ± 3.1[b]
0.05	4	0.5	91.5 ± 2.8
	2	0.5	97.8 ± 1.3
	1	0.5	93.4 ± 1.7
	2	1	90.9 ± 1.2
0.10	2	1	99.4 ± 0.3
	2	0	99.4 ± 0.4
0.20	2	1	99.9 ± 0.2

[a] Average of 5 determinations with standard deviation. Amount of Au^{3+} in solution was 0.5 mg in 0.6 *M* HCl with 15-min agitation.
[b] Duplicate determinations.

TABLE II

REDUCTION AND ISOTOPIC EXCHANGE YIELDS FOR $^{198}Au^{3+}$ WITH VARIOUS INTERFERING IONS

Interfering ion	*Amount (mg)*	*HCl concentration (M)*	% *Yield*[a]
None	—	0.6	99.4 ± 0.3[b]
Na^+	144	1	99.8
Mg^{2+}	80	1	99.8
Al^{3+}	78	1	98.4
Zn^{2+}	417	3	99.1
Mn^{2+}	75	1	99.8
Ga^{3+}	111	2	99.7
PO_4^{3-}	44	1	99.4
VO_3^-	Saturated	1	98.6
TiO^+	Saturated	1	97.6
Cu^{2+}	100	1	96.1
AsO_3^-	65	1	94.9
Fe^{2+}	93	1	91.1
Fe^{3+}	114	1	90.0

[a] Average of duplicate runs. Amount of Au^{3+} in 5 ml solution was 0.5 mg.
[b] Average of 5 replicate runs with standard deviation.

TABLE III

COMBINED REDUCTION–ISOTOPIC EXCHANGE AND COUNTING YIELDS FOR $^{198}Au^{3+}$ AND INTERFERING ISOTOPES

Isotope	*Amount (mg)*	*HCl concentration (M)*	% *Yield*[a]
$^{24}Na^+$	3	1	0.0002
$^{87m}Sr^{2+}$	190	3	$<$ 0.0001
$^{140}La^{3+}$	4	1	0.0009
$^{72}Ga^{3+}$	15	1	$<$ 0.0003
$^{56}Mn^{2+}$	8	4	$<$ 0.0003
$^{64}Cu^{2+}$	9	1 (+ 1 *M* HNO_3)	0.005
$^{69m}Zn^{2+}$	50	1	$<$ 0.004
$^{51}Cr^{3+}$	306	1	0.009
$^{82}Br^-$	19	H_2O only	0.011
$^{60}Co^{2+}$	11	1	0.048
^{239}Np (U)	4 (U)	1	$<$ 0.05[b]
$^{75}Se^{4+}$ (SeO_3^{2-})	10	0.1	1.3
$^{109}Pd^{2+}$ ($PdCl_4^{2-}$)	3	2	3.3
$^{197}Pt^{4+}$ ($PtCl_6^{2-}$)	3	2	3.7
$^{76}As^{3+}$	7	2	21.8
$^{110m}Ag^+$	26	0 (1 *M* HNO_3)	88.7[c]
$^{198}Au^{3+}$	0.5	0.6	71.0 ± 3.9[d]
$^{198}Au^{3+}$	0.5	0.6 (0.05 ml amalgam)	89.0 ± 4.0[e]

[a] Average of duplicate runs, except $^{198}Au^{3+}$, which is average of 5 with standard deviation.
[b] Other low-energy peaks noted. Uranyl acetate irradiated, dissolved, and determined after 1 day.
[c] Initial reduction yield was 94.7%.
[d] Initial R–IE yields are 99.4 ± 0.3% for 5 replicate runs. Difference is due to loss in relative counting efficiency from γ-ray absorption.
[e] Initial R–IE yields are 93.4 ± 1.7% for 5 replicate runs.

Effect of amalgam volume

Recovery data for $^{198}Au^{3+}$ from 15-min runs involving different amalgam volumes and some different indium and gold contents are shown in Table I. Greater amalgam volumes provide more surface area and give yields approaching 100% in shorter times (well under 10 min). This trend has been predicted and discussed by OKASHITA[12].

Effect of solution volume

As solution volume increases, a longer time for attaining equilibrium may be expected. Figure 2 is a plot of percent yield resulting from 15-min agitations as a function of solution volume; it indicates a major decrease when volumes larger than about 6 ml are used under these experimental conditions.

Effect of amount of gold(III) in solution

Figure 3 shows the effect of increased amounts of gold(III) in 5 ml of solution, if all other experimental factors remain constant. Greater than 99% yields of $^{198}Au^{3+}$ may be obtained in 15 min with *ca.* 1 mg of gold(III) present; however, yields fall off severely with increased amounts of gold(III).

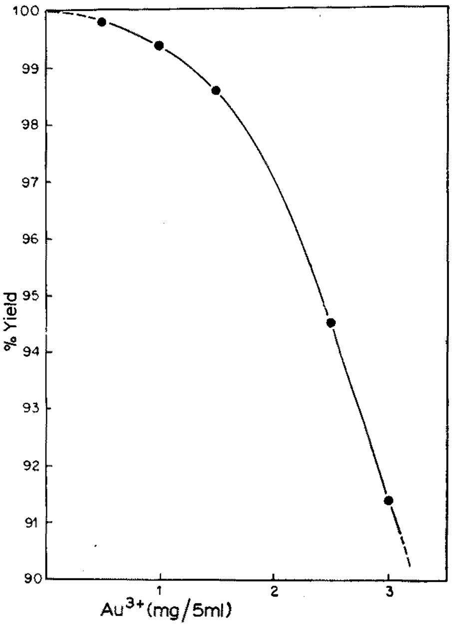

Fig. 3. Effect of dissolved gold(III) upon ^{198}Au R–IE yields.

The reduction–isotopic exchange yields (R–IE) of gold–gold(III) are shown in Table II, and the combined yields (reduction–isotopic exchange plus counting efficiency yield) are shown in Table III. In general, with no interfering ions and low hydrochloric acid concentration, the R–IE yields are quantitative (Table II). The combined yields are dependent upon the amalgam volume employed because of self-absorption caused by mercury. Significant decreases in relative counting efficiency of the amalgam droplet occur between 0.05 and 0.1 ml of amalgam (Table III).

The R–IE yields of $^{198}Au^{3+}$ were similarly observed in the presence of various salts, as summarized in Table II. Most ions tested did not reduce the observed yields below 98%. Moderate amounts of arsenite, copper(II), iron(II) and iron(III) did not reduce the R–IE yields below 90%.

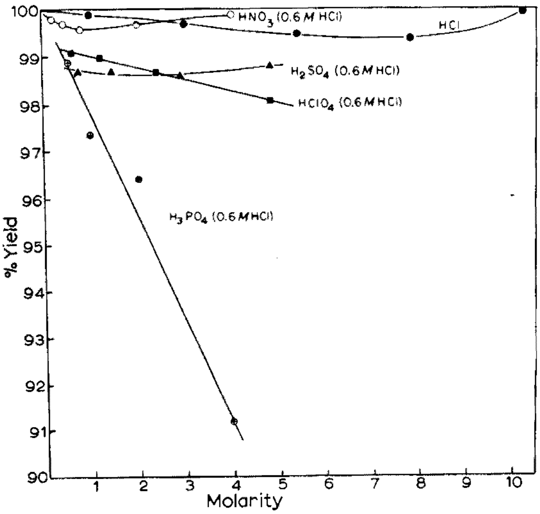

Fig. 4. Effect of acids upon ^{198}Au R–IE yields.

The procedure was tested for ^{198}Au R–IE yields as a function of concentration of various acids present in the system . Figure 4 shows that the presence of acids, with the exception of phosphoric acid, does not appreciably reduce yields below 98%. In fact, higher amounts of hydrochloric, sulfuric and nitric acids tend to *increase* the observed yield slightly. However, it was observed that a certain amount of amalgam decomposition began at the higher levels of sulfuric, nitric and phosphoric acids. Significant decreases in yield occur with increasing concentration of phosphoric acid.

A number of interfering radioisotopes were tested for combined yields by means

TABLE IV

ACTIVATION ANALYSIS AND AMALGAM EXCHANGE SEPARATION OF GOLD IN VARIOUS SAMPLE TYPES

Sample	*Average weight (g)*	*Au*	
		Added (μg)	*Found*[a] *(μg)*
Diabase rock	0.325	22.6	22.7 ± 1.0
Accretion-gley clay	0.231	22.6	22.4 ± 1.7
$CaCO_3$	0.176	22.6	22.5 ± 0.2
Zn metal	0.275	22.6	22.2 ± 0.9
NH_4Br	0.586	22.6	22.4 ± 0.0

[a] Average of duplicate analysis with standard deviation.

of the general procedure in the absence of radioactive $^{198}Au^{3+}$, but with inactive gold present. These results are shown in Table III. The majority tested, representing a sizable portion of the periodic chart, gave only a negligible yield with very little potential γ-ray interference for ^{198}Au. Such isotopes as ^{75}Se, ^{109}Pd, ^{197}Pt, ^{76}As, and ^{110m}Ag interfered from 1.3% up to near quantitative yields (^{110m}Ag was almost quantitative for initial reduction yield).

The results of duplicate analyses performed on diabase rock, clay, calcium carbonate, zinc, and ammonium bromide are shown in Table IV. Comparison of actual gold with gold found is good in both accuracy and precision for all types studied. No interfering radioactivity was observed in the separated fractions.

DISCUSSION

The addition of gold metal to the amalgam definitely promotes a more rapid attainment of equilibrium. Although reduction is the main factor in this process, isotopic exchange does occur and is an advantage. The dissolved indium metal aids in the reduction process by preferential oxidation of indium rather than mercury. When gold amalgam alone was employed in preliminary studies, mercury(I) chloride formed on the amalgam surface and caused non-quantitative yields and poor reproducibility.

The main effect of a larger amalgam volume is to provide more surface area for the occurrence of the reduction and isotopic-exchange processes. As Table I shows, for a given indium–gold concentration, the larger amalgam volume produces better yields (approaching 100%) with better precision. Larger volumes, however, decrease counting efficiency, making the over-all process less precise (see Table I).

Very small amalgam volumes (0.025 ml) decrease R–IE yields but increase counting efficiency. Thus, a compromise in amalgam volume (such as 0.1 ml) must be employed depending upon sample requirements. The counting efficiency of the droplet is the limiting factor that can be ascertained. It is important that amalgam droplets for comparison runs be physically similar (*e.g.* coalesced, if possible) in order to achieve the best counting precision. This is particularly important in actual samples where combined chemical effects may tend to break down, or disperse, the amalgam. Centrifugation for a short time improves this situation.

In a given amalgam volume, the *amounts* of indium or gold metal dissolved do not appreciably affect the R–IE yield. In the 0.05-ml series, the amalgams containing 4 mg of indium and 1 mg of gold metal produced lower yields, possibly owing to a saturated condition inhibiting diffusion.

This is a carrier-type radiochemical procedure, but more than 1 mg of dissolved Au^{3+} will cause low yields (Fig. 3). In such a mass-action effect, indium tends to be completely stripped from the amalgam if the amounts of gold(III) exceed 3–4 mg, and under such circumstances, the formation of mercury(I) chloride is observed. Under the proper conditions, R–IE yields for $^{198}Au^{3+}$ can be made essentially quantitative in a short time (Tables II and III).

In general, most salts and acids individually do not affect the separation. (In practice, the dissolution procedure must be adjusted to conform to those limiting situations.) It is possible that various *combinations* of acids or salts can decrease yields below those predicted for the single interferences.

Very few radioisotopes should cause difficulty with this procedure. Most of those tested were not reduced, and those that were, did not have γ-ray peaks in the same general region. With few exceptions, the gold separated should be immediately countable in an interference-free spectrum.

The reduction of silver under the general procedure gave a nearly quantitative yield (94.7%), and it should be possible to determine this element after some further development. As the ^{110}Pd $(n,\gamma)^{111}$Pd $\xrightarrow[22m]{\beta}$ ^{111}Ag reaction produces a silver isotope, palladium might be determined by this daughter technique. Palladium(II) was reduced only to a minor extent (*ca.* 3%) under these conditions.

The ^{198}Pt$(n,\gamma)^{199}$Pt $\xrightarrow[30m]{\beta}$ ^{199}Au reaction produces a gold isotope. Minor amounts of platinum might also be determined by the proposed technique. Carrier-free ^{199}Au tracer could be added to a sample before irradiation for absolute yield determinations, because ^{199}Au and ^{198}Au γ-rays are compatible.

The various sample types analyzed for added amounts of gold indicate the versatility of the approach. It should be possible to determine gold nearly as low as the calculated sensitivity for many matrices.

The requirements for a successful radiochemical separation have been satisfied —high yield, good decontamination, favorable reproducibility, and fast time of separation, and the method is generally applicable.

Discussions with Dr. N. F. SHIMP and Mr. S. M. KIM and some sample preparation by Mr. D. B. HECK of the Illinois State Geological Survey staff have been most helpful. The cooperation of the Juggernaut Reactor staff at Argonne National Laboratory in producing the various isotopes utilized also is gratefully acknowledged.

SUMMARY

A rapid and simple method for the radiochemical separation of gold after neutron activation. The technique is based on treatment with a dilute indium–gold amalgam, both chemical reduction and isotopic exchange being involved. The counting efficiency for ^{198}Au in small volumes of the amalgam is good. Few interferences occur and the method is applicable to clays, rocks, salts and metals. The possibility of determining silver, platinum and palladium by a similar method is mentioned.

RÉSUMÉ

On propose une méthode rapide et simple pour la séparation radiochimique de l'or, après activation neutronique. La technique est basée sur le traitement avec un amalgame indium–or, il se produit en même temps une réduction chimique et un échange isotopique. On observe peu d'interférences; ce procédé peut s'appliquer aux argiles, roches, sels et métaux. On indique la possibilité de doser argent, platine et palladium par une méthode similaire.

ZUSAMMENFASSUNG

Es wird eine schnelle und einfache Methode für die radiochemische Abtrennung

von Gold nach Neutronenaktivierung beschrieben. Das Verfahren beruht auf der Behandlung mit einem verdünnten Indium–Gold-Amalgam, wobei sowohl chemische Reduktion als auch Isotopenaustausch stattfinden. Der Zählwirkungsgrad für ^{198}Au in kleinen Amalgamvolumina ist gut. Die Störmöglichkeiten sind gering, und die Methode ist anwendbar auf Erdproben, Gesteine, Salze und Metalle. Auf die Möglichkeit der Bestimmung von Silber, Platin und Palladium durch eine ähnliche Methode wird hingewiesen.

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

THE PRECISE DETERMINATION OF URANIUM IN IMPURE URANYL NITRATE AND URANIUM OXIDES*

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(Received October 26th, 1969)

Uranium oxides and uranyl nitrate, particularly those containing uranium enriched in uranium-235, must be analyzed as accurately as possible for uranium. In the usual gravimetric method, uranium compounds are ignited to U_3O_8 and weighed. For accurate analyses, the weight of U_3O_8 must be corrected for the weight of impurities which are usually determined by spectrographic analysis.

For nearly pure materials, this approach is satisfactory, but for uranium compounds containing impurities in excess of a few tenths percent, the errors in the spectrographic analysis become too great for satisfactory corrections in the gravimetric analysis. Consequently, a method is needed to provide precise and accurate uranium results in the presence of such quantities of impurities. Also, such a method could improve gravimetric analyses by helping to elucidate the stoichiometry of oxides containing impurities such as iron, copper, nickel, and chromium. Ideally, such a method should: (1) give a limit of error of $\pm 0.05\%$ or less per determination at the 95% confidence level; (2) be relatively simple and require no expensive equipment or skilled personnel; and (3) should permit the determination of uranium in the presence of several percent impurities.

None of the available methods[1-3] for the very precise measurement of uranium met all of these requirements. Precise determinations can be made coulometrically in the presence of a few certain impurities, but expensive equipment and skilled personnel are required for overall operations; the usual chemical procedures that do not require expensive equipment nor skilled personnel cannot be used when impurities such as iron and copper are present.

The method of DAVIES AND GRAY[4], which involves the reduction of uranium with iron(II) sulfate in strong phosphoric acid, has proven quite valuable, since it permits the accurate determination of uranium in the presence of large quantities of impurities that would interfere in most other redox procedures. As originally conceived, however, the method is not precise enough to meet the established requirements. By making several major modifications in the DAVIES AND GRAY method, it has proved possible to develop a procedure in which uranium in the presence of up to several percent impurities can be determined with a limit of error of $\pm 0.04\%$ per determination at the 95% confidence interval.

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* Presented in part at the Twelfth Annual Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., October 8–10, 1968.

Outline of the procedure

The DAVIES AND GRAY procedure[4] for the titration of uranium in the presence of a wide variety of impurities may be outlined as follows. About 200 mg of uranium is reduced to uranium(IV) with iron(II) in strong phosphoric acid solution. Excess of iron(II) is oxidized to iron(III) with nitrate in presence of molybdate catalyst. The uranium(IV) is titrated to uranium(VI) with potassium dichromate in dilute sulfuric acid in presence of diphenylamine sulfonic acid indicator.

The modified procedure for the precise analysis can be described in general terms as follows. A sample containing about 2.5 g of uranium is dissolved, and the uranium is reduced to uranium(IV) in strong phosphoric acid with iron(II). Excess of iron(II) is oxidized to iron(III) as described above. A weighed slight excess of potassium dichromate is then added to oxidize all the uranium(IV) to uranium(VI), and the excess is determined colorimetrically with diphenylcarbazide so that the uranium-chromate equivalence point can be calculated.

Several variables had to be considered in developing this procedure, the most important being the factors involved in determining a stable end-point that is both accurate and precise. Other variables were the effects of varying the amounts of reagents used or the effects of impurities.

Development of the end-point determination

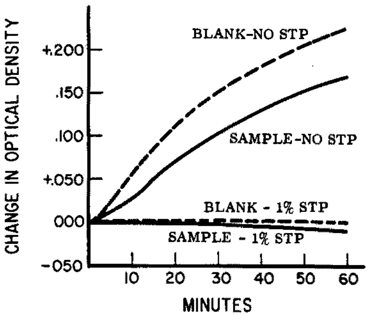
The visual end-point used in the original DAVIES AND GRAY procedure could not be used in the modified procedure because of the presence in the solution of large concentrations of colored ions, particularly chromium(III). The end-point detection technique adopted is a modification of the procedure given by VITA *et al.*[3] in a method for the precise analysis of uranium in pure uranium oxides. In this method, the excess of a known weight of potassium dichromate used to oxidize uranium(IV) is determined by a straightforward colorimetric analysis of chromium(VI) with diphenylcarbazide. With this method of end-point detection, VITA *et al.* reported a limit of error of ±0.015% for the analysis of pure uranium oxides.

Initial application of this approach to the modified DAVIES AND GRAY method was unsatisfactory because of the instability of the purple chromium(VI)–diphenylcarbazide color. The instability verifies the behavior reported by SANDELL[5], who states that in the diphenylcarbazide method for chromium(VI), in the presence of sulfuric acid, iron(III) gives a positive interference that increases with time. The effect observed is demonstrated in Fig. 1. Because of this interference, the dichromate–diphenylcarbazide color had to be measured immediately after its formation. To provide a more reliable analysis and to permit the analysis of several samples at a time, a method for stabilizing the chromate–diphenylcarbazide color was developed. The addition of sodium tripolyphosphate (STP) immediately after color formation gave a solution sufficiently stable for color measurement after 1 h even in the presence of 100 p.p.m. of iron(III). The data demonstrating this stability are also presented in Fig. 1.

Effect of various concentrations of nitric acid and sulfamic acid

The report of DAVIES AND GRAY suggests that nitric acid in excess of 3 ml in the presence of more than 1 mg of molybdenum leads to low results (Table I[4]).

To determine the effect of nitric acid in the modified procedure, ten samples (each containing 2.5 g of uranium) were prepared and fumed to dryness with sulfuric acid. Each of five samples was treated with 5 ml of 1.5 *M* sulfamic acid and with concentrated nitric acid varying in amount from 0.5 to 5 ml. Another five samples were treated with 10 ml of 3 *M* sulfamic acid (*i.e.*, four times the previous amount) and similar amounts of nitric acid. All ten of the samples were carried through the modified procedure; the results (Fig. 2) indicate that the presence of 2 ml of nitric acid without sufficient sulfamic acid will give low results and that samples containing up to 5 ml of nitric acid can be analyzed accurately if sufficient sulfamic acid is present.



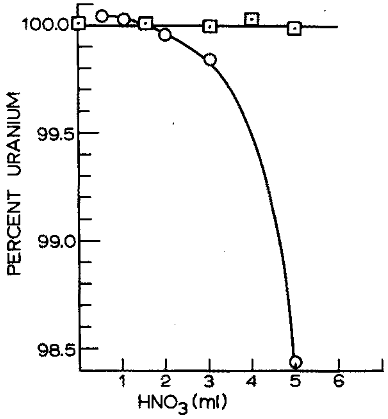


Fig. 1. Stabilization of chromate–diphenylcarbazide color with sodium tripolyphosphate in presence of iron(III) (10 μg Cr/ml).

Fig 2. Effect of nitric acid concentration. (□) 10 ml of 3 *M* sulfamic acid added, (○) 5 ml of 1.5 *M* sulfamic acid added.

TABLE I

EFFECT OF MOLYBDENUM CONCENTRATION

(199.5 mg U added; 3 ml of 16 *M* HNO_3 present)

mg Mo	0	0.1	1	10	100
mg U found	200.0	199.4	199.7	175.6	155.6

Effect of impurities in phosphoric acid

A volume of 110 ml of phosphoric acid was found to be adequate for the complete reduction of uranium with iron(II). The major concern regarding the phosphoric acid was the possibility that it contained oxidizable material as reported by CHERRY[2]. He eliminated the potential bias from this source by preliminary treatment of the phosphoric acid with potassium dichromate. The presence of oxidizable matter in the phosphoric acid used was verified by determining small concentrations of uranium in presence of phosphoric acid either untreated or treated overnight with 0.4 ml of 1 *N* potassium dichromate per liter. The results obtained (Table II) clearly show that a blank correction equivalent to about 0.3 mg of uranium can be attributed to oxidizable material in the phosphoric acid. In 2.5 g of uranium this amount of uranium would give a high bias of 0.012%. Analyses of known amounts

TABLE II

EFFECT OF PRELIMINARY OXIDATION OF PHOSPHORIC ACID ON ACCURACY

mg U taken	*mg U found minus mg U taken*	
	Untreated H_3PO_4	*Treated H_3PO_4*
9.900	+ 0.28	− 0.06
9.900	+ 0.38	+ 0.04
19.900	+ 0.28	− 0.03
160.0	+ 0.18	—

of New Brunswick Laboratory 99.973%* pure dingot metal uranium at the 2.5-g level with both treated and untreated phosphoric acid verified this bias within the limit of error of the method. The eight samples analyzed with untreated phosphoric acid averaged 0.020% higher than the six analyzed with treated acid (*i.e.*, 99.985 *vs.* 99.965% uranium). Therefore, phosphoric acid used in the method was permitted to stand at least overnight with 0.4 ml of 1 *N* potassium dichromate per liter before use.

Effect of impurities

The major impurities usually present in uranium compounds are iron, copper, nickel, molybdenum, and chromium in the range of 0–10 mg/g U. Of these impurities, only copper should be a potential interference. CHERRY[2] reported an interference from copper in both the DAVIES–GRAY titration and his own amperometric titration. The copper interference was confirmed by the analysis of samples containing 2.5 g of uranium plus varying quantities of copper and nickel. These samples were analyzed by the modified procedure; the results are presented in Fig. 3. Nickel up to 1 g gave no interference but copper interfered significantly. As little as 10 mg of copper reduced the uranium result by 0.006%; at the 1-g level, three uranium analyses gave values that were low by 0.24, 0.14 and 0.08%. Since copper(II) ion has been reported to catalyze the air oxidation of uranium(IV), its interference could possibly be minimized by maintaining an inert atmosphere over the sample.

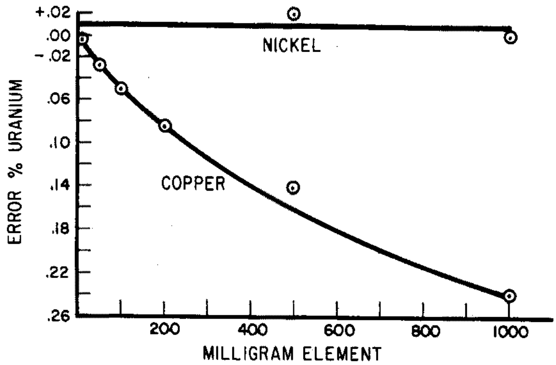


Fig. 3. Interference of copper and nickel.

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* As determined by G. MARINENKO of the National Bureau of Standards by constant-current coulometry.

Precision and accuracy

The precision and accuracy of the method were estimated by six analyses of the New Brunswick Laboratory dingot uranium mentioned previously. The analyses were performed with National Bureau of Standards Lot 136b potassium dichromate (99.98% of theoretical oxidizing power). Analyses of the uranium, which has an established purity of 99.973%, gave an average value of 99.965% uranium with a limit of error of 0.045% at the 95% confidence interval. Thus, the method shows no bias and gives a precision that is more than satisfactory for the purpose for which it is intended.

Comparison with the gravimetric method

The modified procedure was applied to several samples of impure uranium compounds which also had been analyzed by the DAVIES AND GRAY titration and a standard gravimetric procedure with spectrographic corrections for impurities. The results by the precise method agreed well with results obtained by the DAVIES AND GRAY approach, and showed in some cases significant improvement over the gravimetric procedure. This comparison is shown in Table III. Samples were selected to cover the range of impurities generally found in these materials. As can be seen from these data, the proposed method is more reliable than the gravimetric method for

TABLE III

COMPARISON OF GRAVIMETRIC AND PRECISE TITRATION RESULTS

Material	*Impurities (mg/g U)*	*Percent difference*[e]
UNH std.[a]	0.20	+ 0.03[a]
U_3O_8	1.50	− 0.65
	1.60	− 0.05
	2.20	− 0.22
	2.20	− 0.11
	2.50	0.00[b]
	2.10	− 2.38[c]
	3.60	− 1.98[c]
	9.20	+ 0.49[d]
	10.70	+ 0.38[d]
UO_2	0.22	− 0.12

[a] The UNH (uranyl nitrate hexahydrate) standard is a material with relatively low impurity concentration. It has been used as a gravimetric standard for three years, its uranium content having been determined by a precise titration procedure[3].

[b] The major impurity in this material is iron, which is analyzed colorimetrically. Iron at 2000 µg/g U and the other (500 µg/g U) impurities are a combination of several different elements which can be determined satisfactorily by spectrographic analysis. With an iron content correction based on a chemical analysis, the gravimetric and precise titration results are in excellent agreement.

[c] These materials are representative of inhomogenous impure oxides containing U_3O_8 and UO_3. Invariably, they present problems when analyzed gravimetrically and more reliable results can be obtained titrimetrically. These two lots of material containing 28 subsamples were analyzed gravimetrically and then titrimetrically by the DAVIES–GRAY method. The volumetric results were in good agreement with the precise titration results.

[d] These samples contained molybdenum at 2.4 and 7.9 mg Mo/g U respectively as the major contaminant. Chemical molybdenum analyses were made on the original material but not on the ignited samples. Thus the low gravimetric result is probably caused by the fact that some molybdenum was lost during ignition.

[e] Percent difference equals $100\left(\frac{\text{Precise titration result}}{\text{Gravimetric result}} - 1\right)$.

impure samples since the gravimetric results are subject to the error of spectrographic analyses as well as the error in calculating the stoichiometric correction. The proposed method is adaptable to samples containing large concentrations of impurities, and since no long sample preparation procedure is necessary, the method is much faster than other procedures that give comparable precision. It has the additional advantage that no skilled personnel or special equipment are required to perform an analysis.

EXPERIMENTAL

Equipment

A Beckman DU spectrophotometer equipped with 5-cm cells was used.

Reagents

Diphenylcarbazide solution. Dissolve 0.5 g in ethanol and dilute to 100 ml with ethanol. Add one drop of concentrated hydrochloric acid to decolorize and stabilize this solution.

Sulfamate solution, 3 M. Add 300 g of sulfamic acid to 800 ml of water. Add liquid ammonia (*ca.* 30 ml) slowly until all the solid dissolves; dilute to 1 l with water.

Sodium tripolyphosphate solution. Dissolve 100 g of the salt in 800 ml of boiling water. Cool to room temperature, filter, and dilute to 1 l with distilled water.

Iron(II) sulfate solution, 1.25 M. Prepare the solution in 1 *M* sulfuric acid. Add 30–50 g of mossy cadmium metal per liter to prevent oxidation. Any precipitate formed on standing can be redissolved by stirring and gentle heating.

Ammonium molybdate solution, 1%. Dissolve 10 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water and add 10 ml of 1 *M* sodium hydroxide. Dilute to 1 l with distilled water.

Potassium dichromate solution, 0.05 N. Dissolve 4.90266 g of the National Bureau of Standards (NBS Lot 136b) salt in water and dilute to 1 l with water. (The $K_2Cr_2O_7$ weight given is corrected for air buoyancy and for the 99.98% oxidizing power stated by NBS for the material.)

Nitric acid–sulfamic acid mixture. Dilute 320 ml of concentrated nitric acid to about 950 ml with distilled water; add 20 ml of 3 *M* sulfamate solution and dilute to 1 l with distilled water.

Phosphoric acid. Add 1 ml of 1.0 *N* potassium dichromate to each liter of concentrated acid.

Procedure

Weigh to ±0.1 mg a sample of uranium oxides or uranyl nitrate containing about 25 g of uranium, and dissolve it in 75 ml of 8 *M* nitric acid. Add 50 ml of concentrated perchloric acid*, fume to near dryness and allow the sample to cool. Dissolve the residue in 100 ml of distilled water and, if necessary, add 1–2 ml of concentrated hydrofluoric acid and heat the solution to remove any silica residue. Transfer the uranyl perchlorate solution to a *tared* 200-ml volumetric flask and dilute to *ca.* 200 ml with distilled water. Allow the sample to come to room temperature and dilute to 200 ml with distilled water. Weigh the solution and flask to the nearest 10 mg and determine the net weight of uranium solution.

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* Perchloric acid is preferred to nitric acid for sample dissolution because chromium, a common impurity, is present in oxides as $CrUO_4$ which is soluble in perchloric but not in nitric acid.

Pipette 2.0 ml of the prepared uranium solution into a *tared* 25-ml plastic graduated cylinder. Weigh the aliquot and cylinder immediately to obtain the weight of sample taken. Transfer the aliquot to a 400-ml beaker and rinse the cylinder with one 10-ml portion of water, one 5-ml portion of 3 M sulfamic acid solution, and two 20-ml portions of concentrated phosphoric acid, adding all the washings to the beaker. Wash down the sides of the beaker with a further 10 ml of phosphoric acid.

Determine the uranium in the aliquot by the following method[4].

Stir the solution magnetically and add 4 ml of iron(II) sulfate solution from a pipette directly into the sample solution, taking care not to touch the sides of the beaker or to splash any of the sample solution. Add 5 ml of nitric acid–sulfamic acid solution from a pipette, using the solution to rinse the inside of the beaker. Add 2 ml of ammonium molybdate solution (Note 1).

Add 25 ml of 1:1 sulfuric acid and 190 ml of water to the sample by rinsing the sides of the beaker; then mix thoroughly with a magnetic stirrer. Add 7–8 drops of diphenylamine sulfonic acid indicator to the solution, and titrate to a purple end-point with the dichromate solution (Note 2). Determine the uranium in the sample as follows (see Notes 3 and 4):

$$\text{g U/g solution} = \frac{(\text{ml } 0.05\ N\ K_2Cr_2O_7 - \text{blank}) \cdot 5.951}{\text{wt. sample}}$$

Using the above preliminary analysis, weigh to the nearest 0.1 mg, duplicate aliquots, each containing 2.5 g of uranium, into tared 25-ml graduated flasks. At this point, the actual weight of uranium in each weighed aliquot is calculated from the preliminary analysis. Then the weight of solid potassium dichromate needed to oxidize all of the uranium in each aliquot from uranium(IV) to uranium(VI) plus 4 mg of excess is determined as follows:

$$K_2Cr_2O_7\ (\text{g}) = (F \cdot \text{g U}) + 0.004,$$

$$\text{where } F = \frac{\text{mol. wt. } K_2Cr_2O_7}{3\ (\text{atomic wt. U})} \quad \text{(For normal uranium, } F = 0.41198.\text{)}$$

(Example: For 2.500 g normal U, $K_2Cr_2O_7 = 0.41198 \times 2.500 + 0.004 = 1.0340$ g.)

For each aliquot, weigh the calculated amount of potassium dichromate to within 0.1 mg into a 100-ml beaker. Transfer each aliquot to a 1000-ml tall-form beaker that has been calibrated to the 700-ml mark. Wash the flask with distilled water, and add the washings to the samples. Treat each aliquot as follows.

Add 5 ml of 1:1 sulfuric acid, and evaporate the solution to dryness. Dissolve the residue in 15 ml of water, and add 110 ml of phosphoric acid using the acid to rinse the sides of the beaker. While stirring the sample rapidly with a magnetic stirrer, add 10 ml of 3 M sulfamate solution. At this point a fine precipitate of sulfamic acid is formed but does not interfere with the analysis. Immediately add with a pipette 20.0 ml of the iron(II) sulfate solution, taking care to not wet the sides of the beaker. After 1 min, wash down the sides of the beaker with 5.0 ml of nitric acid–sulfamic acid solution. Add 2 ml of ammonium molybdate solution, and stir the samples slowly until a bright green color returns to the sample (about 6–12 min). Continue stirring slowly for an additional 15 min. Add 25 ml of 1:1 sulfuric acid and 300 ml of water to the solution and stir vigorously. Add the weighed potassium dichromate to the solution, rinsing the 100-ml beaker several times with water. Then rinse down the sides of the large beaker with water. Stir the solution vigorously for 10 min to complete the dissolution of the potassium dichromate and to oxidize all the uranium(IV). Dilute the solution to 700 ml with water and again mix thoroughly.

Pipette three 5-ml aliquots of the solution into 100-ml volumetric flasks and dilute the aliquots to about 80 ml with water. To one aliquot, to be used as a blank, add 2 ml of 0.002 *M* ammonium iron(II) sulfate and mix thoroughly. To all three aliquots add 2 ml of diphenylcarbazide solution, and let stand for exactly 1 min. Add 10 ml of 10% sodium tripolyphosphate solution to each aliquot, mix thoroughly, dilute to volume, and again mix thoroughly. Transfer a portion of the blank solution to a 5-cm cell to be used as a reference cell. Transfer each sample solution to the sample cell, and within 30 min, measure their absorbances at 540 nm.

Calculate the excess of dichromate from the absorbance measurements, using a previously determined factor or calibration curve. Then determine the amount of uranium present in the sample as follows (Note 5):

$$\text{g U/g} = [(\text{g } K_2Cr_2O_7 \cdot \text{oxidizing power } K_2Cr_2O_7) + (\text{g } K_2Cr_2O_7 \cdot 0.00031) - \text{excess } K_2Cr_2O_7] \times \frac{\text{atomic wt. uranium} \cdot \text{wt. of sample solution}}{98.064 \cdot \text{wt. aliquot} \cdot \text{wt. sample}}$$

Notes. 1. At this point the solution will turn to a dark brown color that persists for 2–5 min and then disappears. A general rule for standing time after the dark brown color had disappeared is listed in the following table:

Persistence of brown color (min)	*Standing time after disappearance of brown color (min)*
1	5
2	7
3	7
4	10
5	10

2. Accurate detection of the visual end-point requires some practice and experience. The end-point is taken at the last addition of 0.02–0.04 ml of titrant that produces a visible deepening of the purple color in the solution. Another such addition made after the solution has been stirred for 1 min produces no visible color change.

3. The blank may vary occasionally which is attributable to several factors including the reagents used. An accurate method for determining a true blank is as follows. Titrate 4 or 5 weighed portions of a standard uranium solution. The weights taken should be selected to give volumes ranging from 10–45 ml of standard dichromate. Using the method of least squares, fit the values of the titration volumes and corresponding solution weights to a straight line and determine the blank by extrapolating the titration volume to zero uranium solution weight. When new reagents are prepared, a single analysis of about 120–130 mg U will determine the validity of the blank in use.

4. The factor 5.951 applies to normal uranium. For other isotopic compositions of uranium, the factor is obtained by the following calculation: 0.025 · atomic weight uranium. For uranium of isotopic compositions other than normal, the appropriate

atomic weight of uranium should be used for calculating *F*. An analysis can be completed before the uranium isotopic composition is known by arbitrarily using the appropriate factors at a given composition (*e.g.*, normal) in the calculations in both 4 g and 5 g. For the calculation of the final result, however, the correct atomic weight of the uranium must be applied.

5. The $0.00031 \cdot g\ K_2Cr_2O_7$ term is the air buoyancy correction for the weighing of $K_2Cr_2O_7$ with stainless steel weights. The equivalent weight of $K_2Cr_2O_7$ is 98.064.

SUMMARY

A method is presented for the direct determination of uranium in uranium compounds containing up to several percent impurities with a precision of 0.04% at the 95% confidence interval. The method is simple and is a significant improvement over existing methods for analysis of this type of material. A sample containing about 2.5 g of uranium is dissolved in strong phosphoric acid and uranium(VI) is reduced with iron(II). After selective oxidation of the excess of iron(II) with nitrate in presence of molybdate catalyst, a small excess of potassium dichromate is added to oxidize uranium(IV) to uranium(VI). The excess of chromium(VI) is determined colorimetrically with diphenylcarbazide. The method requires some prior knowledge of the uranium content of the sample. It can be applied even in the presence of percent levels of impurities such as iron, nickel, and chromium. Copper, however, at concentrations of more than 1% of the uranium causes a low bias.

RÉSUMÉ

Une méthode est proposée pour le dosage direct de l'uranium dans des composés contenant plusieurs % d'impuretés, avec une précision de 0.04%. Cette méthode est simple et supérieure à celles existant déjà pour ce type de substance. Après dissolution de l'échantillon dans l'acide phosphorique, l'uranium(VI) est réduit par le fer(II). On procède alors à une oxydation sélective du fer(II) en excès, par le nitrate, en présence de molybdate comme catalyseur. On ajoute ensuite un léger excès de dichromate pour oxyder l'uranium(IV) en uranium(VI). Le chrome(VI) en excès est dosé par colorimétrie au moyen de diphénylcarbazide. Il est cependant nécessaire de connaître la teneur approximative un uranium de l'échantillon. Fer, nickel et chrome ne gênent pas. Par contre le cuivre peut gêner.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben für die direkte Bestimmung von Uran in Uranverbindungen, die bis zu einigen Prozent Verunreinigungen enthalten. Die Genauigkeit beträgt etwa 0.04% bei einem Vertrauensbereich von 95%. Das Verfahren ist einfach und stellt eine deutliche Verbesserung gegenüber den bisherigen Methoden zur Analyse derartiger Stoffe dar. Eine Probe, die etwa 2.5 g Uran enthält, wird in starker Phosphorsäure gelöst und Uran(VI) mit Eisen(II) reduziert. Nach selektiver Oxidation des Eisen(II)-Überschusses mit Nitrat in Gegenwart von Molybdat als Katalysator wird ein kleiner Überschuss von Kaliumdichromat hinzugefügt, um Uran(IV) zu Uran(VI) zu oxidieren. Der Überschuss an Chrom(VI) wird kolori-

metrisch mit Diphenylcarbazid bestimmt. Die Methode erfordert gewisse Vorkenntnisse über den Urangehalt der Probe. Sie kann auch in Gegenwart von einigen Prozent Verunreinigungen wie etwa Eisen, Nickel und Chrom angewendet werden. Dagegen stört Kupfer bei Konzentrationen von mehr als 1% des Urangehaltes.

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

SPECTROSCOPIC STUDIES OF RADIO-FREQUENCY INDUCED PLASMA

PART I. DEVELOPMENT AND CHARACTERIZATION OF EQUIPMENT

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(Received September 29th, 1969)

The study of emission spectra of organic compounds in the ultraviolet region of the spectrum has been somewhat neglected in the past, although the parameters which control ultraviolet fluorescence spectra are well known. However, although the technique is useful on a limited basis, it is mostly confined to compounds containing π or n electrons. Further, it is understood that the first transition energies of σ electrons will be in the vacuum ultraviolet region. However, some transitions between upper excited states for all types of electrons may lie in the ultraviolet.

Excitation of such molecules by radiant energy limits the process to molecules that absorb ultraviolet radiation. In an effort to extend the types of molecules which can be examined, it was decided to use a radio-frequency plasma as an excitation source. It was hoped that activation would take place by collision or energy transfer from the plasma gas. The results will be published in a short series of articles of which this is the first.

EXPERIMENTAL

Equipment

The apparatus used consisted of a modified Jarrell-Ash atomic absorption spectrophotometer (model 82000) with a 0.5-m Ebert mount scanning monochromator connected to a Beckman 10-in strip chart recorder (model 1005). The radio-frequency power unit was a Lepel Model T-5-3-MC-J-B with 5 kVA nominal output, operated at a frequency of 8 MHz. The plasma torch was a dual-tube, laminar-flow torch similar to one reported by WENDT AND FASSEL[1]. The plasma tube was clear fused quartz (General Electric type 208) 16 mm i.d., 18 mm o.d., and 125 mm in total length, terminating 5 mm below the bottom turn of the working coil. The coolant tube was of the same type of quartz tubing as the plasma tube but was 20 mm i.d., 24 mm o.d. and 160–300 mm long. The center tube was standard 8-mm borosilicate glass terminating 5 mm below the end of the plasma tube. The gas head was fabricated from brass and had double O-ring seals on the coolant and plasma tubes with a fine screen (80 mesh) at the base of the plasma tube to insure laminar flow in the plasma stream.

Optical arrangement

The two optical systems used are shown in Fig. 1. The first system, in which the torch discharges upwards, was used for general survey work where the total emission was of interest or where a large portion of the plasma was to be investigated. The second system with the torch discharging downwards was used when limited portions of the plasma were to be investigated and when a plasma profile was to be determined.

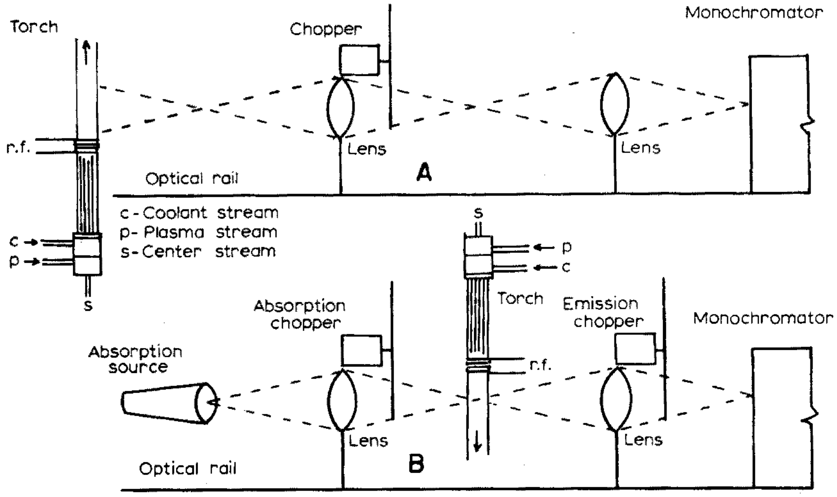

Fig. 1. Schematic diagram of equipment: (A) torch discharging upwards, (B) torch discharging downwards.

Gas manifold

A gas manifold was constructed to service the plasma torch. The system was quite flexible and in general allowed control of the flow rates of the gases to all three tubes and also control of the composition of the gas introduced into the center or coolant tubes. The manifold allowed panel control of binary mixtures of argon and air, argon and oxygen, argon and nitrogen, or argon and helium. Through the use of auxiliary inputs, corrosive gases or high pressure gases could also be controlled. The gas-control manifold also contained a silica-gel drying tower, an ascarite tower and an argon pre-heater. The argon pre-heater, in addition to heating the gas, also served to remove oxygen. The pre-heater was a 3-foot section of 0.5-in copper tubing wrapped with a 800-W heater.

Plasma initiation

In order to initiate the plasma it was necessary to operate the plasma with argon in all three streams and either introduce an ungrounded carbon rod into the coil until the plasma became self-sustaining or to cause initial ionization of the argon by means of an external spark coil which was removed after initiation. Initiation of the plasma discharge usually required reducing the coolant stream flow rate to *ca.* 6 l/min and using a minimum power level of approximately 2 kVA. Initiation was usually obtained by using a spark coil as a matter of convenience.

Sample introduction. Physical introduction into the r.f. cell.

Five methods of sample introduction were investigated and used throughout this work. The simplest method used was for gaseous samples which were introduced through a metering valve and rotameter into a simple mixing chamber where it was either mixed with the appropriate amount of carrier gas as necessary, or introduced directly into the torch without addition of carrier gas.

Liquid samples were much more difficult to introduce. The simplest method of sample introduction involved allowing a controlled amount of carrier gas to pass over, or bubble through, the liquid in a modified gas-washing bottle. The amount of sample introduced depended to a first approximation on the amount of carrier gas, the temperature and the vapor pressure of the liquid. This system was particularly useful when the exact amount of sample introduced was not important (*e.g.* in qualitative work) or when very small samples were to be introduced over extended periods of time. The advantages of this system were simplicity and the availability of two independent methods of controlling the rate of sample introduction, *i.e.* temperature and flow rate of carrier gas. The disadvantages included the difficulty of calibration by repeated weighing and the tendency of the carrier gas flow rate to fluctuate slightly when the carrier gas was allowed to bubble through the liquid sample.

When large samples were required or the samples were solutions containing non-volatile solutes, the aspirator portion of a Beckman total-consumption burner was mounted in a side arm of the coolant tube and the sample was aspirated directly into the discharge. Limited control of rate of sample introduction was possible by adjusting the flow rate (pressure) of the aspirating gas. This system worked best when the torch discharged downwards. Variations in the rate of sample introduction were reduced by force-feeding the liquid through a fine capillary aspirator and using the aspirator only as a means of introducing carrier gas. It was found to be advantageous to use the entire burner and introduce additional carrier gas through the fuel section to stabilize the system. The main disadvantage of this system was that the system was applicable only for introduction of large samples into the discharge above the base of the discharge.

Two other related systems were also used to introduce samples into the plasma torch. These systems involved the use of a motorized drive–syringe system in conjunction with a heated chamber or block. In the first of these methods, the syringe was fitted with a 26-gauge needle and introduced through a silicone rubber system into a preheated stream of carrier gas into a heated block similar to the system used in gas chromatography. In the second of these methods, the syringe was attached to the aspirator section of a fine-capillary, total-consumption burner which was mounted in a 250-ml heated glass vaporization chamber where the sample was mixed with additional carrier gas before going into the torch. These last two methods were used when quantitative intensity data were required for single bonds or lines, or for other short quantitative experiments. One problem with this system was the fluctuations in sample feed rate caused by the tendency of the syringe to leak and seize up.

Location of sample introduction

There were three places in the plasma where it was possible to introduce samples. They could be introduced (*a*) into the center stream in which case a portion of the sample would be introduced directly into the core of the discharge, (*b*) into the coolant stream in which case the sample would, for the most part, be expected to pass by the core and only limited mixing would be expected, or (*c*) the straight coolant tube could be replaced with a "Tee" shaped coolant tube and the sample could be injected directly into the tail-flame with or without carrier gas. This latter method was also used on occasion to inject the sample into the secondary region.

The amount of sample which could be accommodated was very dependent on where the sample was introduced. For example, when air was examined, only 2 mg sec^{-1} could be introduced into the center stream, representing a composition of *ca.* 20% air and 80% argon in the center stream. However, pure nitrogen (22 l min^{-1}) could be introduced into the coolant stream, or through the "Tee" into the tail flame.

In the case of organic liquids, approximately ten times as much sample could be handled in the coolant stream as in the center stream without extinguishing the plasma. The amount of sample introducible into the coolant stream and tail-flame was limited only by the build up of carbonaceous material on the coolant tube or condensation in the torch head of liquid sample. This latter problem was minimized by operating in the discharge downward position.

Mode of operation

There were found experimentally two distinct sets of flow conditions under which a plasma was sustainable. These modes can be distinguished from each other on the basis of whether the coolant or plasma stream flows faster. With argon in all three streams, the flow rates shown in Table I were representative.

TABLE I

FLOW CONDITIONS FOR SUSTAINABLE PLASMA

(All numbers represent l min^{-1})

Coolant stream	15.0–18.0	Coolant stream	5.0–8.0
Plasma stream	0.4– 0.5	Plasma stream	4.4–4.8
Center stream	0.4– 0.8	Center stream	0.4–0.8
Total	15.8–19.3	Total	9.8–13.6

A large region was found between these two extremes in which it was not possible to maintain a plasma discharge. Experiments performed on the torch with smoke added to the gas streams one at a time, with no discharge indicated that in both cases the coolant and plasma streams were laminar in flow until well above the normal region of the secondary region. The center streams in both cases were very turbulent.

Studies indicated that in the case of high coolant flow rates, the coolant stream flowed with greater velocity than the plasma stream and caused circulation of the plasma stream. The circulation inside the plasma stream was downward and toward the outside, thus tending to create a hollow area in the center of the plasma stream. The center stream was introduced into this area. The center stream had little effect on the plasma in the case. In the other case where the plasma flowed faster than the coolant stream, most of the circulation appeared to be due to the center stream. In this case the circulation was from the outside toward the inside and the center stream flow rate controlled the length and diameter of the discharge core. At higher power levels or upon introduction of most samples into the coolant stream, it was necessary to have a center-stream flow to prevent the retracting core from dropping down into the plasma tube and destroying the center tube. Rapid reduction of the coolant flow rate or a drastic increase in the plasma flow rate caused the plasma to extinguish. In the case of operation with the plasma stream having a flow rate greater than the coolant stream, the coolant stream had little effect on the actual operation of the torch other than protecting the coolant tube from the high-temperature core. In fact the torch could be operated for short periods of time, *ca.* 3 min, without the coolant stream flowing. The flow rates of the plasma and center streams could be varied over a large range without extinguishing the plasma, provided that they were both varied in the same direction. Several experiments were performed to determine if it was possible to change slowly from one region to the other by changing the velocities of the coolant stream and plasma stream while maintaining a plasma discharge. These experiments indicated that there was a large area where the differences in velocities were not sufficient to cause circulation. It should be noted that it appeared from visual observations that in order to cause circulation, it would be necessary to reverse the direction of circulation in the core while maintaining a discharge, which did not seem to be a reasonable procedure. However, this could be done when the reversal took place rapidly enough to prevent the plasma from dissipating.

The description of the plasma discharge reported by WENDT AND FASSEL[1] for their laminar-flow torch indicated that their results were quite similar to those obtained with the present torch operating in the high flow mode. The discharge obtained with this torch operating in the low flow mode appeared to be quite similar to that which they reported even in the case when the coolant and plasma gases were not introduced tangentially. These authors maintain, however, that in their torch the recirculation was accomplished by forming a vortex in the gas stream by virtue of tangential introduction of the gas and that this arrangement produces sufficient reverse flow to maintain the plasma.

Function of the coolant tube

Coolant tubes with internal diameters of 20–24 mm and lengths of 160–600 mm were studied. Also investigated were coolant tubes that ended in a "Tee" with and without restrictions in the side pieces and coolant tubes with side arms in the coolant tube to allow introduction into the discharge above the base of the discharge. A series of these latter tubes were made in which the position of the side arm differed 15 mm from tube to tube. Thus it was possible to determine an injection profile by changing coolant tubes in increments of 15 mm.

The gas velocities were calculated for various sizes of coolant tubes at a standard flow rate of 332 cm^3 sec^{-1} in the coolant stream, 5.3 cm^3 sec^{-1} in the plasma stream and 13.3 cm^3 sec^{-1} in the center stream.

The data are reported in Table II. It was found experimentally with a support gas (argon) plasma that a discharge could be maintained for at least a short period of time at 1 kVA in each of these torches. However, it was found that the larger diameter tubes (23-mm i.d. and greater) tended to overheat and the discharge core was noticeably less stable. Variations of flow rates in the various torches indicated that there was a considerable change (increase) in stability, shape of the core and secondary region at a coolant stream velocity of *ca.* 300 cm sec^{-1}. Between 300 and 500 cm sec^{-1} these regions remained stable and tended to elongate only slightly with increasing velocity. At flow rates giving velocities above 500 cm sec^{-1} the discharge again became unstable and the base of the discharge increased in diameter giving the discharge a somewhat nail-like appearance rather than a pencil-like appearance.

TABLE II

CALCULATED GAS VELOCITIES FOR DIFFERENT COOLANT TUBES

Coolant tube		*Coolant stream*			*Plasma tube*		*Plasma stream*			*Center tube*		*Center stream*		
o.d. *(cm)*	*i.d.* *(cm)*	*c.-s. A*[a] *(cm²)*	*v* *(cm sec⁻¹)*	*R* *(cm³ sec⁻¹)*	*o.d.* *(cm)*	*i.d.* *(cm)*	*c.-s. A* *(cm²)*	*v* *(cm sec⁻¹)*	*R* *(cm³ sec⁻¹)*	*o.d.* *(cm)*	*i.d.* *(cm)*	*c.-s. A* *(cm²)*	*v* *(cm sec⁻¹)*	*R* *(cm³ sec⁻¹)*
2.5	2.3	1.62	205	332	1.8	1.6	1.50	5.5	8.3	0.8	0.7	0.38	35	13.3
			82	133				50	75					13.3
2.4	2.2	1.26	264	332	1.8	1.6	1.50	5.5	8.3	0.8	0.7	0.46	35	13.3
			106	133				50	75					13.3
2.35	2.15	1.14	290	332	1.8	1.6	1.50	5.5	8.3	0.8	0.7	0.38	35	13.3
			117	133				50	75				35	13.3
2.3	2.1	0.92	360	332	1.8	1.6	1.50	5.5	8.3	0.8	0.7	0.38	35	13.3
2.2	2.0	0.60	555	332	1.8	1.6	1.50	5.5	8.3	0.8	0.7	0.38	35	13.3

[a] *c.-s. A* = cross-sectional area; v = velocity; R = flow rate.

The same experiments were repeated introducing hydrocarbon vapor into the center stream at concentrations high enough to produce yellow flares throughout the discharge and large quantities of soot. Observation of the yellow flares in the region of the core indicated that the flares tended to be going both with and against the general gas flow in cases where the coolant tube was between 20 and 21.5-mm i.d. and the flow rates were such that the velocities were between 300 and 500 cm sec^{-1} in the coolant stream. At higher or lower velocities and with larger coolant tubes, the flow of the flares appeared to be mainly upwards. It must be pointed out, however, that it was difficult to observe fully the interior of the discharge.

EMISSION SPECTRA OBSERVED

Argon plasma

The induction-coupled plasma torch had appeared as a bright flame with three distinctly different regions or zones. The brightest region, the core, originated within the working coil and extended beyond the coil. This region was *ca.* 15 mm in diameter at its base and extended *ca.* 40 mm to its tip. The core was brilliant, blue-white and non-transparent. The secondary or transition region which appeared above the core had the same general shape as the core but extended *ca.* 75 mm from the base of the discharge and, while still bright, was significantly weaker than the core. The secondary

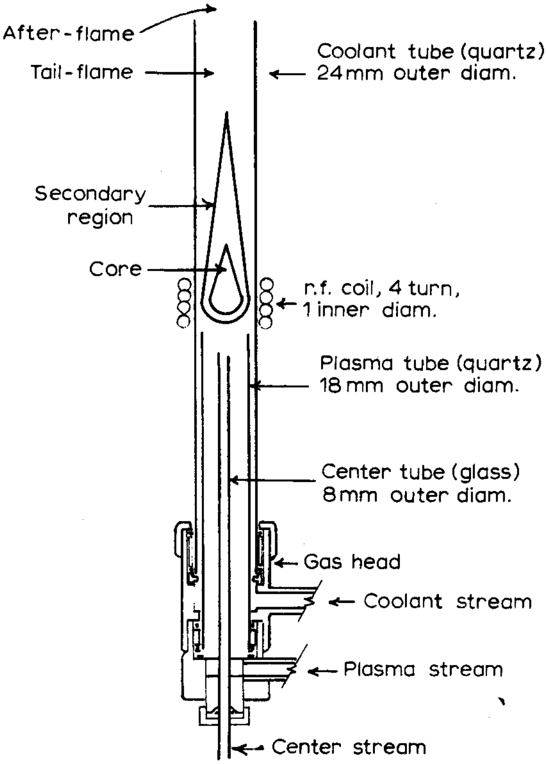

Fig. 2. Schematic diagram of plasma torch and optical regions in the plasma discharge.

region was semi-transparent and appeared white rather than blue-white. The remainder of the coolant tube was filled with a faint blue transparent discharge. This portion of the discharge is referred to as the tail-flame. The region beyond the end of the cool-

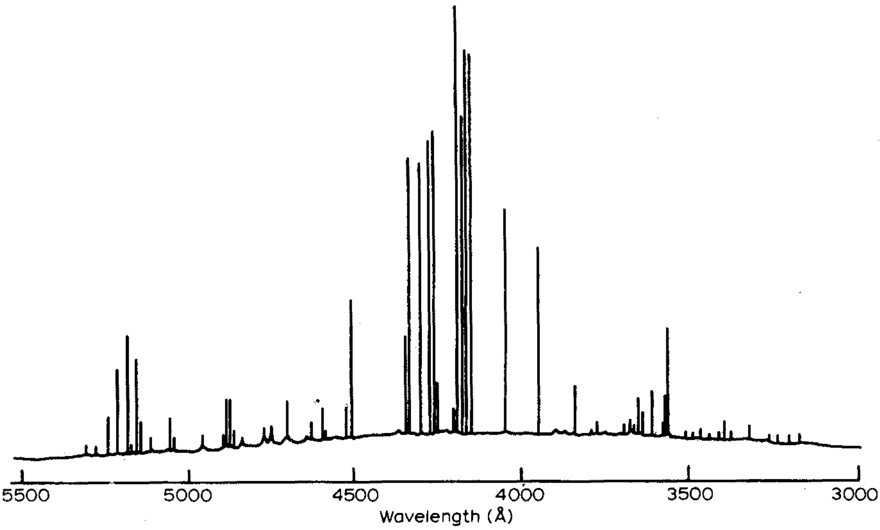

Fig. 3 Spectrum of dry argon.

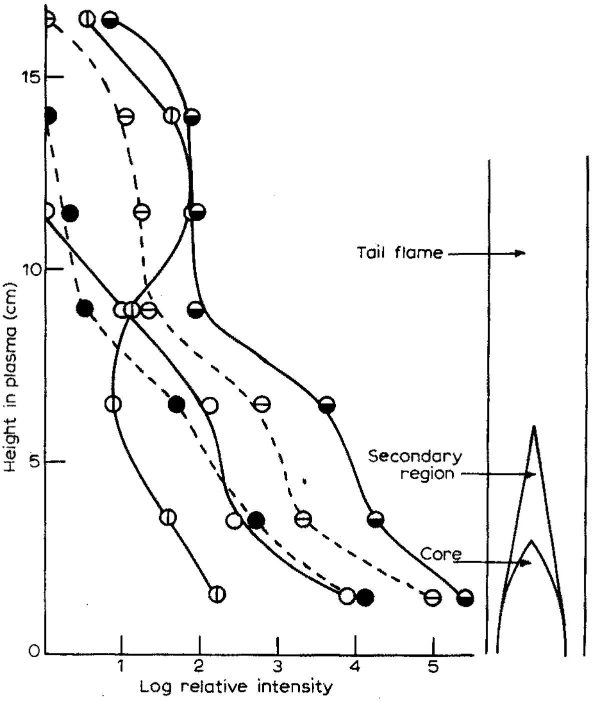

Fig. 4. Plasma profile of emission for moist argon: (⦶) 3089 Å (OH), (⊖) 3949 Å (Ar), (○) 4150 Å (continuum), (◒) 4201 Å (Ar), (●) 4861 Å (H).

ant tube is referred to as the after-flame. In this case, however, there was no significant after-flame and the name is introduced only for the sake of completeness. Operating in the low flow mode there was less distinction between the core and secondary region. Both zones were somewhat thinner and longer and the boundary between the two was unclear.

The torch and various visible regions are shown in Fig. 2. Spectroscopic studies of the plasma indicated that the strongest emission signal from all regions of the plasma was the 4201 Å atomic argon line. The relative intensities for this line from the core, secondary region and tail-flame were found to be 23,000: 11,000:7. The spectrum obtained from the secondary region of the tail-flame is shown in Fig. 3. The intensities of various lines and bands and the continuum in the three regions are shown in Fig. 4, which gives the plasma profile for some of the more important lines and bands. The spectra obtained from the argon plasma in the core and secondary region included an intense continuum extending from below 3000 Å to *ca.* 5000 Å. The intensity of this continuum, relative to the strongest emission line, varied depending on the condition of the coolant tube, the r.f. coupling and power, and the amount of water vapor and other impurities present in the argon support. The continuum was, however, always prominent in the spectrum recorded from the core or secondary region. A well developed spectrum of atomic argon was emitted from the core and secondary region; however, only one line indicative of A(II) (4806 Å) was found in the core region and this line was weak. The tail-flame region showed the stronger atomic argon lines at reduced intensities. These emission lines have excitation potentials up to 15 eV, and their presence indicated large concentration of metastable argon atoms in the tail-flame. The after-flame, or the region beyond the end of the coolant tube, gave spectra containing even weaker atomic argon lines and the 3064 Å OH-band system.

The emission intensities fell off very quickly with increasing distances from the end of the coolant tube. The OH-band system was the last emission to disappear.

The power requirements of the plasma

The plasma was found to be self-sustaining at power levels above 0.70 kVA. The power level had a strong effect on the overall intensity of the emission spectrum. The principal effect appeared to be a general overall increase in the intensity. There were, however, at higher power levels some additional argon lines that appeared and a few weak hydrogen lines. Continuous operation was not possible at power levels above 1.75 kVA with pure argon because the plasma attacked the quartz tubing. Figure 5 shows the response of several spectral features to changes in power level. Short-term operation was found to be practical to power levels of 2.5 kVA.

When a short coolant tube was used, the after-flame emitted band spectra characteristic of O_2, N_2, OH and weak bands which were apparently due to NH and N_2^+. When the coolant tube was very short, as in the case of the torch reported by GREENFIELD *et al.*[2], the secondary region extended beyond the end of the coolant tube into the atmosphere and these band systems became more prominent and the continuum increased. The results of this torch configuration were quite similar to those obtained when large air samples were introduced into the coolant stream. When the torch head was clean and no sample was being introduced, the core and secondary region were quite stable and the tail-flame wandered only slightly. Continuous monitoring of the 4201 Å argon line with the instrument set to read full-scale deflection gave

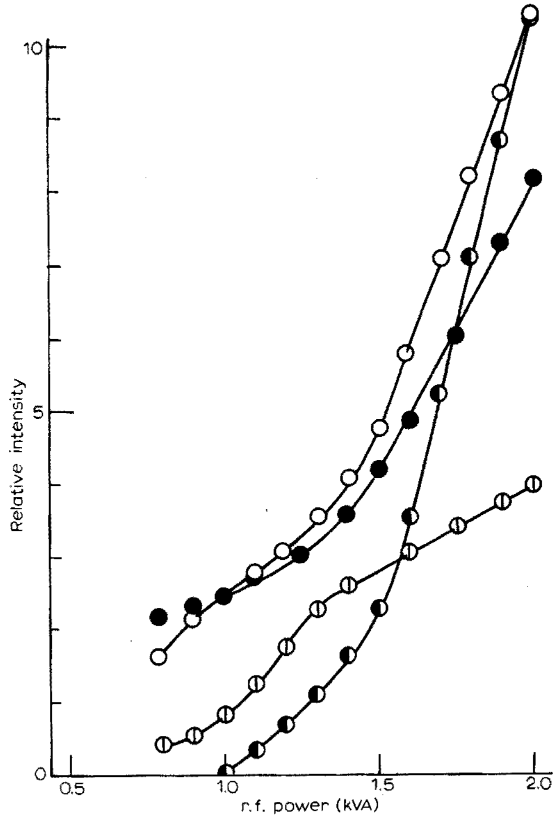

Fig. 5. Effect of r.f. power on emission intensity for moist argon: (○) 3089 Å (OH), (◐) 4150 Å (continuum), (●) 4201 Å (Ar), (⌽) 4861 Å (H).

a signal-to-noise ratio of 100:1 to 200:1, with a maximum variation from the mean of 2% over 3 successive 20-min runs produced over a period of 2 h. Over short periods of time, *ca.* 1 or 2 days, the system may be shut down and started up again and the readings reproduced within 1–2% without readjustment of the equipment.

Great care had to be taken when recording the emission spectrum from the core and at times from the secondary region, in order to prevent saturation of the photomultiplier. It was often found that partial saturation of the photomultiplier occurred at voltages as low as 500 V. This partial saturation caused the line-to-background ratio to be erroneously small.

Emission spectra of water

When water vapor was introduced into either the coolant or center streams, moderately strong OH bands (3064 Å) were emitted from all regions of the plasma and the overall intensity of the plasma was decreased while the amount of heat dissipated increased. Balmer-series hydrogen lines were also found. These lines were very strong and quite broad from the core and secondary region and were stronger when the sample was introduced into the core than when the sample was introduced into the coolant stream. The hydrogen lines rapidly weakened in the tail-flame and disap-

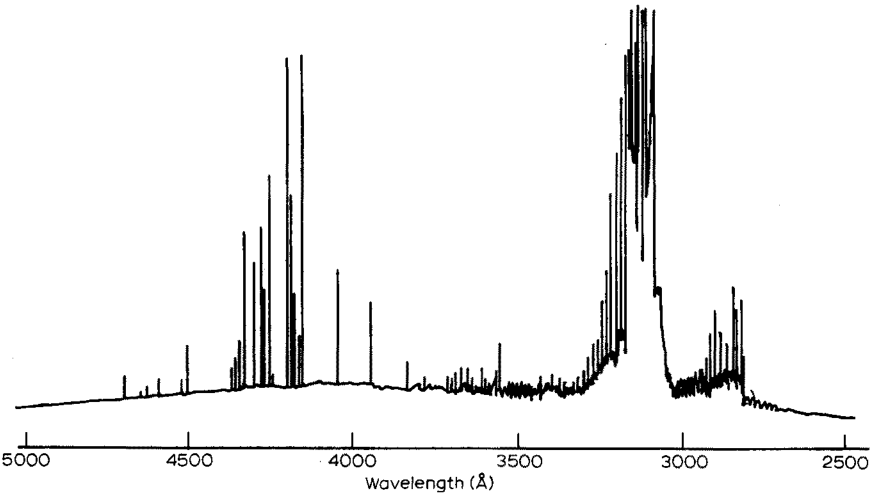

Fig. 6. Spectrum of water.

peared before the end of the coolant tube was reached. The 2800-Å OH band was also found occasionally but was only approximately 10% as strong, in favorable cases, as the 3064-Å OH band. Low concentrations of water, for example, had little effect on the intensities of the argon lines and almost no visual effect. At higher concentrations the core retracted and elongated while the secondary region became less distinctive. The introduction of water vapor into the core caused a considerable increase in the intensity of the continuum and thus reduced the line-to-background ratio of the argon. The intensity of the 3064 Å OH band was found to increase from the core to the tail-flame while the effect on the Balmer-series hydrogen was reversed. The OH bands were found to increase in intensity with increases in the radio-frequency power. The spectrum is shown in Fig. 6.

Emission spectra of simple gases

Nitrogen, oxygen, helium and air were investigated as samples. The gaseous sample was introduced through a rotameter and metering valve into the stream of interest and mixed with argon in a mixing chamber. In all cases, it was possible to replace all of the argon with sample gas in the coolant stream without extinguishing the plasma discharge. However, it was necessary in some cases to increase the power level to as high as 2.0 kVA to maintain the discharge. In the case of nitrogen and helium, all of the argon could be replaced in the center tube, but in the case of air or oxygen, pure gas samples could not be introduced into the center stream at low power levels. In all cases, as the amount of sample gas in the argon increased, the minimum amount of power required to maintain the plasma discharge also increased. Pure samples in the coolant stream required approximately twice the minimum power (*ca.* 1.4 kVA) needed to maintain the plasma discharge with argon only. With a sample size of *ca.* 0.1 l min^{-1} the spectra obtained when samples were introduced into the center and coolant streams could be compared directly. In general, introduction of any of the gases into the center stream resulted in severe contraction of the core, a reduction in the line-to-background ratio and reduction of line and band intensities in the spectrum obtained of the core and secondary region and to a lesser extent from the tail-flame. Introduction of sample gases into the tail-flame via the "Tee" in the coolant tube, as would be expected, did not appear to affect the core or secondary region, but often drastically changed the spectrum of the tail-flame.

As nitrogen replaced argon in the coolant stream, the tail-flame of the plasma discharge turned pink to reddish-orange and the after-flame increased in length. With pure nitrogen coolant, the red after-flame extended over 60 cm beyond the end of the coolant stream. In all cases the introduction of a given sample resulted in the same line and band spectra. When nitrogen was introduced, the spectra obtained from all three regions of the plasma discharge showed the second positive nitrogen system and at higher power levels, particularly from the core and secondary region, bands of the first negative nitrogen system appeared, originating with N_2^+. The red emission was probably due to the first positive nitrogen system. The two nitrogen band systems observed, along with literature values, are given in Fig. 7, which shows the spectrum

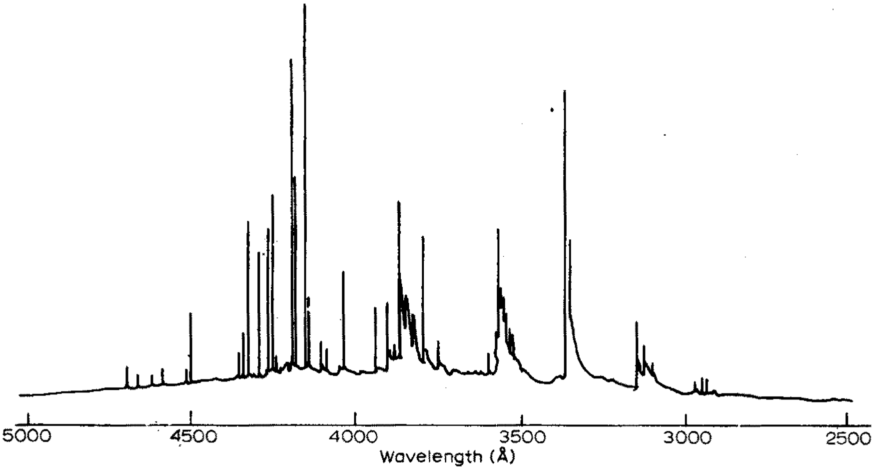

Fig. 7. Spectrum of dry nitrogen.

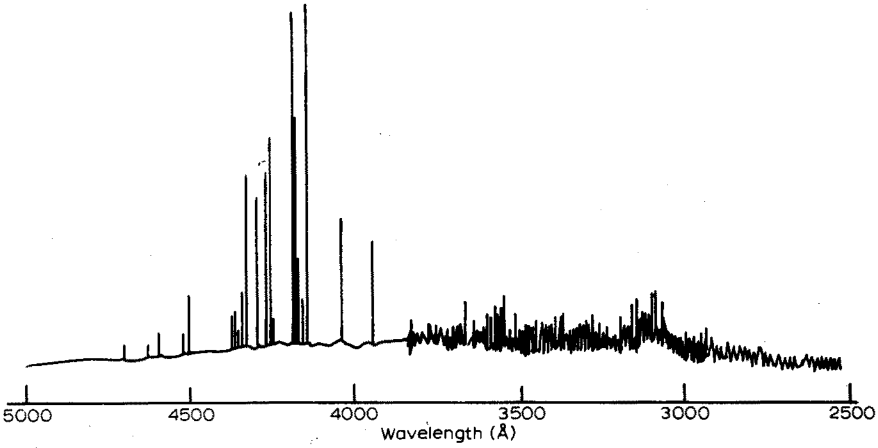

Fig. 8. Spectrum of dry oxygen.

obtained from the lower portion of the tail-flame when nitrogen was introduced as a sample into the coolant stream. Atomic nitrogen lines are probably present in the spectrum at 4100, 4110, 3830, 4915 and 4935 Å, but these lines are too weak or too close to strong argon lines for positive identification.

Introduction of oxygen, even at low levels, caused severe reduction in the line intensities. At higher concentrations, a poorly developed oxygen band system appeared. The system was too poorly developed for positive identification of band heads but appeared to be the Schumann-Runge system. The spectrum obtained from the tail-flame of the plasma discharge is shown in Fig. 8. Introduction of helium had no effect on the spectrum obtained as far as the number of emission lines and bands are concerned, but did cause a slight reduction in the intensities of the argon lines and an increase in the intensity of the OH bands and the continuum. No emission lines characteristic of helium were found under the conditions employed in these experiments. Helium coolant caused the plasma to radiate a noticeably greater amount of heat than any other coolant. Introduction of air, as would be expected, produced an effect which was a mixture of the effects produced by oxygen and nitrogen. Nitrogen and oxygen bands were prevalent as in the case of either gas and the line-to-background ratio decreased along with a smaller decrease in the line intensities. The OH bands became very prominent and the NO γ-system appeared. This spectrum is shown in Fig. 9.

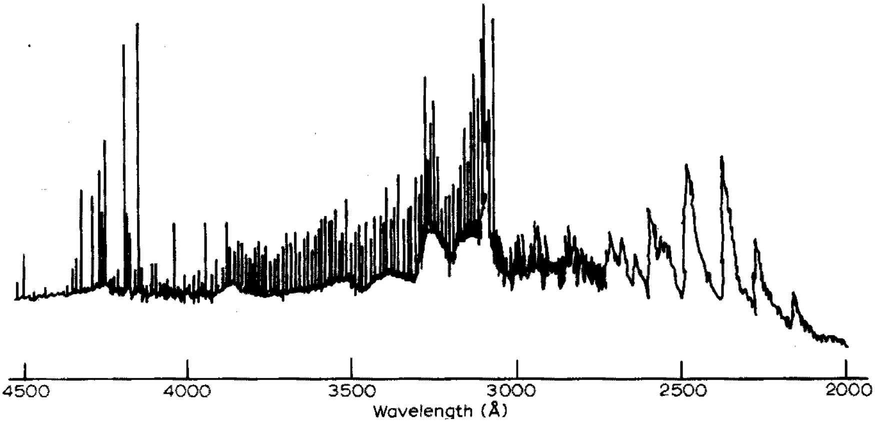

Fig. 9 Spectrum for torch with air coolant at 4.0 kVA power.

The NO γ-system bands are considered later under the discussion on nitrogen oxides. The effect of power on the various band systems is shown in Fig. 10.

With an air coolant, the plasma was operated at power levels up to 4.0 kVA. At a power level of 4 kVA the secondary region became an extension of the core. The spectrum gave an average signal-to-background ratio of 1 at a signal-to-noise ratio of 10–20 for full scale deflection. Fairly strong and well developed NO γ-system bands and N_2^+ bands were found along with fairly strong, poorly developed O_2 bands and moderately strong, well developed N_2 and NH bands. Atomic nitrogen lines could not be definitely identified although they appeared to be present as weak lines at 4100 and 4110 Å. A large number of argon lines were still present in the spectral region 4000–5000 Å. At this point it is interesting to note that the 4159 and 4201 Å argon lines corresponded to electronic transitions of *ca.* 14.7 eV. These transitions were from an

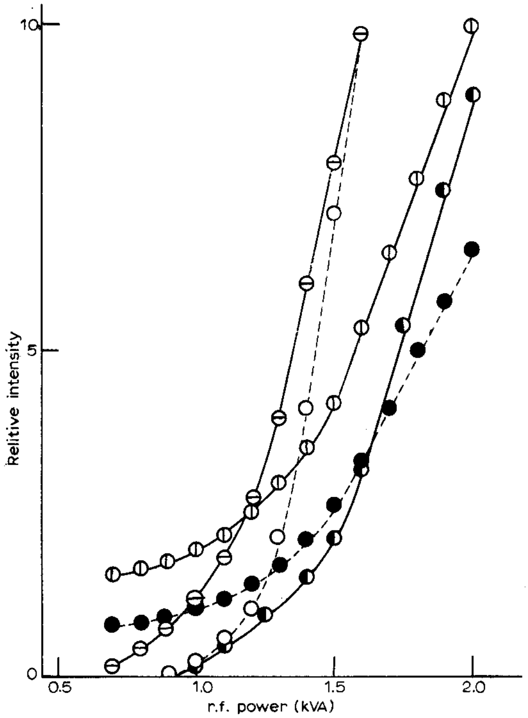

Fig. 10. Effect of r.f. power on emission intensity for moist nitrogen: (⦶) 3360 Å (NH or N_2), (⊖) 3371 Å (NH or N_2), (○) 3915 Å (N_2^+), (●) 3949 Å (Ar), (◐) 4150 Å (continuum).

excited state to a metastable state with an energy of the order of 11.5 eV. The first and second positive nitrogen systems represented transitions from excited states with energies of the order of 7.4 and 11.0 eV respectively. It was also interesting that the ionization potential of helium at 24.6 eV was in all probability far beyond the energy available in this argon-based plasma; in fact, it appeared from data reported by CHANDLER[3] that there are no prominent helium transitions expected at this low energy level. Thus the effects caused by helium would be due to dilution and most likely to changes in the heat capacity of the plasma. While considering energy levels, it should also be noted that the first ionization potential for molecular nitrogen (15.5 eV) is reported to be only 0.2 eV less than the ionization potential of argon. The absence of atomic oxygen lines could be explained on the basis that the major oxygen lines (7772, 7774 and 7775 Å) fell outside the range of the photomultiplier used.

SUMMARY

A highly stable and quiet induction-coupled radio-frequency plasma torch capable of continuous operation has been developed. The electronic spectra produced by various organic compounds when introduced into the plasma have been studied. Results indicate that the tendency is for the molecules to be shattered in the plasma and to emit electronic spectra typical of functional groups.

RÉSUMÉ

Une étude spectroscopique par radiofréquence est effectuée sur le plasma. On examine les spectres électroniques produits par divers composés organiques, introduits dans le plasma. Les résultats montrent que les molécules ont tendance à être brisées dans le plasma et à émettre des spectres électroniques typiques de groupes fonctionnels.

ZUSAMMENFASSUNG

Es wurde ein hochstabiler induktionsgekoppelter Radiofrequenz-Plasmabrenner entwickelt, der für kontinuierliche Arbeitsweise geeignet ist. Die Elektronenspektren, die durch verschiedene organische Verbindungen im Plasma hervorgerufen werden, wurden untersucht. Wie die Ergebnisse zeigen, neigen die Moleküle dazu, im Plasma zu zerfallen und Elektronenspektren zu emittieren, die für funktionelle Gruppen charakteristisch sind.

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

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

PART III. ABSORPTION OF RADIATION FROM HOLLOW CATHODES*

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(Received October 13th, 1969)

As mentioned previously[1] the purpose of the present investigation is threefold: (*a*) to indicate sources of spectral interferences in flame photometry and atomic absorption, (*b*) to add to the knowledge of physical and chemical processes in flames employed for analytical work, and (*c*) to study the development of analytical methods for the determination of organic compounds by flame spectroscopy.

Spectral interferences produced in atomic absorption by scattering and by absorption by various flame species are described in Part II[1]. In this third part of the investigation, absorption of atomic resonance radiation by flames and solvents has been studied.

EXPERIMENTAL

The experimental conditions were the same as those used to obtain the data reported previously[1].

Hollow-cathode lamps from Atomic Spectral Lamps, Pty. Ltd., Beckman Instruments, Inc., and Perkin Elmer Corp. were used.

RESULTS AND DISCUSSION

Absorption of atomic ground state lines by flames and solvents

Absorption of atomic lines originating in the ground state by flames is illustrated in Fig. 1 which shows absorption by the oxyhydrogen flame of the bismuth 3068-Å line. The beam (1–1.5 cm in diameter) from the hollow cathode was passed once through the flame 3 cm above the tip of the burner. Strong absorption of the aluminum 3082-Å and 3092-Å lines by oxyhydrogen flames was also observed (the zinc 3076-Å line was not absorbed significantly).

Absorption by the flame at low wavelengths is illustrated in Fig. 2. When nitroethane was introduced the absorption was increased.

Absorption by flames into which organic solvents were aspirated and of organic solvent sprays (with no flame burning) were obtained for various atomic resonance lines, as shown in Tables I and II. The beam from the hollow-cathode lamp was passed through the flame or spray three times by means of reflection. The highest pass

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* Taken in part from the Ph.D. Dissertation of V. J. SMITH, Louisiana State University, Baton Rouge, 1969.

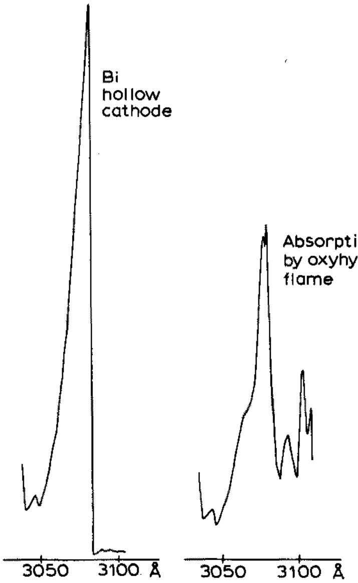

Fig. 1. Absorption of Bi 3068-Å line by the oxyhydrogen flame.

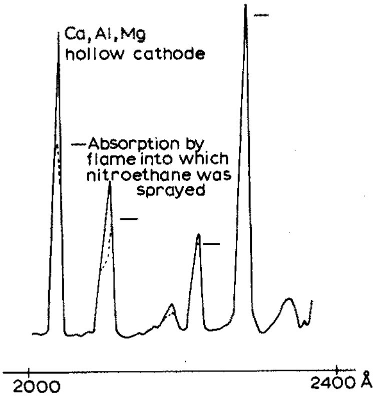

Fig. 2. Absorption produced by spraying nitroethane into the oxyhydrogen flame of lines from the Ca–Al–Mg multielement hollow cathode.

was 4–5 cm above the tip of the burner, and the lowest pass was 0.8 cm above the burner, which was in the reaction zone of the flame. The diameter of the beam at the highest pass was 1–1.5 cm and at the lowest pass it was approximately 1 cm. Absorption signals obtained from the oxyhydrogen flame by itself were subtracted from absorption signals resulting when solvents were aspirated into the flame (Table I). Instrumental slit and gain settings for the different resonance lines were comparable (except at 3233 Å, 3302 Å, 3860 Å, and 4044 Å), the slits were significantly wider (>0.10 mm) than at the other wavelengths shown in Tables I and II.

Table I shows relatively large absorption signals at 3233 Å, 3302 Å, 3860 Å and 4044 Å. Except as noted in Table III, emission signals from unmodulated flames (obtained by blocking the beam from the lamp and recording any signals from the flames) were zero. Table III shows emission from unmodulated flames at 3233 Å, 3302 Å, 3860 Å, and 4044 Å, however. These relatively large absorption and emission signals recorded in Tables I and III were caused by the relatively wide slits used (>0.10 mm) at these wavelengths. At 3233 Å the observed absorption and emission can probably be attributed to OH, PO and SO_2 fragments[1]. At 3302 Å, 3860 Å, and 4044 Å the observed absorption and emission can probably be attributed to PO and SO_2 radicals[1].

Tables IV and V show the effects of the slit width on absorption at 3248 Å, 3383 Å, and 4227 Å. Instrumental parameters other than the slit width were similar. The beam from the hollow cathode was passed once through the flame at a distance of 3 cm above the tip of the burner. Signals from the flame were subtracted from signals produced when solvents were aspirated into the flame. Absorption and emission signals were produced mainly by PO and SO_2 fragments[1].

The relatively large absorption signals shown in Table I at 5890 Å were attributed to sodium impurity. Emission and absorption by sodium impurity has been illustrated also in figures presented in previous Parts of this series[1]. Atomic absorption analyses for sodium are more sensitive at 5890 Å than at 3302 Å[2].

Table I also shows significant absorption signals at short wavelengths. Absorption was especially pronounced for the oxyhydrogen flame by itself and for flames resulting when benzene, anisole, butylamine, pyridine, nitroethane, triethyl phosphate, thiophene, or dimethyl sulfoxide was introduced. Absorption by the oxyhydrogen flame at low wavelengths was attributed to oxygen molecules[3-6]. The small increase in the absorption signal generally produced by aspirating a solvent (*e.g.* cyclohexane) into the flame may be partly caused by an increase in the size of the flame, and hence an increase in the number of oxygen molecules in the light path.

Table II shows absorption signals produced by several organic solvent sprays with no flame burning. Relatively intense absorption is produced at low wavelengths by benzene, anisole, butylamine, pyridine, nitroethane, and thiophene, and absorption by pyridine is significant at wavelengths as high as 2659 Å. These signals resulted from absorption by whole solvent molecules.

Benzene exhibits a strong absorption maximum at 2020 Å (ε_{max} 6900) and a weak absorption maximum at 2550 Å (ε_{max} approximately 200)[7-9]. Table II shows absorption of the magnesium 2025-Å line by benzene, but no significant absorption of the other resonance lines investigated. Anisole has a strong absorption maximum at 2690 Å (ε_{max} 1480)[9,10]. Table II shows absorption by anisole at wavelengths less than 2226 Å. The amine group has an absorption maximum at 1950 Å (ε_{max} 2800)[8]. Butylamine absorbed appreciably at wavelengths less than 2349 Å. Pyridine has a strong absorption maximum at 1950 Å (ε_{max} 6000) and a maximum at 2510 Å (ε_{max} 1700)[8,9]. Table II shows pyridine absorbing at wavelengths less than 2796 Å. Nitroethane has a strong absorption maximum at 2010 Å (ε_{max} 4850) and a weak absorption maximum at approximately 2800 Å ($\varepsilon_{max} < 20$)[10-12]. The nitroethane spray absorbed appreciably at wavelengths less than 2349 Å. Thiophene has a strong absorption maximum at 2310 Å (ε_{max} 5620)[7,9]. Table II shows that thiophene absorbed at wavelengths less than 2492 Å.

No significant absorption was observed for cyclohexane, distilled water, butanol, amyl acetate, methyl isobutyl ketone, acetic acid, tributyl phosphate, triethyl phosphate, dimethyl sulfoxide, chloroform, or butyl chloride solvent sprays. Absorption was not observed for these solvents, for benzene at wavelengths close to 2550 Å, for anisole at wavelengths close to 2690 Å, or for nitroethane at wavelengths close to 2800 Å, because (*a*) the molecules did not absorb in the ultraviolet region or at the wavelengths investigated, or (*b*) the absorption (ε_{max}) was relatively weak[7,8,13,14].

The relatively small absorption signals shown in Table II that are approximately constant for a solvent at all of the wavelengths investigated are probably due to scattering of the light by the solvent drops.

The relatively high absorption signals at short wavelengths that resulted when benzene, anisole, butylamine, nitroethane, and thiophene were aspirated into the flame may be attributed mainly to absorption by whole, unburned solvent molecules (see Tables I and II). Absorption by pyridine and thiophene molecules in the flame was also observed in absorption spectra obtained with a source of continuous emission[1]. The relatively high absorption signals observed when triethyl phosphate and

TABLE I

ABSORPTION OF ATOMIC RESONANCE LINES BY OXYHYDROGEN FLAMES INTO WHICH ORGANIC SOLVENTS WERE

Sample[a]	% *Absorption*[b] *of atomic resonance lines (wavelengths in Å)*											
	Mg 2025	*Zn 2138*	*Pt 2148*	*Pb 2170*	*Cu 2226*	*Be 2349*	*Co 2407*	*Cu 2492*	*Co 2521*	*Pt 2659*	*Mg 2796*	*Pb 2833*
Flame	13	5	3	6	3	0	2	1	1	0	0	2
Benzene	15	5	4	4	1	2	1	0	0	0	0	0
Cyclohexane	1	3	3	2	0	1	0	0	0	0	0	0
Distilled water	0	0	1	1	0	0	0	0	0	0	0	0
Butanol	1	0	1	0	0	0	0	0	0	0	0	0
Amyl acetate	2	2	2	2	0	0	0	0	0	0	0	0
Methyl isobutyl ketone	3	2	4	2	0	0	0	0	0	0	0	0
Anisole	4	6	6	6	2	0	0	0	0	0	0	0
Acetic acid	1	2	1	1	0	0	0	0	0	0	0	0
Butylamine	6	8	8	5	2	2	0	0	0	0	0	0
Pyridine	4	4	6	3	2	1	2	2	4	0	0	0
Nitroethane	9	6	11	4	2	0	0	0	0	0	0	0
Tributyl phosphate	2	4	2	2	1	1	0	0	0	0	0	1
Triethyl phosphate	5	9	5	6	2	3	2	2	3	2	2	2
Thiophene	24	28	33	32	18	22	16	6	6	4	4	5
Dimethyl sulfoxide	10	12	11	12	5	4	4	2	2	2	2	2
Chloroform	2	0	1	1	0	0	0	0	0	0	0	0
Butyl chloride	2	3	3	2	0	0	0	0	0	0	0	0

[a] Gas flow rates: oxygen 3.5 l min^{-1}, hydrogen 10 l min^{-1}.
[b] ± 2% Absorption.

TABLE II

ABSORPTION OF ATOMIC RESONANCE LINES BY SOLVENT SPRAYS[a]

Sample[a]	% *Absorption*[b] *of atomic resonance lines (wavelengths in Å)*											
	Mg 2025	*Zn 2138*	*Pt 2148*	*Pb 2170*	*Cu 2226*	*Be 2349*	*Co 2407*	*Cu 2492*	*Co 2521*	*Pt 2659*	*Mg 2796*	*Pb 2833*
Benzene	58	4	4	4	2	2	3	3	4	4	2	4
Cyclohexane	3	1	3	2	1	1	2	1	2	2	2	2
Distilled water	4	4	5	4	3	2	4	2	4	4	4	4
Butanol	1	2	3	2	1	1	2	2	2	2	2	2
Amyl acetate	5	6	7	6	4	4	6	4	5	6	4	6
Methyl isobutyl ketone	6	6	6	6	4	4	6	4	6	6	6	6
Anisole	12	23	27	20	6	2	4	2	4	6	3	4
Acetic acid	4	3	4	4	2	2	3	2	2	3	2	4
Butylamine	16	22	28	24	14	6	4	4	4	4	3	4
Pyridine	8	4	4	6	4	10	16	15	20	11	5	5
Nitroethane	42	34	34	24	8	4	5	4	4	5	5	6
Tributyl phosphate	2	1	3	4	2	2	2	2	2	3	2	3
Triethyl phosphate	4	4	5	5	4	4	5	4	4	5	4	6
Thiophene	29	62	70	68	60	80	36	2	3	2	2	4
Dimethyl sulfoxide	4	4	5	4	2	2	2	2	2	3	2	4
Chloroform	4	2	2	3	0	1	2	2	2	2	2	2
Butyl chloride	2	3	3	4	2	2	4	2	2	4	2	4

[a] No flame. Oxygen flow rate: 3.5 l min^{-1}.
[b] ±2% Absorption.

SPRAYED

Mg 2852	*Zn* 3076	*V* 3184	*Li* 3233	*Cu* 3248	*Ag* 3281	*Na* 3302	*Ag* 3383	*Cr* 3579	*Fe* 3860	*W* 4009	*K* 4044	*Ca* 4227	*Ba* 5536	*Na* 5890	*Li* 6708	*K* 7665
0	0	0	17	0	1	0	0	0	0	0	0	0	0	0	0	1
0	0	0	8	0	0	2	0	0	0	0	1	0	0	0	0	0
0	0	0	6	0	0	2	0	0	0	0	0	0	0	0	0	0
0	0	0	3	0	0	0	0	0	0	0	0	0	0	2	0	0
0	0	0	2	0	0	0	0	0	0	0	0	0	0	2	0	0
0	0	0	3	0	0	0	0	0	0	0	0	0	0	6	0	0
0	0	0	3	0	0	1	0	0	0	0	0	0	0	29	0	0
0	0	0	6	0	0	2	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0	0	0	0	14	0	0
4	0	0	2	0	0	1	0	0	0	0	0	2	0	4	0	0
0	0	0	5	0	0	1	0	0	2	0	0	0	0	0	0	0
0	0	0	3	0	0	0	0	0	0	0	0	0	0	2	0	0
2	0	0	25	0	2	16	0	0	7	0	13	0	0	2	0	0
2	2	2	39	2	3	24	1	0	18	0	24	1	0	0	1	2
4	3	3	34	2	2	28	1	0	3	0	6	0	0	0	0	0
2	2	1	21	0	1	10	0	0	2	0	2	0	0	2	0	0
0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0

Mg 2852	*Zn* 3076	*V* 3184	*Li* 3233	*Cu* 3248	*Ag* 3281	*Na* 3302	*Ag* 3383	*Cr* 3579	*Fe* 3860	*W* 4009	*K* 4044	*Ca* 4227	*Ba* 5536	*Na* 5890	*Li* 6708	*K* 7665
4	4	4	4	3	4	2	4	2	3	4	3	4	3	4	4	4
2	2	2	2	2	2	2	1	2	2	3	2	2	2	2	2	4
4	4	5	4	3	4	3	3	6	5	4	4	4	5	4	4	6
2	2	3	4	2	2	2	2	2	2	2	2	2	2	3	2	4
6	6	8	8	6	6	6	5	6	7	8	6	8	6	8	8	10
6	6	8	6	6	6	5	6	6	6	8	6	8	6	6	7	9
4	5	6	5	4	4	4	4	5	4	4	4	6	4	6	6	4
4	4	4	5	3	4	3	2	4	4	4	2	3	4	4	4	4
4	4	6	6	3	4	4	3	4	5	5	4	4	4	5	6	7
4	4	5	5	4	4	4	3	4	5	4	4	4	4	4	4	5
6	6	7	5	6	6	4	5	6	6	6	5	6	6	6	7	8
2	4	4	3	2	2	2	2	3	4	4	3	3	4	4	3	4
6	6	7	6	5	6	5	4	6	8	6	5	6	6	6	6	8
2	3	4	4	4	4	2	2	3	3	4	3	4	4	4	4	5
2	3	4	4	3	2	3	2	4	5	4	3	3	4	4	4	4
2	2	3	3	2	2	2	2	2	2	3	2	2	2	2	2	4
3	4	5	3	4	2	2	2	3	4	4	4	4	3	4	4	6

TABLE III

EMISSION SIGNALS FROM UNMODULATED FLAMES

Sample[a]	*% Emission*[b]			
	Li 3233 *Å*	*Na* 3302 *Å*	*Fe* 3860 *Å*	*K* 4044 *Å*
Flame	4			
Benzene	3			
Cyclohexane	2			
Distilled water	4			
Anisole	3			
Butylamine	1			
Pyridine	2			
Nitroethane	1			
Tributyl phosphate	18		1	
Triethyl phosphate	16	10	2	3
Thiophene	16	18		
Dimethyl sulfoxide	17			

[a] Gas flow rates: oxygen 3.5 l min^{-1}; hydrogen 10 l min^{-1}.
[b] ±2% Emission.

TABLE IV

ABSORPTION OF ATOMIC RESONANCE LINES BY OXYHYDROGEN FLAMES INTO WHICH ORGANIC SOLVENTS WERE SPRAYED. EFFECT OF SLIT WIDTH

Sample[a]	*% Absorption*[b] *of atomic resonance lines*					
	Cu (3248 Å)		*Ag (3383 Å)*		*Ca (4227 Å)*	
	Slit 0.10	*0.50*	*0.08*	*0.50*	*0.10*	*0.50*
Flame	0	3	0	0	0	0
Benzene	0	4	0	2	0	0
Pyridine	0	4	0	2	0	0
Tributyl phosphate	0	16	0	18	0	20
Triethyl phosphate	0	2	0	15	0	6
Thiophene	0	7	0	16	0	4
Dimethyl sulfoxide	0	12	0	14	0	2

[a] Gas flow rate: oxygen 3.5 l min^{-1}; hydrogen 10 l min^{-1}.
[b] ±2% Absorption.

TABLE V

EMISSION SIGNALS FROM UNMODULATED PLAMES. EFFECT OF SLIT WIDTH

Sample[a]	*% Emission*[b]					
	Cu (3248 Å)		*Ag (3383 Å)*		*Ca (4227 Å)*	
	Slit 0.10	*0.50*	*0.08*	*0.50*	*0.10*	*0.50*
Flame	0	0	0	0	0	1
Benzene	0	1	0	0	0	0
Pyridine	0	2	0	0	0	0
Tributyl phosphate	0	19	0	6	0	13
Triethyl phosphate	0	53	0	30	0	46
Thiophene	0	35	0	23	0	2
Dimethyl sulfoxide	0	8	0	2	0	0

[a] Gas flow rates: oxygen 3.5 l min^{-1}; hydrogen 10 l min^{-1}.
[b] ± 2% Emission.

dimethyl sulfoxide were aspirated into the flame must be due to species produced in the flame since there was no significant absorption observed for the sprays (Tables I and II). Absorption produced by triethyl phosphate at low wavelengths may be due to the P_2 fragment[3]. Absorption produced by dimethyl sulfoxide at low wavelengths is probably due to sulfur dioxide[6,15]. Some of the absorption produced in the same region by thiophene is probably also due to sulfur dioxide.

CONCLUSION

Absorption signals produced by organic solvent sprays (with no flame burning) and by species formed in oxyhydrogen flames from flame gases and organic solvents have been presented for selected atomic resonance lines.

Results reported in this third Part as well as in previous Parts of this series, indicate sources of spectral interferences in flame photometry and atomic absorption. However, "although it is desirable for a user to... have some information regarding interference possibilities,... until enough is on record regarding his particular instrument, the information to be found in the literature must be regarded as a warning of what might happen"[16].

SUMMARY

Absorption produced at selected atomic-resonance wavelengths by species formed in oxyhydrogen flames from flame gases and organic solvents has been studied. Results indicate sources of spectral interferences in atomic absorption spectroscopy.

RÉSUMÉ

On a étudié l'absorption produite à certaines longueurs d'onde de résonance atomique par des particules formées dans des flammes oxyhydrogène de mélanges gaz et solvants organiques. Les résultats indiquent les sources d'interférences spectrales dans la spectroscopie par absorption atomique.

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

PHOTON SELF-ABSORPTION CORRECTIONS FOR THE MINIMIZATION OF SYSTEMATIC ERRORS IN 14-MeV NEUTRON ACTIVATION ANALYSIS

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(Received October 8th, 1969)

In comparative 14-MeV neutron activation analysis of thick samples, high precision and accuracy can be obtained provided appropriate measures are taken to ensure homogeneity of the incident neutron flux, and corrections are made for self-absorption in the sample and standard. An earlier study[1] shows the necessity for these procedures in the precise and accurate analysis for oxygen in samples of widely varying composition. Our recent work[2,3] describes techniques which permit the evaluation of systematic errors resulting from absorption of fast neutrons and γ-rays by the sample during the irradiation and measurement of induced radioactivity processes, respectively. The successful conclusion of these studies prompted further investigation into the possibility of applying the developed techniques to the determination of photon attenuation correction factors for the general case.

The significance of obtaining accurate empirical relationships which would predict attenuation correction factors in the general case cannot be over-emphasized. Such information would permit the use of any standard for the determination of an element in any matrix. Also, the use of such correction factors would improve the accuracy of general analyses with 14-MeV neutrons.

In most cases, γ-spectrometry associated with activation analysis involves measurement of photopeaks resulting from direct nuclear level transitions or annihilation of positrons. From the previous study[3], it was concluded that the attenuated sample thickness, as given by the slope of the photon correction factor line as a function of the linear absorption coefficient, would be independent of the primary γ-energy and dependent only upon the efficiency of the detector system for degraded γ-ray contribution within the region of interest. Therefore, it was surmised that the slope for photopeak counting would be greater than that measured for the integral counting of γ-rays between 4.8 and 8.0 MeV from ^{16}N decay in oxygen analysis, and would approximate a value equivalent to one half the geometrical sample diameter. It was also surmised that annihilation photons would exhibit a small change in the slope because of bremsstrahlung contributions under the annihilation photopeak.

The neutron attenuation behavior, however, would remain unchanged if the removal cross-section theory was valid, since this theory assumes that neutrons whose energy have been degraded do not take part in subsequent nuclear reactions within the sample. Confirmation of this could easily be obtained if the nuclear reactions

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chosen showed a wide range in their threshold energies. It was realized that before 14-MeV neutron activation analysis can be considered as a precise and accurate analytical technique and applied routinely to general analysis, experimental verification of the assumptions stated above would be needed.

The approach to this problem was to use the already proven techniques[2,3] and apply them to samples suitably selected to give the required information. By the judicious choice of samples, the effect of different reaction threshold energies on the previously established[3] neutron attenuation correlation for the attenuation of fast neutrons, and the γ-ray and positron energy dependence on the photon attenuation correction factors, could be evaluated. The effect of sample density and other factors such as bremsstrahlung contribution in the photopeak regions, could also be measured. The empirical determination of the photon attenuation correction factors for the general case would considerably expand the capability of the 14-MeV neutron activation facility to include numerous semi-micro and macroconstituent analyses of elements in diverse matrices. The technique would also have the advantage of both speed and versatility, and be comparable in precision and accuracy to many chemical and instrumental methods presently employed in the certification of Standard Reference Materials.

SELECTION OF SAMPLES

The selection criteria for samples are described under separate headings denoting the particular effect being investigated.

Effect of threshold energy on neutron attenuation

The selection criteria suggested the use of two or more nuclear reactions producing the same radioisotope but having much lower threshold energies than the *ca.* 9 MeV required to initiate the $^{16}O(n,p)^{16}N$ reaction which was used in the determination of the neutron attenuation correction curve described earlier[3]. In addition, it was necessary to find compounds containing the appropriate target element whose weights when encapsulated in the standard irradiation containers, would reflect reasonable differences between the calculated γ-ray linear absorption coefficients for sample and standard. Phosphorus and silicon adequately satisfy the target requirements utilizing the reactions: $^{31}P(n,\alpha)^{28}Al$, $E_t = +1.9541$ MeV; and $^{28}Si(n,p)^{28}Al$, $E_t = +3.0445$ MeV. Compounds containing each element were selected so that in the measurement of the 1.78-MeV ^{28}Al γ-ray, no interference from γ-rays of other elements would be experienced. For the experiments, several pairs (sample–standard) were selected from the list shown in Table I. Each pair contained the element of interest; *e.g.*, the simultaneous irradiation of $Ca_3(PO_4)_2$ (sample) and $Sn_2P_2O_7$ (standard) would represent one such pair.

Effect of photopeak energy

In the nuclear reaction $^{56}Fe(n,p)^{56}Mn$, 0.845-MeV γ-rays are produced from the decay of ^{56}Mn. Photon attenuation at this energy can be compared to that at 1.78 MeV. Two samples, iron oxide (Fe_2O_3) and tris(1-phenyl-1,3-butanediono)iron(III) (SRM 1079a), for which the difference in the calculated γ-ray linear absorption coefficients was significant, were selected.

TABLE I

LIST OF COMPOUNDS USED FOR STUDY OF THRESHOLD-ENERGY EFFECTS

Phosphorus compounds	*Silicon compounds*
1. $Ca_3(PO_4)_2$	Silicon carbide (SRM 112)[a]
2. $Ba_3(PO_4)_2$	$C_{48}H_{40}O_4Si$ (SRM 1066)[a]
3. $Sn_2P_2O_7$	Borosilicate glass (SRM 93)[a]
4. $Co_3(PO_4)_2$	Silica brick (SRM 102)[a]

[a] These numbers identify NBS Standard Reference Materials.

Effect of positron energy

This effect can be evaluated by selecting two or more nuclear reactions in which positrons of different E_{max} are emitted. Since the attenuation of β-particles depends on the density of the sample, it was important to consider pairs of samples having the same density. The reactions $^{121}Sb(n,2n)^{120}Sb$, $E_{\beta^+} = 1.70$ MeV, and

$$^{92}Mo(n,2n)\,^{91m}Mo \xrightarrow[66\ sec]{IT} {}^{91}Mo,\ E_{\beta^+} = 3.44\ \text{MeV},$$

appear to satisfy these conditions when the metals or the oxides (MoO_3, Sb_2O_3) are used. It is possible to prepare samples of the oxides in equivalent-volume irradiation containers having equal weights of each oxide. Similarly, the metals packed in the containers have approximately the same density. The difference in the calculated linear absorption coefficient between a Mo–MoO_3 or Sb–Sb_2O_3 pair is significant. Further, pairs of samples were selected possessing approximately the same β^+ attenuation characteristics, but in which positrons of different energies are emitted. To assist in this selection, it was necessary to calculate the β^+ linear absorption coefficients for two samples having different positron energies. These can be estimated from the empirical equation given by EVANS[4].

$$\frac{\mu^{\beta^+}}{\varrho} = \frac{17}{E^{1.14}} \qquad (1)$$

where μ^{β^+} = linear absorption coefficient (cm^{-1}), ϱ = sample density (g/cm^3), and E = maximum energy of positron (MeV).

For two samples whose absorption coefficients are identical, the comparative form,

$$\frac{\varrho\text{Sb}}{\varrho\text{Mo}} = \frac{E_{Sb}{}^{1.14}}{E_{Mo}{}^{1.14}} \qquad (2)$$

is used. By substituting the respective positron energies, a ratio of the densities can be calculated. Since the sample containers have equivalent volumes, eqn. (2) also gives the weight ratio. For example, in the attenuation of 3.44-MeV β^+ emission from ^{91}Mo decay, 32.80 g and 23.58 g of Mo and MoO_3 respectively, correspond to the attenuation of 1.19 MeV β^+ emission from ^{13}N decay from 10.01 g and 7.19 g of ammonium nitrate and glycine respectively.

Effect of sample density

By using the same positron emitter in three different irradiated matrices, such as ^{91}Mo in molybdenum metal, molybdenum trioxide and sodium molybdate dihydrate, the effect of sample density on the attenuation of annihilation quanta can be observed. Pairs of samples were selected to give a substantial difference in the calculated linear absorption coefficients for the annihilation radiation.

Combined effect of sample density and positron energy

A pair of copper-containing samples such as copper(II) sulfide and bis(1-phenyl-1,3-butanediono)copper(II) (SRM 1080) provides an opportunity to measure a combination of these effects. The ^{63}Cu(n,2n)^{62}Cu reaction results in the emission of a 2.9-MeV positron. Data from this experiment can be compared to other experiments which involve positron energy and density changes.

A criterion for sample selection was to acquire, as far as possible, only those in which a single energy group of positrons would be observed. Some of the essential nuclear data[5] relevant to the selected samples are summarized in Table II. Threshold energies were obtained from a recent report[6].

TABLE II

INDUCED NEUTRON REACTIONS IN SELECTED SAMPLES

Reaction	*Half-life*	*Threshold energy E_t (MeV)*	*E_{β^+} (MeV)*	*E_γ (MeV)*
^{31}P(n,α)^{28}Al	2.31 m	+ 1.9541		1.78
^{28}Si(n,p)^{28}Al	2.31 m	+ 3.0445		1.78
^{56}Fe(n,p)^{56}Mn	2.576 h	+ 2.9242		0.845
^{14}N(n,2n)^{13}N	10.0 m	+10.5529	1.19	
^{121}Sb(n,2n)^{120}Sb	15.9 m	+ 9.250	1.70	
^{92}Mo(n,2n)^{91}Mo	15.49 m	+12.580	3.44	
^{63}Cu(n,2n)^{62}Cu	9.8 m	+10.841	2.91	

EXPERIMENTAL

Equipment

The fast neutron activation facility at the National Bureau of Standards has been updated from that described in earlier work[3]. A new Cockcroft-Walton neutron generator rated at 2.5 mA maximum beam output and 200 kV acceleration voltage was recently installed. The 4 × 3 in NaI(Tl) detectors previously described[3] have been replaced by equivalent size detectors matched for gain-shift stability and resolution. Fundamentally, however, the mode of operation was the same as described previously[3].

Experimental procedure

Because of changes in both the irradiation and counting geometry, the neutron and γ-ray (4.8–8.0 MeV) attenuation calibration lines were redetermined. The method used was identical to that described earlier[3]. In photopeak counting, half-life checks were made to ensure purity of the counted species. Where necessary, adjustments were made for long-lived radioactive contamination in the energy region of interest. The general experimental procedure was similar to that discussed previously[3].

The photon attenuation correction factors were obtained by first correcting for neutron attenuation and then attributing the difference between the observed and theoretical elemental contents of the two samples to γ-attenuation[3].

In an effort to automate all necessary calculations, values for σ_R (microscopic removal cross-section for 14.5-MeV neutrons) for the elements were stored in the

TABLE III

MICROSCOPIC REMOVAL CROSS-SECTIONS OF ELEMENTS FOR 14.5-MeV NEUTRONS

Element	*Atomic weight*	σ_R[a] *(barns)*	*Element*	*Atomic weight*	σ_R[a] *(barns)*
Hydrogen	1.00797	0.66	Tin	118.69	2.12
Lithium	6.939	0.73	Antimony	121.75	2.15
Beryllium	9.0122	0.77	Tellurium	127.60	2.18
Boron	10.811	0.79	Iodine	126.9044	2.20
Carbon	12.01115	0.80	Cesium	132.905	2.25
Nitrogen	14.0067	0.93	Barium	137.34	2.68
Oxygen	15.9994	1.03	Lanthanum	138.91	2.29
Fluorine	18.9984	0.94	Cerium	140.12	2.31
Sodium	22.9898	1.03	Praseodymium	140.907	2.33
Magnesium	24.312	1.08	Neodymium	144.24	2.35
Aluminum	27.9815	1.03	Promethium	147	2.37
Silicon	28.086	1.05	Samarium	150.35	2.39
Phosphorus	30.9738	1.17	Europium	151.96	2.41
Sulfur	32.064	1.12	Gadolinium	157.25	2.43
Chlorine	35.453	1.18	Terbium	158.924	2.47
Potassium	39.102	1.26	Dysprosium	162.50	2.48
Calcium	40.08	1.25	Holmium	164.930	2.50
Scandium	44.956	1.30	Erbium	167.26	2.51
Titanium	47.90	1.30	Thulium	168.934	2.53
Vanadium	50.942	1.36	Ytterbium	173.04	2.57
Chromium	51.996	1.32	Lutetium	174.97	2.58
Manganese	54.9380	1.42	Hafnium	178.49	2.60
Iron	55.847	1.39	Tantalum	180.948	2.63
Cobalt	58.9332	1.51	Tungsten	183.85	2.65
Nickel	58.71	1.52	Rhenium	186.2	2.68
Copper	63.54	1.55	Osmium	190.2	2.70
Zinc	65.37	1.58	Iridium	192.2	2.71
Gallium	69.72	1.60	Platinum	195.09	2.74
Germanium	72.59	1.63	Gold	196.967	2.77
Arsenic	74.9216	1.66	Mercury	200.59	2.79
Selenium	78.96	1.69	Thallium	204.37	2.80
Bromine	79.909	1.72	Lead	207.19	2.82
Rubidium	85.47	1.78	Bismuth	208.980	2.82
Strontium	87.62	1.80	Thorium	232.038	2.97
Yttrium	88.905	1.83	Uranium	238.03	3.01
Zirconium	91.22	1.86			
Niobium	92.906	1.89			
Molybdenum	95.94	1.91			
Ruthenium	101.07	1.97			
Rhodium	102.905	2.00			
Palladium	106.4	2.02			
Silver	107.870	2.05			
Cadmium	112.40	2.08			
Indium	114.82	2.10			

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[a] Microscopic removal cross-section.

TABLE IV

NEUTRON ATTENUATION CORRECTION FACTORS AND CALCULATED ABSORPTION DATA (14.5-MeV)
(Sample diameter = 1.45 cm; sample volume = 8 cm^3; X[a] = 0.4 cm; slope = 0.9682 ± 0.05515 cm[b]; intercept = 1.0010 ± 0.00074[c])

Sample					*Standard*					*$\Delta\Sigma_R$*[d] *(cm^{-1})*	*Neutron attenuation correction factor*
Name	*Weight (g)*	*Σ_R (cm^{-1})*	*μ_0 (cm^{-1})*	*$e^{-\mu_0 X}$*	*Name*	*Weight (g)*	*Σ_R (cm^{-1})*	*μ_0 (cm^{-1})*	*$e^{-\mu_0 X}$*		
C_6H_5COOH	7.9129	0.0567	0.0255	0.9899	C_6H_5COOH	7.9129	0.0567	0.0255	0.9899	0.0000	1.0000 ± 0.00643
$C_6H_{12}O_6$	8.6288	0.0682	0.0284	0.9887	H_2O	8.0056	0.0787	0.0276	0.9890	0.0105	1.0098 ± 0.00902
C_6H_5COOH	7.9129	0.0567	0.0255	0.9899	H_2O	8.0056	0.0787	0.0276	0.9890	0.0219	1.0252 ± 0.00842
CH_3OH	6.2307	0.0654	0.0214	0.9915	H_2O	8.0056	0.0787	0.0276	0.9890	0.0132	1.0123 ± 0.00847
H_2O	8.0056	0.0787	0.0276	0.9890	$C_6H_{12}O_6$	8.6288	0.0682	0.0284	0.9887	−0.0105	0.9924 ± 0.01067
H_2O	8.0056	0.0787	0.0276	0.9890	C_6H_5COOH	7.9129	0.0567	0.0255	0.9899	−0.0219	0.9813 ± 0.01399
H_2O	8.0056	0.0787	0.0276	0.9890	CH_3OH	6.2307	0.0654	0.0214	0.9915	−0.0132	0.9890 ± 0.01190

[a] Value of X is the estimated slope of the γ-attenuation line (Table V).
[b] Weighted standard error of the slope based on the number of points determined (least squares analysis).
[c] Weighted standard error of the intercept based on the number of points determined (least squares analysis).
[d] $\Delta\Sigma_R$ is calculated from the difference (Σ_R (standard) − Σ_R (sample)).

TABLE V

γ-RAY ATTENUATION CORRECTION FACTORS AND CALCULATED ABSORPTION DATA (4.8–8.0 MeV)
(Sample diameter = 1.45 cm; sample volume = 8 cm^3; slope = 0.5488 ± 0.01400 cm[a]; intercept = 0.9971 ± 0.00188[b])

Sample				*Standard*				*$\Delta\Sigma_R$*[c] *(cm^{-1})*	*$\Delta\mu_0$*[d] *(cm^{-1})*	*Neutron attenuation correction factor*[e]	*γ-Attenuation correction factor*
Name	*Weight (g)*	*Σ_R (cm^{-1})*	*μ_0 (cm^{-1})*	*Name*	*Weight (g)*	*Σ_R (cm^{-1})*	*μ_0 (cm^{-1})*				
C_6H_5COOH	7.9129	0.0567	0.0255	C_6H_5COOH	7.9129	0.0567	0.0255	0.0000	0.0000	1.0010 ± 0.00074	1.0000 ± 0.00643
C_6H_5COOH	7.9129	0.0567	0.0255	PbO	40.8331	0.0530	0.2159	−0.0037	0.1904	0.9975 ± 0.00076	1.1015 ± 0.01005
C_6H_5COOH	7.9129	0.0567	0.0255	Bi_2O_3	42.5601	0.0600	0.2220	0.0033	0.1965	1.0043 ± 0.00076	1.1133 ± 0.00947
C_6H_5COOH	7.9129	0.0567	0.0255	Fe_2O_3	11.5925	0.0321	0.0419	−0.0246	0.0164	0.9775 ± 0.00151	1.0051 ± 0.00891
PbO	40.8331	0.0530	0.2159	C_6H_5COOH	7.9129	0.0567	0.0255	0.0037	−0.1904	1.0046 ± 0.00077	0.8918 ± 0.00930
Bi_2O_3	42.5601	0.0600	0.2220	C_6H_5COOH	7.9129	0.0567	0.0255	−0.0033	−0.1965	0.9978 ± 0.00076	0.9012 ± 0.01071
Fe_2O_3	11.5925	0.0321	0.0419	C_6H_5COOH	7.9129	0.0567	0.0255	0.0246	−0.0164	1.0251 ± 0.00158	0.9870 ± 0.01110

[a] Weighted standard error of the slope based on the number of points determined (least squares analysis).
[b] Weighted standard error of the intercept based on the number of points determined (least squares analysis).
[c] $\Delta\Sigma_R$ is calculated from the difference (Σ_R (standard) − Σ_R (sample)).
[d] $\Delta\mu_0$ is calculated from the difference (μ_0 (standard) − μ_0 (sample)).
[e] From a least squares fit of data in Table IV.

computer memory as part of a program used to calculate the macroscopic removal cross-section for the sample. These values are tabulated in Table III. For those elements for which the removal cross-section was not known, interpolations from a plot made from available values[7] were made. This table can be used in the evaluation of the macroscopic removal cross-section for any compound[3]. The linear absorption coefficients for the various γ-energies of interest were calculated by means of published values[8] and equations described previously[3]. After the photon attenuation correction factors had been determined, the calibration lines were checked by performing analyses of Standard Reference Materials, the predicted correction factors from the calibration lines being applied.

RESULTS AND DISCUSSION

The data and results of neutron and γ-ray (4.8–8.0 MeV) correction factors are tabulated in Tables IV and V, respectively. The correction factor curves are shown in Figs. 1 and 2 as a function of the difference in the absorption coefficients between sample and standard. Analogous results for photopeak and annihilation radiation analyses are shown in Tables VI and VII respectively. The attenuation behavior of both sources of γ-radiation is shown in Fig. 3. All correction plots are on semilog coordinates. The analyses of some typical Standard Reference Materials are tabulated in Table VIII.

One of the important points established in this study was that related to the effect of threshold energy on the neutron attenuation line. The nuclear reactions given in Table II, have a range of threshold energies from 1.95 to 12.58 MeV. When corrected for the coulombic barrier, the range of reaction threshold energies is from 6.2 to 12.6 MeV. Throughout this range, the neutron attenuation follows a simple exponential law dependent only upon the calculated macroscopic removal cross-section difference between the sample and standard. Within the precision of the present measurements, the results are consistent with the removal cross-section theory. The removal cross-sections given in Table III can now be used with confidence in correcting for this systematic error, provided that the sample size is not unduly large when compared to the removal mean free path for 14.5-MeV neutrons. By definition, the removal mean free path is the inverse of the calculated macroscopic removal cross-section for the sample.

In comparing the slopes of the three γ-ray attenuation correction factor lines shown in Figs. 2 and 3, a significant difference is observed. This difference is attributed to the differences in the counting efficiencies for the three cases. For example, in Fig. 2 primary photons of 6.1-MeV energy may undergo degradation and still possess sufficient energy to be counted within the large window (4.8–8.0 MeV) used in oxygen analysis. This essentially improves the efficiency of counting and is reflected in the reduced attenuation correction factor. If this is true, then both lines in Fig. 3 should have equivalent slopes, since only the photopeak-energy γ-rays were being counted. Experimentally, however, this was not observed; in fact, the slope for photopeak analysis was *ca.* 1.4 times that for the annihilation γ-rays. This observed difference may be attributed to improved efficiency due to counting of bremsstrahlung along with the annihilation γ-rays.

It must be recognized that there will be a higher contribution from brems-

TABLE VI

γ-RAY ATTENUATION CORRECTION FACTORS AND CALCULATED ABSORPTION DATA (PHOTOPEAK ANALYSIS)

(Sample diameter = 1.45 cm; sample volume = 8 cm^3; slope = 1.0419 ± 0.03046 cm[a]; intercept = 0.9953 ± 0.00162[b])

Sample				*Standard*				$\Delta\Sigma_R$[c] *(cm^{-1})*	$\Delta\mu_0$[d] *(cm^{-1})*	*Neutron attenuation correction factor*[e]	*γ-Attenuation correction factor*
Name	*Weight (g)*	*Σ_R (cm^{-1})*	*μ_0 (cm^{-1})*	*Name*	*Weight (g)*	*Σ_R (cm^{-1})*	*μ_0 (cm^{-1})*				
$Ca_3(PO_4)_2$	4.6709	0.0162	0.0276	$Sn_2P_2O_7$	15.9548	0.0403	0.0897	0.0241	0.0621	1.0242 ± 0.00165	1.0571 ± 0.01111
$Ba_3(PO_4)_2$	17.1836	0.0402	0.0955	$Ca_3(PO_4)_2$	4.6709	0.0162	0.0276	−0.0240	−0.0679	0.9787 ± 0.00148	0.9281 ± 0.00501
$Ba_3(PO_4)_2$	17.9896	0.0419	0.1000	$Sn_2P_2O_7$	15.9548	0.0403	0.0897	−0.0016	−0.0103	0.9995 ± 0.00061	0.9873 ± 0.00998
$Ba_3(PO_4)_2$	17.9896	0.0419	0.1000	$Co_3(PO_4)_2$	10.9875	0.0341	0.0630	0.0078	0.037	1.0080 ± 0.00079	1.0364 ± 0.01103
$C_{48}H_{40}O_4Si_4$	7.8237	0.0543	0.0486	SiC	14.8830	0.0516	0.0882	−0.0027	0.0396	0.9985 ± 0.00072	1.0332 ± 0.00898
Silica brick	12.3809	0.0479	0.0734	$C_{48}H_{40}O_4Si_4$	7.8237	0.0543	0.0486	0.0064	−0.0248	1.0072 ± 0.00077	0.9611 ± 0.01255
Borosilicate glass	12.3068	0.0496	0.0727	SiC	14.8830	0.0516	0.0882	0.0020	0.0155	1.0029 ± 0.00073	1.0142 ± 0.01012
$C_{30}H_{27}O_6Fe$	7.3995	0.0510	0.0667	Fe_2O_3	16.6918	0.0462	0.1381	−0.0048	0.0714	0.9965 ± 0.0076	1.0812 ± 0.01235

[a] Weighted standard error of the slope based on the number of points determined (least squares analysis).
[b] Weighted standard error of the intercept based on the number of points determined (least squares analysis).
[c] $\Delta\Sigma_R$ is calculated from the difference (Σ_R (standard) − Σ_R (sample)).
[d] $\Delta\mu_0$ is calculated from the difference (μ_0 (standard) − μ_0 (sample)).
[e] From a least squares fit of data in Table IV.

TABLE VII

γ-RAY ATTENUATION CORRECTION FACTORS AND CALCULATED ABSORPTION DATA (ANNIHILATION PEAK ANALYSIS)

(Sample diameter = 1.45 cm; sample volume = 8 cm^3; slope = 0.7055 ± 0.02798 cm[a]; intercept = 0.9947 ± 0.00292[b])

Sample				*Standard*				$\Delta\Sigma_R$[c] *(cm^{-1})*	$\Delta\mu_0$[d] *(cm^{-1})*	*Neutron attenuation correction factor*	*γ-Attenuation correction factor*
Name	*Weight (g)*	*Σ_R (cm^{-1})*	*μ_0 (cm^{-1})*	*Name*	*Weight (g)*	*Σ_R (cm^{-1})*	*μ_0 (cm^{-1})*				
MoO_3	23.5852	0.0617	0.2518	Mo	32.8033	0.0492	0.3481	−0.0125	0.0963	0.9892 ± 0.00119	1.0725 ± 0.00911
$Na_2MoO_4\cdot 2H_2O$	15.7681	0.0628	0.1706	Mo	32.8033	0.0492	0.3481	−0.0136	0.1775	0.9870 ± 0.00120	1.1131 ± 0.01032
MoO_3	23.5852	0.0617	0.2518	$Na_2MoO_4\cdot 2H_2O$	16.1505	0.0643	0.1747	0.0026	−0.0771	1.0031 ± 0.00074	0.9422 ± 0.00521
Sb_2O_3	23.5839	0.0450	0.2648	Sb	32.8012	0.0436	0.3719	−0.0014	0.1071	0.9997 ± 0.00061	1.0801 ± 0.00894
NH_2CH_2COOH	7.1960	0.0569	0.0829	NH_4NO_3	10.0108	0.0715	0.1135	0.0146	0.0306	1.0150 ± 0.00121	1.0202 ± 0.00876
$C_{20}H_{18}O_4Cu$	8.0354	0.0526	0.0900	CuS	23.5873	0.0496	0.2451	−0.0030	0.1551	0.9982 ± 0.00073	1.1051 ± 0.01001

[a] Weighted standard error of the slope based on the number of points determined (least squares analysis).
[b] Weighted standard error of the intercept based on the number of points determined (least squares analysis).
[c] $\Delta\Sigma_R$ is calculated from the difference (Σ_R (standard) − Σ_R (sample)).
[d] $\Delta\mu_0$ is calculated from the difference (μ_0 (standard) − μ_0 (sample)).
[e] ~~From a least squares fit of data in Table IV~~

strahlung under the 0.51-MeV peak than under higher-energy peaks, provided that the bremsstrahlung end-point energy extends beyond the maximum γ-ray energies being considered. This type of preferred contribution under the 0.51-MeV annihilation peak would result in a reduced attenuation correction factor. It might also be said that similar contributions would also occur with γ-rays from direct nuclear transitions,

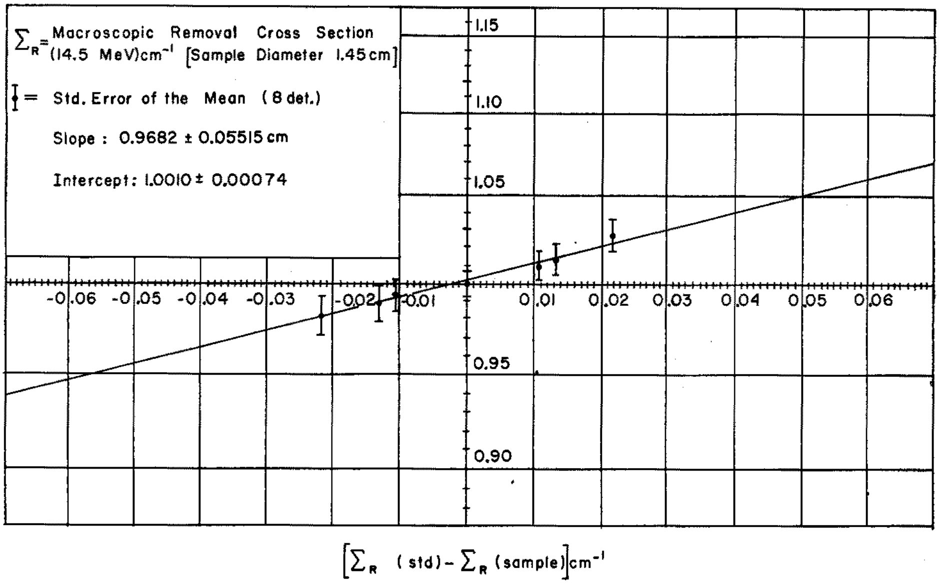

Fig. 1. 14.5-MeV Neutron attenuation correction factor curve.

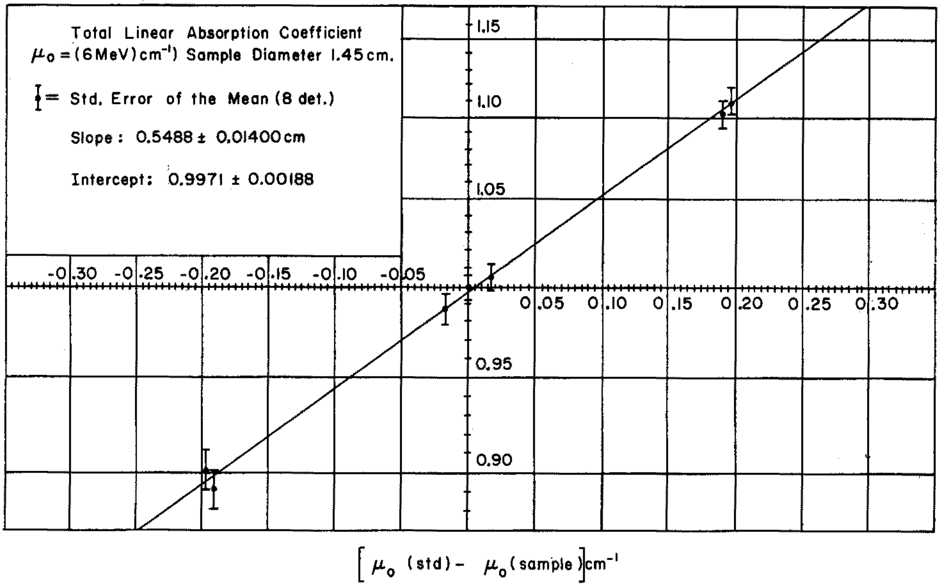

Fig. 2. 4.8–8.0 MeV γ-ray attenuation correction factor curve.

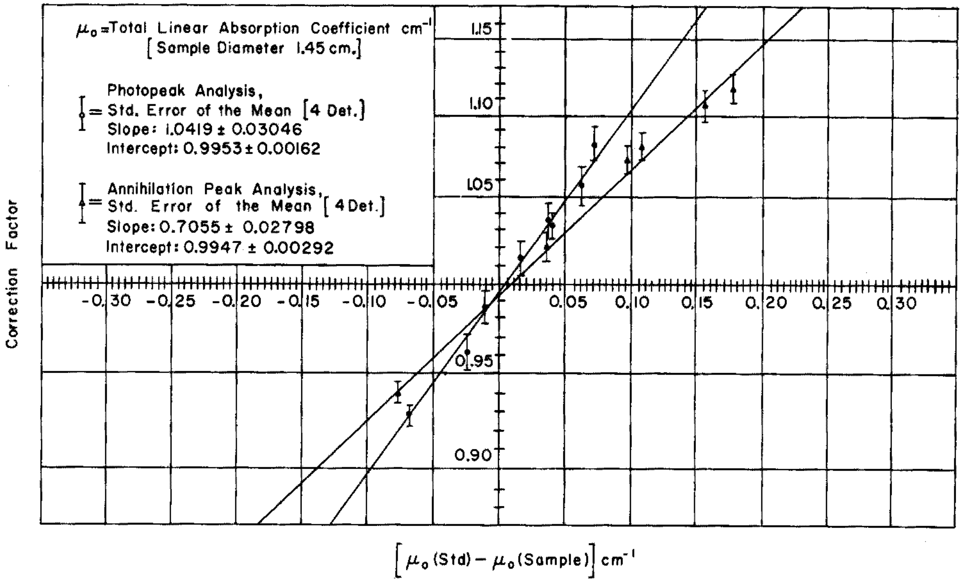

Fig. 3. Photopeak and annihilation peak γ-ray attenuation correction factor curve.

TABLE VIII

ANALYSIS OF STANDARD REFERENCE MATERIALS

Standard Reference Material	*Element determined*	*Concentration (%)*	
		14-MeV Neutron activation analysis	*Certified*[b] *value*
Cobalt cyclohexanebutyrate 1055a	Cobalt	17.49 ± 0.11[a]	17.4 ± 0.17
Silver 2-ethyl hexanoate 1077	Silver	42.49 ± 0.42[a]	42.4 ± 0.42
Magnesium cyclohexanebutyrate 1061a	Magnesium	6.69 ± 0.04[a]	6.8 ± 0.14
Octaphenylcyclotetrasiloxane 1066	Silicon	14.16 ± 0.11[a]	14.1 ± 0.14

[a] Weighted standard error of the weighted mean (4 determinations).

[b] As per NBS Certificate.

provided that the maximum β-energy was significantly greater than the photopeak being considered. In addition, poor resolution of the detector system would enhance the bremsstrahlung contributions because a wider energy range is included. However, it should be recognized that the slopes of all the attenuation curves give a measure of the attenuated sample thickness, and this thickness is dependent only upon the geometry of counting and the physical sample diameter or thickness. In keeping with this, it can be seen that counting of different γ-ray energies shown in Fig. 3 has no effect on the exponential behavior of photon attenuation.

Another interesting fact is illustrated in Fig. 3. The calibration line representing the attenuation of 0.51-MeV annihilation γ-rays appears to be independent of the positron energy, and any effect is negligible.

For the least-squares fitting of all the attenuation lines, calculations were performed on a multi-access computer facility. A code based on the Gram-Schmidt

Orthonormalization process was used. It is clear that the straight-line function should intercept the origin (0,1 point). There seems to be no evidence that the computed values of intercepts of these lines differ from the origin, judging from their respective standard errors based on 6–8 points for each line.

The correction factors determined in this study were used in the analyses of several Standard Reference Materials. A comparison of results using the 14-MeV neutron activation technique with the certified values is shown in Table VIII. Good agreement and comparable precision in the final results are observed.

The assistance and continuous cooperation from NBS staff members F. C. RUEGG, M. STALBIRD, F. A. LUNDGREN and GILBERT W. SMITH are greatly appreciated. Computational assistance given by E. PRZYBYLOWICZ (Research Associate from Eastman Kodak Company at the National Bureau of Standards, 1968) is gratefully acknowledged.

SUMMARY

In comparative 14-MeV neutron activation analysis for oxygen, systematic errors are evidenced if attenuation of incident neutrons and induced γ-radioactivity by a thick sample is ignored. The present study pertains to the general case of measurement where photopeaks resulting from either direct nuclear transitions or from positron annihilation are counted. A quantitative evaluation of these attenuation processes is presented. The results show that the photon attenuation correction factor is related to the difference between the calculated linear absorption coefficients for sample and standard through a simple exponential expression. The slopes of the respective correction factor lines are compared with that for integral γ-counting in oxygen analysis. Differences in the magnitudes of the slopes are discussed. The results of this study are consistent with the removal cross-section theory describing 14-MeV neutron attenuation over a wide range of threshold energies. Typical analyses of Standard Reference Materials, with these correction factors, are given.

RÉSUMÉ

Lors du dosage de l'oxygène par activation neutronique comparative à 14 Me-V, des erreurs systématiques peuvent se produire si on ne tient pas compte de l'atténuation des neutrons incidents et de la radioactivité induite par un échantillon épais. On présente une évaluation quantitative de ces processus d'atténuation. Les résultats montrent que le facteur de correction de cette atténuation photonique dépend de la différence entre les coefficients d'absorption linéaire calculés pour l'échantillon et l'étalon par une expression exponentielle simple. Les pentes des courbes de facteurs de correction respectifs sont comparées avec celles du comptage intégral dans l'analyse de l'oxygène. Diverses analyses typiques de substances de référence sont données, utilisant ces facteurs de correction.

ZUSAMMENFASSUNG

Bei der vergleichenden Aktivierungsanalyse mit 14 MeV-Neutronen für die

Bestimmung von Sauerstoff treten systematische Fehler auf, wenn die Verluste der einfallenden Neutronen und der induzierten Radioaktivität durch eine dicke Probe nicht berücksichtigt werden. Die vorliegende Untersuchung behandelt den allgemeinen Fall einer Messung, bei der Photopeaks gezählt werden, die entweder durch direkte Kernübergänge oder durch Positronenvernichtung entstehen. Es wird eine quantitative Auswertung dieser Verluste vorgelegt. Die Ergebnisse zeigen, dass der Korrekturfaktor für die Photonenverluste mit der Differenz zwischen den berechneten linearen Absorptionskoeffizienten für die Probe und für den Standard durch einen einfachen Exponentialausdruck verknüpft ist. Die betreffenden Korrekturfaktor-Kurven werden mit jenen für die integrale γ-Zählung bei der Sauerstoffanalyse verglichen und Unterschiede diskutiert. Die Ergebnisse dieser Untersuchung stimmen überein mit der Theorie des Abfang-Querschnittes, die die Verluste der 14 MeV-Neutronen über einen weiten Bereich von Schwellenenergien beschreibt. Es wird über typische Analysen von Standard-Vergleichsproben berichtet, die mit diesen Korrekturfaktoren ausgeführt wurden.

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

DETERMINATION OF THE OXYGEN-TO-URANIUM RATIO IN HYPOSTOICHIOMETRIC URANIUM DIOXIDE*

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(Received October 24th, 1969)

In general, the reactor fuel uranium dioxide is hyperstoichiometric. However, if a specimen of this material is heated at temperatures near or above 2000° in either inert or reducing atmospheres hypostoichiometric UO_{2-y} is formed[1]. As far as is known, the UO_{2-y} so obtained is composed upon cooling of uranium metal in a matrix of $UO_{2.000}$[1-3].

For the determination of the overall oxygen-to-uranium ratio in UO_{2-y}, the following methods have been mentioned in the literature[2,3].

(*a*) The sample is oxidized in air:

$$3\ UO_{2-y} \xrightarrow{O_2} U_3O_{8.000}$$

and the O/U ratio is calculated from the increase in weight.

Alternatively, dissolution in nitric acid can be followed by conversion to U_3O_8:

$$3\ UO_{2-y} \xrightarrow{HNO_3} 3\ UO_2^{2+} \rightarrow U_3O_8$$

and the O/U ratio is calculated from the increase in weight.

(*b*) Partial oxidation of the sample in air is followed by reduction in hydrogen:

$$UO_{2-y} \xrightarrow{O_2} UO_{2+x} \xrightarrow{H_2} UO_{2.000} + x\ H_2O$$

The O/U ratio is calculated from the increase in weight for the overall reaction:

$UO_{2-y} \rightarrow UO_{2.000}$

(*c*) Hydride formation is used, the free uranium metal in UO_{2-y} being converted first to uranium hydride, after which the hydride is decomposed:

$$2\ UO_{2-y} \xrightarrow{H_2} (2-y)\ UO_{2.000} + y\ UH_3 \rightarrow 2\ UO_{2-y} + 1\tfrac{1}{2}y\ H_2\uparrow$$

In this case the O/U ratio is calculated from the amount of released hydrogen.

The methods described under (*a*) are simple and reliable. However, adsorbed moisture in the samples may cause erroneous results[3], and on account of the small increases in weight, large samples are needed.

Method (*b*) does not appear to have any advantage over methods (*a*), and it has the serious drawback that the $UO_{2.000}$ finally formed shows considerable reactivity (with oxygen and water)[3].

Method (*c*) is more attractive, but has the disadvantages[2] that uranium metal

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* This paper was presented at the Thirteenth Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tennessee, U.S.A., October, 1969.

occluded within the UO_2-grains may not form the hydride and thus will escape subsequent detection; and a considerable blank is obtained, which makes the use of large samples inevitable.

For the determination of the O/U ratio in small samples of hypostoichiometric uranium dioxide, none of the methods mentioned above is attractive. For this reason the merits of a new method wherein the sample is dissolved in concentrated phosphoric acid have been studied. During dissolution the valency of uranium in $UO_{2.000}$ will remain unchanged[4], while the metallic uranium present is converted to uranium(IV) and an equivalent amount of hydrogen is released. Hence the overall reaction should be:

$$UO_{2-y} \xrightarrow{H^+} U^{4+} + (2-y)\, H_2O + y\, H_2 \uparrow$$

The O/U ratio is calculated from the amount of hydrogen released. If uranium(III) is present in the UO_{2-y}, it is also converted to uranium(IV) during dissolution and the same overall reaction will occur.

For the measurement of the amount of hydrogen, the method used involves removal of the hydrogen from the phosphoric acid solution by a helium stream. The hydrogen is stripped from the helium by Molecular Sieve 5A powder at liquid nitrogen temperature. Afterwards the hydrogen is desorbed from the molecular sieve at room temperature and determined by gas chromatography[5].

This method was tested successfully on metallic uranium samples of about 1 mg. With samples of UO_{2-y} weighing 30–140 mg, the O/U ratios measured corresponded quite acceptably with the values obtained by gravimetric method (*a*) on 1000-mg samples.

EXPERIMENTAL

Chemicals

Helium. The cylinder gas used contained the following maximum concentrations of impurities: 0.5 p.p.m. hydrogen, 8 p.p.m. nitrogen, 1 p.p.m. oxygen, 14 p.p.m. argon by weight.

Linde Molecular Sieve 5A. This was used as 30–60 mesh powder obtained from 1/16-in pellets by grinding and sieving. This powder was heated at 300° for 4 h in a helium stream before use.

Phosphoric acid. Analytical-grade phosphoric acid was heated to 250° in air for removal of water in excess.

Hydrazine sulphate solution. 0.1 *M* in water.

Equipment

The helium cylinder gas was first passed through a reduction valve and then through a tube filled with Molecular Sieve held at liquid nitrogen temperature in order to reduce the concentrations of the impurities to a level where they did not cause a measurable blank. Then the gas was introduced into the apparatus.

The apparatus used was a slightly modified version of the instrument for the determination of hydrogen, nitrogen and oxygen in water[5]. The general layout is shown in Fig. 1. Calibration was performed with hydrogen generated coulometrically in a hydrazine sulphate solution[6].

Dissolution tube A was made of quartz; the other parts of A, electrolysis cell B, water trap C, four-way valves V_1, V_2 and their connecting leads were made of pyrex. All the other tubing, absorption column D and chromatographic column E, were made of stainless steel. Columns D and E had an internal diameter of 4 mm and a total length of 75 and 200 cm, respectively; they were filled with Molecular Sieve powder. Eight-way valve V_3 was made of stainless steel and Teflon. A catharometer detector F was used.

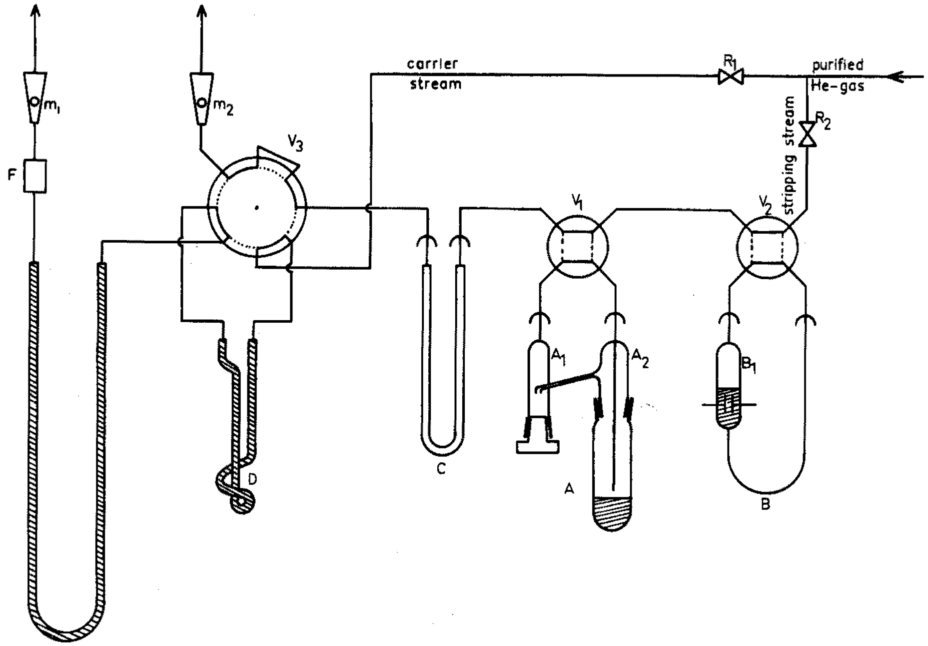

Fig. 1. Diagram of equipment used. (A) Dissolution system with dissolution tube A and water trap A_1, (B) system for the coulometric generation of hydrogen with electrolysis cell B_1 filled with an aqueous hydrazine sulphate solution and equipped with platinum electrodes and a porous sintered bottom plate for dispersion of the stripping gas, (C) water trap to be kept at liquid nitrogen temperature, (D) H_2-absorption tube filled with molecular sieve and kept at liquid nitrogen temperature during stripping, (E) chromatographic column filled with molecular sieve and kept at room temperature, (F) katharometer detector, (R_1, R_2) flow regulators, (m_1, m_2) flow meters, (V_1, V_2) four-way valves, (V_3) eight-way valves.

The helium carrier gas stream was adjusted to a speed of 100 ml/min (at atmospheric pressure) with regulator R_1; the stripping gas stream was adjusted at a speed of 10 ml/min with R_2. Dissolution tube A was heated with a small electric tube furnace.

Procedure

About 0.3–1.2 mg of metallic uranium mechanically cleaned and stored in a dry atmosphere, or about 30–140 mg of a crushed sample of hypostoichiometric uranium dioxide was placed in dissolution tube A; valves V_{1-3} were placed in the position shown in Fig. 1 and trap C and column D were immersed in liquid nitrogen.

After the addition of about 5 ml of phosphoric acid to the dissolution tube A, this tube was connected to the rest of system A and valve V_1 was turned 90°. After a few seconds valve V_3 was turned 45°, so that the stripping gas was passed through absorption column D, while the carrier gas was led directly to the chromatographic column E. Then the temperature of the phosphoric acid in tube A was increased gradually to 350° and it was kept at this value until *ca.* 10 min after the generation of hydrogen in the tube had ceased (total duration of the process about 20–60 min).

After this period the furnace was removed and valve V_3 was turned 45°, so that the carrier gas was passed through the absorption column before going to the chromatographic column. After the chromatographic recorder had returned to its original position the Dewar flask with liquid nitrogen was removed from absorption tube D and the tube was allowed to warm up in air to room temperature. During the warming up, hydrogen and the other gases present were desorbed from the Molecular Sieve and eluted through the chromatographic column. The height of the peak for hydrogen in the chromatogram was used for the determination of its quantity.

Calibration

For calibration purposes valves V_1 and V_3 were placed in the positions of Fig. 1 while V_2 was turned 90°. Coulometrically a known amount of hydrogen in the range of 25–500 µl (corrected to 0° and 76 cm pressure) was generated. The procedure for hydrogen stripping and measurement was the same as that mentioned above.

RESULTS AND DISCUSSION

The results of the determinations are collected in Tables I and II.

The values in Table I show that the proposed method can be used for the analysis of metallic uranium. The mean value of the measurements is about 1% low, but this

TABLE I

AMOUNT OF HYDROGEN RELEASED DURING DISSOLUTION OF METALLIC URANIUM IN PHOSPHORIC ACID

Theoretical value of released hydrogen (%)	100.0
Mean of measured values (%)	98.8
Extremes (%)	95.9/104.0
Standard deviation (%)	3.3
Number of determinations	7
Sample aliquots (mg)	0.32–1.21
Volumes of released H_2 (µl)	56–236

TABLE II

DETERMINATION OF THE O/U RATIOS IN 4 SAMPLES OF HYPOSTOICHIOMETRIC URANIUM DIOXIDE

Samples	*A*	*B*	*C*	*D*
Gravimetric values of O/U	1.929/1.928	1.933/1.935	1.954/1.955	1.994/1.992
Means	1.929	1.934	1.955	1.993
Sample aliquots (mg)	*ca.* 1000	*ca.* 1000	*ca.* 1000	*ca.* 1000
Mean values of O/U ratios according to the H_3PO_4-method	1.927	1.932	1.960	1.9886
Extremes	1.947/1.918	1.940/1.924	1.970/1.951	1.9925/1.9857
Standard deviations	0.009	0.005	0.005	0.0018
Number of determinations	16	18	15	19
Sample aliquots (mg)	31.1–53.8	35.3–78.7	43.3–77.4	36.6–137.0
Volumes of H_2 (µl)	141–348	196–455	155–240	35.0–162

deviation is considerably smaller than the value of the standard deviation. A standard deviation of about 3% is quite a normal value for the procedure of gas collection and measurements.

For the figures mentioned in Table II small sintered pellets were used, showing a radial increase in O/U ratio: in sample A, O/U ratios of 1.918 and 1.921 were measured for the inner core of the pellet while values of 1.947 and 1.943 were measured for its outermost layer. The other sample aliquots used in Table II were chosen at random from the crushed pellets.

On account of the small samples (30–140 mg) used in the proposed method, the inhomogeneity of the samples resulted in rather high values of the standard deviations. In the case of gravimetric analysis much more sample material (*ca.* 1000 mg) was used, so that the problem of inhomogeneity became less important here. The mean values of the O/U ratios obtained by the phosphoric acid method correspond quite reasonably with the values obtained by gravimetry if an accuracy within ±0.004 O/U units is claimed for the gravimetric method[3]. On account of the inhomogeneity of the samples, it is not possible to give experimentally verified figures about the accuracy and precision of the method. It is assumed that the accuracy and precision of the collecting and measuring procedure will be the limiting factor.

In the present measurements no hydrogen blanks were detected.

In connection with the long dissolution time and the restricted absorbing capacity for hydrogen of the Molecular Sieve, the speed of the stripping gas flow must be low.

All impurities in the samples that generate hydrogen during dissolution in phosphoric acid will interfere in the determinations.

During the dissolution process, the temperature of the phosphoric acid has to be kept below 400°. At higher temperatures considerable dehydration occurs, resulting in a considerable increase in the viscosity of the solution.

For the determination of the O/U ratio, samples weighing 30–140 mg were used; these generated hydrogen volumes of 35–455 μl. This range can be extended to the lower side without any objection. If the limited sensitivity of the catharometer becomes the restricting factor, an ionisation detector with a radioactive source can be used[5].

It stands to reason that any other sensitive and accurate method for the determination of the total amount of hydrogen in the stripping gas can be used for the measurements.

The authors wish to thank G. VERSTEEG and A. J. G. ENGEL of RCN for supplying the samples.

SUMMARY

For the determination of the oxygen-to-uranium ratio in hypostoichiometric uranium dioxide, a method was developed in which the sample is dissolved in phosphoric acid. During dissolution, all uranium present is converted to uranium(IV) while an amount of hydrogen equivalent to the degree of hypostoichiometry is released. The O/U ratio is determined from the amount of released hydrogen. Satisfactory results, in accordance with those obtained gravimetrically on 1-g samples, can be obtained on 30–140 mg samples.

RÉSUMÉ

On a développé une méthode de détermination du rapport oxygène/uranium dans un dioxyde d'uranium hypostoechiométrique, avec dissolution de l'échantillon dans l'acide phosphorique. Au cours de la dissolution tout l'uranium est converti en uranium(IV) tandis qu'une certaine quantité d'hydrogène est libérée, équivalente au degré d'hypostoechiométrie. Le rapport O/U est déterminé à partir de la quantité d'hydrogène libérée. Des résultats satisfaisants correspondant à ceux trouvés par gravimétrie avec des échantillons de 1 g, ont été obtenus avec des prises de 30–140 mg.

ZUSAMMENFASSUNG

Für die Bestimmung des Verhältnisses Sauerstoff zu Uran in unterstöchiometrischem Urandioxid wurde eine Methode entwickelt, bei der die Probe in Phosphorsäure gelöst wird. Während des Auflösevorganges wird das gesamte vorhandene Uran in Uran(IV) überführt, wobei eine Wasserstoff-Menge freigesetzt wird, die dem Grad der Unterstöchiometrie äquivalent ist. Das Verhältnis O/U wird aus der entwickelten Wasserstoff-Menge ermittelt. Befriedigende Ergebnisse, die im Einklang mit jenen stehen, die gravimetrisch bei Proben von 1 g zu erhalten sind, können bei Proben von 30–140 mg erhalten werden.

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

CATALYTIC DETERMINATION OF SUBMICROGRAM AMOUNTS OF SELENIUM(IV) BY MEANS OF THE OXIDATIVE COUPLING REACTION OF PHENYLHYDRAZINE-*p*-SULFONIC ACID WITH 1-NAPHTHYLAMINE

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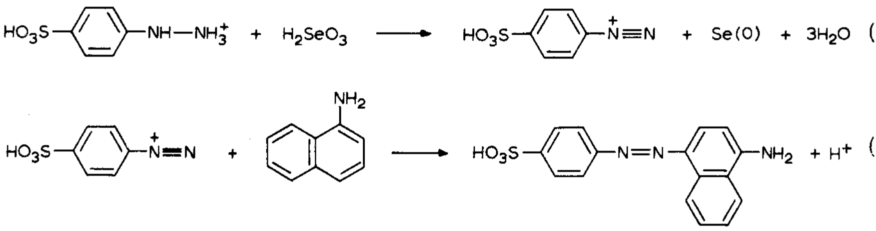
(Received September 15th, 1969)

Catalytic methods for the determination of selenium are few. One method is based on the catalytic effect of selenium(IV) on the reduction of methylene blue[1-3], and the other on the catalytic reduction of 1,4,6,11-tetraazanaphthacene by submicrogram amounts of selenium(IV)[4,5].

KIRKBRIGHT AND YOE[6] have determined microgram amounts of selenium(IV) by the oxidative coupling reaction of phenylhydrazine-*p*-sulfonic acid with 1-naphthylamine. The catalytic action of vanadium on the oxidation of phenylhydrazine-*p*-sulfonic acid by chlorate has been used in the determination of submicrogram amounts of vanadium(V)[7]. In this paper, a method of determination of submicrogram amounts of selenium(IV) based on the catalytic effect of selenium on the same reaction is described.

DEVELOPMENT OF THE METHOD

Phenylhydrazine-*p*-sulfonic acid is oxidized by selenous acid to *p*-diazobenzenesulfonic acid, which is coupled with 1-naphthylamine to form a colored azo dyestuff ($\lambda_{max} = 525$ nm):



(1)

(2)

$$Se(0) + ClO_3^- + 2H^+ \longrightarrow H_2SeO_3 + Cl^- \qquad (3)$$

Elemental selenium produced by the reaction (1) is oxidized again to selenous acid

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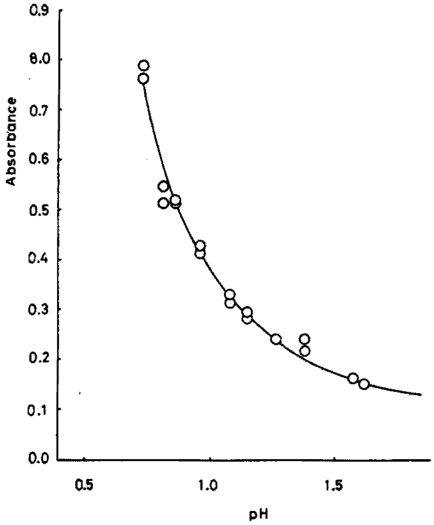
by chlorate in acid medium. As a result of the regeneration of selenium(IV) by reaction (3), the oxidation of phenylhydrazine-*p*-sulfonic acid is catalyzed by a minute amount of selenium.

Effect of temperature

Although the reaction proceeds faster at higher temperatures, the reagent blank is also increased at temperatures higher than 60°. Thus the reaction temperature was fixed at 50° and a reaction time of 60 min was chosen for the sake of high sensitivity and reproducibility.

Effect of pH

Figure 1 illustrates the effect of pH on the rate of formation of the dyestuff; the rate is faster at lower pH. However, below pH 0.7 reagent blanks are very high, so that the measurements become unreliable. Thus the reaction was carried out in the pH range 0.8–1.2. As is evident from Fig. 1, the pH should be carefully adjusted.



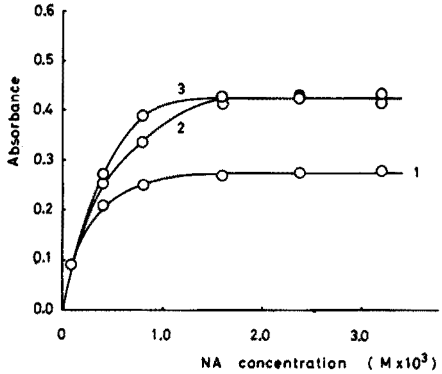


Fig. 1. Effect of pH: reaction time, 60 min; reaction temperature, 50.0 ± 0.1°; phenylhydrazine-*p*-sulfonic acid, $3.0 \cdot 10^{-3}$ *M*; 1–naphthylamine, $2.4 \cdot 10^{-3}$ *M*; $KClO_3$, $2.4 \cdot 10^{-2}$ *M*; Se(IV), 1.00 µg/25 ml.

Fig. 2. Effect of reagent (1-naphthylamine) concentrations: reaction time, 60 min; reaction temperature, 50.0 ± 0.1°; pH, 0.96; phenylhydrazine-*p*-sulfonic acid: (1) $1.2 \cdot 10^{-3}$ *M*, (2) $2.4 \cdot 10^{-3}$ *M*, (3) $3.0 \cdot 10^{-3}$ *M*; $KClO_3$, $2.4 \cdot 10^{-2}$ *M*; Se(IV), 1.00 µg/25 ml.

Effect of reagent concentrations

The results for the effect of changes in 1-naphthylamine and phenylhydrazine-*p*-sulfonic acid concentrations are shown in Fig. 2. The absorbance remained constant over the concentration range $1.6 \cdot 10^{-3}$–$5.6 \cdot 10^{-3}$ *M* 1-naphthylamine in the case of $3.0 \cdot 10^{-3}$ *M* phenylhydrazine-*p*-sulfonic acid. A slight decrease in absorbance was observed beyond a 1-naphthylamine concentration of $3 \cdot 10^{-3}$ *M*.

With consideration to the solubility of phenylhydrazine-*p*-sulfonic acid and the sensitivity, the concentration of the hydrazine was fixed at $3.0 \cdot 10^{-3}$ *M* and that of 1-naphthylamine at $2.4 \cdot 10^{-3}$ *M*.

Effect of chlorate concentration

Though the rate of formation of the azo dyestuff increases gradually with increasing concentration of chlorate at moderate concentration of chlorate (Fig. 3), constant and sufficient amounts of potassium chlorate should be used. A chlorate concentration of $2.4 \cdot 10^{-2}$ *M* is recommended.

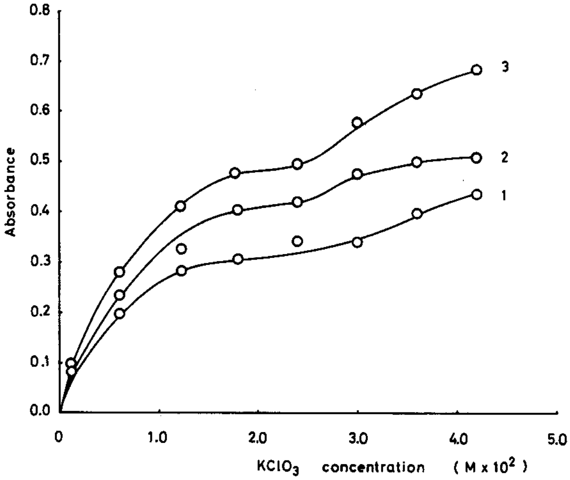


Fig. 3. Effect of $KClO_3$ concentration: reaction time, 60 min; reaction temperature, 50.0 ± 0.1°; pH: (1) 1.08, (2) 0.96, (3) 0.87; phenylhydrazine-*p*-sulfonic acid, $3.0 \cdot 10^{-3}$ *M*; 1-naphthylamine, $2.4 \cdot 10^{-3}$ *M*; Se(IV), 1.00 μg/25 ml.

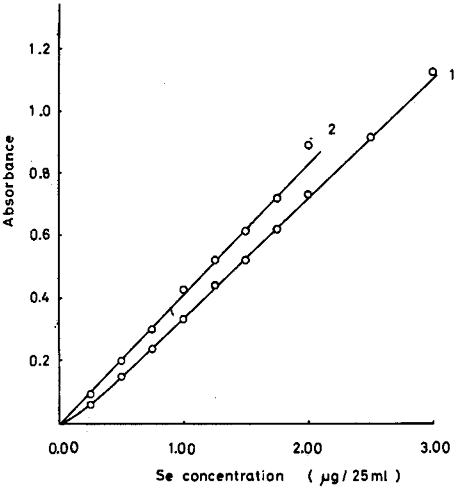


Fig. 4. Working curves for selenium. Conditions as in recommended procedure. pH: (1) 1.08, (2) 0.96.

Calibration graphs

Typical working curves for the recommended procedure are shown in Fig. 4. The sensitivity of the present method is about twenty times as high as the stoichiometric method proposed by KIRKBRIGHT AND YOE[6]. The present method provides an effective molar absorbance of $7.2 \cdot 10^5$ for selenium(IV).

Effect of diverse ions

The presence of the following elements caused no interference with the determination of 1.00 μg of selenium(IV), at least up to the specified amounts: Na(I) (50 mg), NH_4^+ (50 mg), K(I) (20 mg), Ca(II) (10 mg), Ba(II) (10 mg), Mg(II) (1 mg), Ni(II) (1 mg), Cd(II) (1 mg), Zn(II) (1 mg), Pb(II) (1 mg), Mn(II) (1 mg), As(V) (1mg), Al(III) (0.1 mg), Te(IV) (1 mg), Se(VI) (10 μg), Sn(II) (10 μg), Sn(IV) (10 μg), Ce(III) (10 μg), Co(II) (10 μg), SO_4^{2-} (100 mg), Cl^- (100 mg), NO_3^- (30 mg), ClO_4^- (10 μg), SO_3^{2-} (10 μg). It should be emphasized that tellurium(IV) and selenium(VI) do not interfere with the proposed method of determination of selenium(IV). The color of the cobalt aquo ion interferes at higher concentration.

Ions with oxidizing power give rise to a positive interference (Table I). Iron(III) and iron(II) form violet precipitates with 1-naphthylamine. Copper(II), cerium(IV), vanadium(V) and chromium(VI) act as catalysts in the color development. Nitrite (>1 mg) forms an orange product.

The interfering metals can be easily removed by the extraction of oxinates.

TABLE I

EFFECT OF DIVERSE IONS ON THE DETERMINATION OF 1.00 μg OF SELENIUM BY THE RECOMMENDED PROCEDURE

Ion added	μg	*Se found (μg)*	*Ion added*	μg	*Se found (μg)*
Fe(II)	10	2.32	V(V)	1	2.57
Fe(III)	10	3.00	NO_2^-	1000	2.75
Cu(II)	10	1.78	I^-	10	1.64
Ce(IV)	10	1.44	Br^-	10	1.42
Cr(VI)	10	1.65			

EXPERIMENTAL

Reagents

Stock selenium solution (1 mg of Se/ml). Dissolve 2.20 g of anhydrous sodium selenite (dried at 120° for 2 h) in 1 l of 0.1 *M* hydrochloric acid. Standardize the solution iodimetrically. Prepare a working solution of 1.00 μg of Se/ml by suitable dilution with 0.1 *M* hydrochloric acid.

*$2.5 \cdot 10^{-2}$ M Phenylhydrazine-*p*-sulfonic acid solution.* Dissolve 471 mg of phenylhydrazine-*p*-sulfonic acid (Tokyo Chemical Industry Co., Ltd., Japan) in 100 ml of 0.1 *M* hydrochloric acid by gentle warming. Prepare the solution fresh daily.

$3.0 \cdot 10^{-2}$ M 1-Naphthylamine solution. Purify 1-naphthylamine by vacuum sublimation. Dissolve 215 mg of purified 1-naphthylamine in 50 ml of 0.1 *M* hydrochloric acid. Prepare the solution fresh daily.

Other reagents used were of analytical grade.

Apparatus

Hitachi Perkin-Elmer Model 139 spectrophotometer; Horiba Model F-5 pH meter; Taiyo Model C-550 circulating bath.

Recommended procedure

To 12 ml of sample solution (about 0.2–0.3 *M* in hydrochloric acid) containing not more than 3.0 μg of selenium(IV) in a 50-ml volumetric flask, add 5 ml of 1.0 *M* acetic acid, 3 ml of 0.2 *M* potassium chlorate, 2 ml of 1-naphthylamine solution and 3 ml of phenylhydrazine-*p*-sulfonic acid solution, and then mix the solution. Heat the mixture at 50.0 ± 0.1° for 60 min. Pipette *ca.* 5 ml of the solution into a dry test tube immersed in an ice bath. Then measure the absorbance at 525 nm in a 10-mm cell preferably within 20 min, against a distilled water reference. Net absorbance were obtained by subtracting a blank absorbance.

The authors wish to thank Professor M. KAMADA, Department of Chemistry, Faculty of Science, Kagoshima University, for his stimulating and helpful discussions and Professor K. MŌRI, Chemical Institute, the College of Liberal Arts, Kagoshima University, for kindly providing research facilities.

SUMMARY

In the presence of potassium chlorate, selenium catalyzes the oxidation of phenylhydrazine-*p*-sulfonic acid and the *p*-diazobenzenesulfonic acid formed is coupled with 1-naphthylamine to form an intensely colored azo dyestuff. By means of this catalytic reaction, submicrogram amounts of selenium(IV) can be easily determined. The method is simple and sensitive, and there are few interferences.

RÉSUMÉ

En présence de chlorate de potassium, le sélénium catalyse l'oxydation de l'acide phénylhydrazine-*p*-sulfonique. L'acide *p*-diazobenzènesulfonique formé est copulé avec la 1-naphtylamine pour donner un azocolorant intensément coloré. On peut ainsi doser facilement des quantités de sélénium(IV) de l'ordre du submicrogramme. Cette méthode est simple et sensible et ne présente que peu d'interférences.

ZUSAMMENFASSUNG

In Gegenwart von Kaliumchlorat katalysiert Selen die Oxidation von Phenylhydrazin-*p*-sulfonsäure; die gebildete *p*-Diazobenzolsulfonsäure koppelt mit 1-Napthylamin zu einem stark gefärbten Azofarbstoff. Mit Hilfe dieser katalytischen Reaktion können Submikrogramm-Mengen Selen(IV) leicht bestimmt werden. Die Methode ist einfach und empfindlich, und es gibt nur geringe Störmöglichkeiten.

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

THE FORMATION CONSTANTS OF EUROPIUM(III)–SALICYLATE COMPLEXES AND THEIR EXTRACTION INTO ISOAMYL ALCOHOL

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(Received November 19th, 1969)

In connection with studies of the synergic liquid–liquid extraction of ternary complexes of the lanthanides[1], it was necessary to know the formation constants of complexes of europium(III) with salicylate ions. Few lanthanide–salicylate systems have previously been studied and only values for the stability constants K, for the 1:1 complexes have been reported[2].

Preliminary experiments showed that lanthanides could be extracted from an aqueous salicylate medium by higher aliphatic alcohols and the present paper details the investigations with europium(III) and isoamyl alcohol which lead to the evaluation of the relevant distribution and formation constants.

The distribution of salicylic acid alone between isoamyl alcohol and aqueous phases of different pH values but constant ionic strength (0.1 M sodium perchlorate) was first studied with the results shown in Table I. Here the distribution coefficient D_{Sal} represents the ratio (total concentration of salicylate in the organic phase)/(total concentration of salicylate in the aqueous phase). The values $\mathrm{p}K_1{}^{\mathrm{T}}=2.973$ and $\mathrm{p}K_2{}^{\mathrm{T}}=13.592$ have been reported[3] for the thermodynamic dissociation constants of salicylic acid ($\mathrm{H_2Sal}$) at 25°. By using the Davies approximation the value $K_1=[\mathrm{H^+}][\mathrm{HSal^-}]/[\mathrm{H_2Sal}]=1.77\cdot10^{-3}$ at $\mu=0.1$ M was calculated ($\mathrm{p}K_1=2.75$). This is appreciably lower than any value measured directly[4] in a medium of constant ionic strength, *viz.* 3.14 (18°; $\mu=0.1$ M), 2.98 (20°; $\mu=0.1$–0.15 M KCl), 2.82 (25°; 0.1 M $\mathrm{NaClO_4}$) and 2.88 (30°; $\mu=0.1$ M KCl). We have somewhat arbitrarily adopted the value $\mathrm{p}K_1=2.85$ but find that the stability constants finally calculated are not very sensitive to the changes in this.

Over the pH range studied (2.23–5.67), only the species $\mathrm{H_2Sal}$ and $\mathrm{HSal^-}$ need be considered in the aqueous phase. Although dimerisation of salicylic acid occurs in benzene[1] it is negligible in methyl isobutyl ketone[5] and can reasonably be expected to be small or negligible in other polar or hydroxylic solvents (such as isoamyl alcohol) that can act as acceptors for hydrogen bonds.

If then the partition equilibrium is represented by the equation

$$\begin{aligned} D_{\mathrm{Sal}} &= [\mathrm{H_2Sal}]_{\mathrm{org}}/([\mathrm{H_2Sal}]+[\mathrm{HSal^-}]) \\ &= p_0/\{1+(K_1/[\mathrm{H^+}])\} \qquad (1) \end{aligned}$$

where $p_0=[\mathrm{H_2Sal}]_{\mathrm{org}}/[\mathrm{H_2Sal}]$ and the subscript org distinguishes species in the organic phase, we would expect the product $D_{\mathrm{Sal}}\{1+(K_1/[\mathrm{H^+}])\}$ to be constant ($=p_0$) for all pH values. The penultimate column of Table I shows that this is not the case with

TABLE I

DISTRIBUTION OF SALICYLIC ACID BETWEEN ISOAMYL ALCOHOL AND AN AQUEOUS PHASE OF CONSTANT IONIC STRENGTH

(μ = 0.1 *M* sodium perchlorate at 22°)

pH	D_{sal} *(experimental)*	$D_{sal}(1+K_1/[H^+])$	D_{sal} *(calculated)*[a]
2.23	92.33	114.5	88.2
2.69	69.0	116.8	64.7
3.46	20.77	115.4	21.6
4.09	5.53	101.6	6.06
4.27	3.90	106.5	4.11
4.46	2.63	109.8	2.73
4.64	1.88	117.8	1.86
4.70	1.72	123.5	1.64
4.80	1.36	122.6	1.33
4.90	1.13	127.9	1.08
5.56	0.298	153.1	0.326
5.67	0.294	194.5	0.279

[a] Calculated from eqn. (4) with the values $p_0 = 109.3$ and $k = 0.114$.

the present system: the product actually increases with pH, indicating that some species other than salicylic acid is partitioning into the organic phase.

It was found that sodium salicylate was appreciably soluble in isoamyl alcohol and its distribution between organic and aqueous phases can be taken into account through the following equilibria, *viz.*

$$[Na^+][HSal^-] \rightleftharpoons [Na^+]_{org}[HSal^-]_{org} \rightleftharpoons [Na^+HSal^-]_{org}$$

governed by

$$p_1 = [Na^+]_{org}[HSal^-]_{org}/[Na^+][HSal^-] \quad (2)$$

and $$K_{org} = [Na^+HSal^-]_{org}/[Na^+]_{org}[HSal^-]_{org} \quad (3)$$

If K_{org} is sufficiently large, *i.e.* if the ion-pair or molecular species NaHSal is not significantly dissociated in the organic phase, then

$$D_{sal} = ([H_2Sal]_{org} + [Na^+HSal^-]_{org})/([H_2Sal] + [HSal^-])$$

$$= \{p_0 + (p_1K_{org}[Na^+]K_1/[H^+])\}/\{1 + (K_1/[H^+])\}$$

or

$$D_{sal}\{1 + (K_1/[H^+])\} = p_0 + k(K_1/[H^+]) \quad (4)$$

for $k = p_1K_{org}$ $[Na^+]$ may be regarded as constant since the ionic strength was maintained at 0.1 *M* with sodium perchlorate. A least-squares treatment of the experimental data leads to $p_0 = 109.3$ and $k = 0.114$. Values of D_{sal} calculated from eqn. (4) are given in the final column of Table I.

The hypothesis that the species $[NaHSal]_{org}$ was appreciably dissociated in the organic phase was discarded in the light of trial calculations. The value found for the distribution coefficient $p_0 = 109.3$ is much higher than that reported[5] for chloroform ($p_0 = 3$) but similar to that found for another polar solvent, hexone, for which $p_0 = 324$[5].

The distribution of europium(III) between an aqueous phase containing salicylate ions (and maintained at $\mu = 0.1\ M$ with sodium perchlorate) and an equal volume of isoamyl alcohol was followed radiometrically by using ^{152,154}Eu as tracer. The results are summarised in Table II. On the assumption that only the formally uncharged species $Eu(Hsal)_3$ will extract into the organic phase we can write

TABLE II

THE DISTRIBUTION OF EUROPIUM(III) BETWEEN ISOAMYL ALCOHOL AND AQUEOUS PHASES OF VARIABLE ACIDITY AND CONSTANT IONIC STRENGTH

($\mu = 0.1\ M$ sodium perchlorate at 22°)

pH	$-\log[Hsal]^a$	$\log D_{Eu}$	*pH*	$-\log\,[HSal]^a$	$\log D_{Eu}$
A. $[H_2Sal]_{total} = 3.125 \cdot 10^{-3}\ M$			D. $[H_2Sal]_{total} = 5.056 \cdot 10^{-2}\ M$		
6.41	2.564	−1.53	5.86	1.383	0.42
4.90	2.827	−1.79	5.47	1.436	0.97
4.18	3.303	−2.55	5.30	1.474	1.02
			5.05	1.554	0.98
B. $[H_2Sal]_{total} = 1.418 \cdot 10^{-2}\ M$			4.84	1.647	0.93
6.00	1.925	−0.26	4.71	1.718	0.79
5.55	1.974	−0.05	4.33	1.975	0.60
5.18	2.061	−0.11	4.28	2.104	0.51
5.02	2.118	−0.19			
4.82	2.210	−0.29	E. $[H_2Sal]_{total} = 1.344 \cdot 10^{-1}\ M$		
4.51	2.396	−0.41	5.94	0.952	1.73
4.32	2.535	−0.71	5.70	0.976	1.59
3.98	2.817	−1.44	5.55	0.998	1.28
			5.05	1.129	1.06
C. $[H_2Sal]_{total} = 2.53 \cdot 10^{-2}\ M$			4.75	1.270	0.96
6.50	1.653	0.06			
6.07	1.669	0.10	F. $[H_2Sal]_{total} = 5.162 \cdot 10^{-1}\ M$		
5.57	1.695	0.41	6.52	0.343	1.66
5.20	1.803	0.34	6.25	0.351	1.70
4.92	1.910	0.27	6.10	0.358	1.78
4.89	1.923	0.12	5.77	0.383	1.79
4.75	1.996	−0.03	5.57	0.409	1.82
4.68	2.036	−0.05	5.55	0.412	1.80
4.39	2.231	−0.34	5.32	0.460	1.73
			5.18	0.499	1.78
			5.04	0.549	1.76
			4.09	1.161	1.17

[a] Calculated by eqn. (7). $[Eu]_{inactive} = 0.97 \cdot 10^{-5}\ M$; $[^{152,154}Eu] \sim 10^{-7}\ M$.

$$D_{Eu} = \frac{[Eu(HSal)_3]_{org}}{([Eu^{3+}] + [Eu(HSal)^{2+}] + [Eu(HSal)_2{}^{+}] + \ldots}$$

$$= p_c\beta_3[HSal^-]^3 / \sum_0^N \beta_n[HSal^-]^n \qquad (5)$$

where $p_c = [Eu(HSal)_3]_{org}/[Eu(HSal)_3]$

and $\beta_n = [Eu(HSal)_n]^{3-n}/[Eu^{3+}][HSal^-]^n$

Equation (5) can be expressed in the more convenient form

$$\log D_{\mathrm{Eu}} = \log p_c\beta_3 + 3 \log [\mathrm{HSal}^-] - \log \sum_0^N \beta_n [\mathrm{HSal}^-]^n \tag{6}$$

The value of the term $[\mathrm{HSal}^-]$ can readily be calculated from the equation expressing the mass-balance of salicylic acid, *viz.*

$$[\mathrm{H_2Sal}]_{\mathrm{total}} = [\mathrm{H_2Sal}]_{\mathrm{org}} + [\mathrm{H_2Sal}] + [\mathrm{HSal}^-] + [\mathrm{Na^+HSal^-}]_{\mathrm{org}}$$

$$+ \sum_1^N n[\mathrm{Eu(HSal)}_n] + 3\,[\mathrm{Eu(HSal)_3}]_{\mathrm{org}}$$

$$= [\mathrm{HSal}^-]\,\{(p_0+1)\,(K_1/[\mathrm{H}^+]) + 1 + k\}$$

Since the terms involving europium at tracer levels can be neglected, by introducing the values previously determined for p_0 and k, we obtain

$$[\mathrm{HSal}^-] = [\mathrm{H_2Sal}]_{\mathrm{total}}/(1.114 + 78.22 \cdot 10^3[\mathrm{H}^+]) \tag{7}$$

Figure 1 shows a plot of log D_{Eu} against $-\log\,[\mathrm{HSal}^-]$. In agreement with eqn. (6), the tangent to the curve through the experimental data has a limiting slope of 3 for low values of $[\mathrm{HSal}^-]$. At high salicylate concentrations the curve approaches the value log $p_0 = 1.8(0)$. By using Dyrssen and Sillén's two-parameter method[6] (which *postulates* that $K_1/K_2 = K_2/K_3 = 10^{2b}$ and that $\beta_3 = K_1K_2K_3 = 10^{3a}$), we calculate a = 1.62 and 2b = 0.965 whence log $\beta_3 = 1.486$, log K_1 = a + 2b = 2.59, log K_2 = a = 1.62 and log K_3 = a − 2b = 0.65. The experimental data are represented tolerably well by a curve (Fig. 1 solid continuous line *a*) calculated from eqn. (6) with these stability constants and the partition coefficient $p_c = 10^{1.80}$.

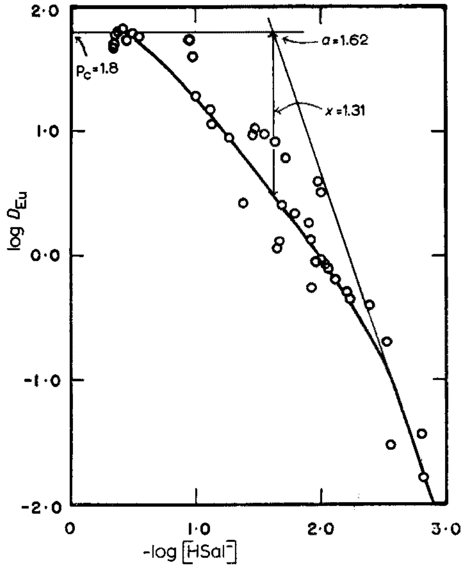

Fig. 1. The relationship between the distribution constant for europium(III) and the concentration of salicylic acid.

TABLE III

STABILITY CONSTANTS FOR 1:1 LANTHANIDE–SALICYLATE COMPLEXES

Element	*La*	*Ce*	*Pr*	*Nd*	*Eu*[a]
Atomic no.	57	58	59	60	63
log K_1	2.64	2.66	2.68	2.70	2.59

[a] Present work. Valid for $\mu = 0.1$ M $NaClO_4$ and 22°. All other values from ref. (2) data, valid for 30° and 0.1 M KCl.

The value for the stability of the 1:1 species $Eu(HSal)^{2+}$ is of the same order as that reported for other lanthanides (Table III).

The data are not directly comparable as the measurements for the lighter rare-earths were made at 30° and in 0.1 M potassium chloride. However, the enthalpy change in reaction between iron(III) and salicylic acid is known to be negative[7] ($K_1 = 15.95$ at 15° and 15.69 at 35°) and it is reasonable to predict that slightly larger values would apply for 20–25°. The value log $K_1 = 2.59$ now found for europium would therefore appear not to follow the trend shown by complexes of lanthanum, cerium, praseodymium and neodymium with this and other hydroxycarboxylic acids[8] but there may well be no anomaly since the "gadolinium break" which invariably leads to a reduction in the formation constant normally occurs in the region Sm–Eu–Gd. Without a knowledge of K_1 for the species $Sm(HSal)^{2+}$, it is impossible to confirm this explanation.

EXPERIMENTAL

The liquid–liquid extraction of salicylic acid

Solutions of AnalaR salicylic acid of known concentration (*ca.* 10^{-2} M) adjusted to a definite pH with either perchloric acid or sodium hydroxide were made up to 10 ml and to an ionic strength of 0.1 M with sodium perchlorate and equilibrated with an equal volume of isoamyl alcohol (10 ml) by being shaken in stoppered test-tubes for about 18 h at room temperature (22°). After phase separation (assisted if necessary by centrifugation), the pH of the aqueous phase was measured and the concentration of salicylic acid determined spectrophotometrically. To this end a 2-ml aliquot portion of the aqueous phase was treated with 2–3 ml of concentrated perchloric acid (to convert all ions into the species H_2Sal) and diluted to 100 ml. The absorbance of this solution was measured at 302 nm (where isoamyl alcohol transmits freely) with a Unicam SP500 spectrophotometer. The distribution coefficient was calculated from

$$D_{sal} = \frac{(\text{initial O.D. of aqueous phase}) - (\text{final O.D. of aqueous phase})}{(\text{final O.D. of aqueous phase})}$$

Extraction of europium(III)-salicylate

An aqueous mixture (10 ml) of radioactive tracer $^{152,154}Eu$ ($< 10^{-7}$ M) containing inactive europium(III) perchlorate (*ca.* 10^{-5} M) as carrier and sodium salicylate of various concentrations ($3 \cdot 10^{-1}$–$5 \cdot 10^{-1}$ M) was shaken with an equal volume of isoamyl alcohol in a stoppered test-tube for 2–4 h. The pH of the aqueous phase was adjusted by adding either perchloric acid or sodium hydroxide and the ionic strength brought to 0.1 M with sodium perchlorate. After equilibration and centrifugation, the phases were separated and the pH of the aqueous phase was measured with a Radiometer pH-meter. Aliquot portions of each of the phases (2 ml) were assayed radiometrically with an I.D.L. γ-scintillation counter equipped with a Tl-doped sodium iodide crystal. Background counts were subtracted but no correction for decay was necessary since $t_{\frac{1}{2}} = 5.3$ years.

Each solvent, isoamyl alcohol and water, was presaturated with the other to prevent changes in phase volume on equilibration.

SUMMARY

The distribution of salicylic acid (H_2Sal) between isoamyl alcohol and aqueous buffers of constant ionic strength ($\mu = 0.1$ M $NaClO_4$) was investigated over a range of pH values. The partition coefficient was found to be 109.3 and sodium salicylate was also found to be extracted to a small extent. The liquid–liquid extraction of europium(III) as its salicylate into isoamyl alcohol was investigated radiometrically. The partition coefficient log $p_c = 1.8(0)$ and the successive stability constants, $K_1 = 10^{2.59}$, $K_2 = 10^{1.62}$ and $K_3 = 10^{0.65}$, were evaluated.

RÉSUMÉ

On examine le partage de l'acide salicylique (H_2Sal) entre alcool isoamylique et tampons aqueux de force ionique constante ($\mu = 0.1$ M $NaClO_4$), en fonction du pH. Le coefficient de partage est de 109.3; le salicylate de sodium est faiblement extrait. L'extraction liquide–liquide de l'europium(III), sous forme de salicylate, dans l'alcool isoamylique est examinée par radiométrie. Le coefficient de partage évalué est log $p_c = 1.8$; les constantes de stabilité successives sont: $K_1 = 10^{2.59}$, $K_2 = 10^{1.62}$ et $K_3 = 10^{0.65}$.

ZUSAMMENFASSUNG

Die Verteilung von Salicylsäure (H_2Sal) zwischen Isoamylalkohol und wässrigen gepufferten Lösungen konstanter Ionenstärke ($\mu = 0.1$ M $NaClO_4$) wurde für eine Reihe von pH-Werten untersucht. Der ermittelte Verteilungskoeffizient beträgt 109.3; ausserdem wurde gefunden, dass in geringem Masse auch Natriumsalicylat extrahiert wird. Die Verteilung von Europium(III) als Salicylat zwischen Isoamylalkohol und wässriger Lösung wurde radiometrisch untersucht. Es wurden der Verteilungskoeffizient log $p_c = 1.8(0)$ und die aufeinander folgenden Stabilitätskonstanten $K_1 = 10^{2.59}$, $K_2 = 10^{1.62}$ und $K_3 = 10^{0.65}$ ermittelt.

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

COMPLEXES FORMED IN THE CHLOROFORM EXTRACTION OF NICKEL WITH OXINE

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(Received October 4th, 1969)

Although the extraction and colorimetric determination of nickel with oxine (8-hydroxyquinoline) has been frequently investigated[1-5], little is known about the complexes extracted into the organic phase. SEKIDO[6] has reported that nickel oxinate could be extracted once into chloroform, but it precipitated again when the concentration of oxine was low, and that as the presence of a large excess of oxine was indispensable for preparing a stable nickel extract, the nickel must be extracted in the form of a nickel oxinate combined with neutral oxine molecules. STARÝ[7] has concluded that nickel is extracted as a simple chelate, $NiOx_2$, from the difference in the pH of 50% extraction for 0.01 and 0.1 M oxine solutions in chloroform.

This paper reports a more detailed study of the distribution equilibrium of nickel with oxine to give more definite information on the extractable nickel–oxine complexes.

EXPERIMENTAL

Materials and apparatus

Chloroform containing 0.5% (v/v) ethanol was used.

A ^{63}Ni radiotracer of 99.9% purity was used in all the extraction experiments.

Reagents and chemicals were all of guaranteed reagent grade and were used without further purifications.

A Shimadzu-Bausch-Lomb Spectronic 20 Colorimeter and the accessory 0.5-in diameter test tubes, a 2π gas flow counter, and a pH meter with a glass and 3.33 M calomel electrode pair were used.

Distribution measurements of nickel

A volume (5 ml) of a solution of oxine in chloroform (0.01–0.1 M) and an equal volume of an aqueous solution containing nickel ion labelled with ^{63}Ni at a constant ionic strength of 0.1 M were equilibrated by shaking in a glass-stoppered cylindrical tube for 1 h, an adequate time for the attainment of equilibrium. The pH of the aqueous phase was adjusted by addition of perchloric acid and sodium hydroxide. Small amounts (<0.002 M) of acetate or borate were added to buffer the aqueous phase. The presence of such amounts of these salts was verified not to alter the distribution ratio of nickel within experimental error. The ionic strength was kept constant by addition of sodium perchlorate. The mixtures were then centrifuged for 5 min. After the phase separation, an aliquot of the organic phase (0.1, 0.5 or 1.0 ml) was pipetted out on a stainless steel planchet, heated at 200° to remove excess of oxine and counted on a 2π gas flow counter. The residual organic phase was removed for the absorbance measurement.

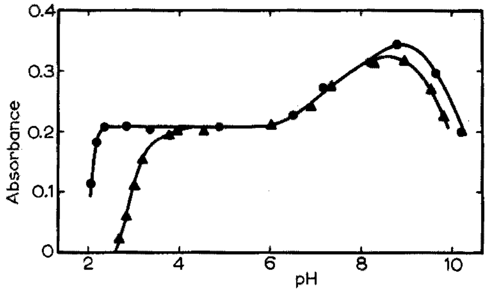
Part of the aqueous phase (2 ml) was transferred to another glass tube, the pH was adjusted to 3.5–8 with sodium hydroxide, and the nickel in the solution was extracted into an equal volume of a 0.1 M oxine solution in chloroform. The radioactivity of the organic extract, which was measured as described above, was taken as the radioactivity of the aqueous phase. The distribution ratio of nickel was defined as the ratio of the radioactivity of an aliquot of the organic phase to that of an equal volume of the aqueous phase. The pH of the aqueous phase was measured after the phase separation.

The experiments were all carried out in a temperature-controlled room at 20°.

RESULTS AND DISCUSSION

Absorption spectra of nickel–oxine complexes in the organic phase

Figure 1 shows the effect of pH on the absorbance (400 nm) of nickel complexes in the organic extract. The absorbance was measured against a chloroform blank, but the absorbance by excess of reagent was negligible at 400 nm. For 0.01 M oxine, the absorbance increases from pH 2.5 and then reaches a constant value in the pH region 4–6. A further increase in the absorbance is observed at pH 6–9. The gradual increase in the absorbance at pH 6–9 is due to changes in the extractable nickel complex, but not due to an increase in the extraction efficiency, because nickel is completely extracted ($\log D_{Ni} > 1.5$) throughout the pH region 4–9 for 0.01 M oxine and $7.64 \cdot 10^{-5}$ M nickel (see Fig. 3). Precipitations were noticed at the interface of organic and aqueous phases above pH 10. Similar trends were also observed for 0.1 and 0.03 M oxine solutions.



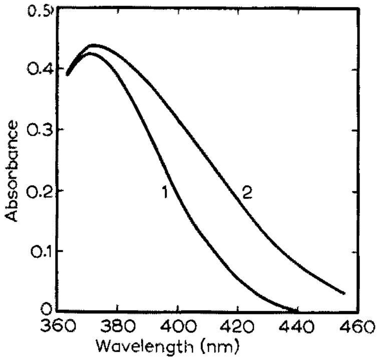


Fig. 1. The effect of pH on the absorbance of nickel complexes in the organic phase. The initial concentration of nickel in the aqueous phase: $7.64 \cdot 10^{-5}$ M. The initial concentration of oxine in the organic phase: (●) 0.100 M; (▲) 0.0100 M.

Fig. 2. Absorbance spectra of nickel–oxine complexes in the organic extracts measured against reagent blank. The organic extract was prepared at (1) pH 3.5 and (2) pH 8.5.

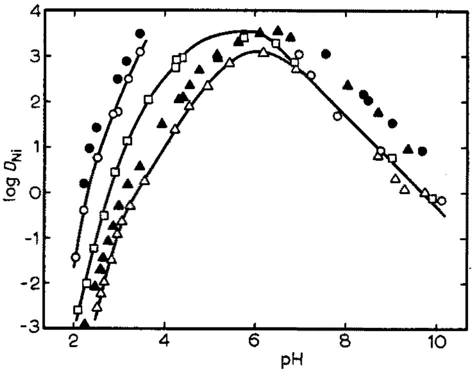
The absorbance spectra for the nickel complexes extracted at pH 3.5 and 8.5

with 0.1 *M* oxine in chloroform are given in Fig. 2. An absorbance maximum appears at about 370 nm for both cases, but the absorbance is distinctly higher at longer wavelengths for the pH 8.5 extract. The spectrum of the nickel–oxine complex extracted at pH 8.5 is essentially the same as that reported[5,6], but that at pH 3.5 has not previously been reported. These spectra are reversibly changed to each other by shaking an organic extract for more than 5 min with an aqueous solution at the desired pH.

Previous work[1-5] on these complexes has been mainly concerned with the development of analytical methods, and little attention has been given to the attainment of the extraction equilibrium; the quantitative extraction of nickel in the low pH region, which is possible by prolonged shaking, has been overlooked.

Distribution of nickel at low pH

The distribution ratio of nickel, D_{Ni}, is shown as a function of pH in Fig. 3. The initial concentrations of nickel were $9.0 \cdot 10^{-7}$ *M* and $7.64 \cdot 10^{-5}$ *M*. The distribution ratio is a little higher for the stronger solutions, which suggests the presence of some polymerized complexes in addition to the monomeric species in the organic phase in such solutions. Since the distribution ratio of nickel proved to be independent of the initial nickel concentration below 10^{-5} *M*, it is reasonable to assume that only monomeric species are present when $9.0 \cdot 10^{-7}$ *M* nickel is used. The shapes of the distribution curves for the two concentrations of nickel tested are very similar (Fig. 3).



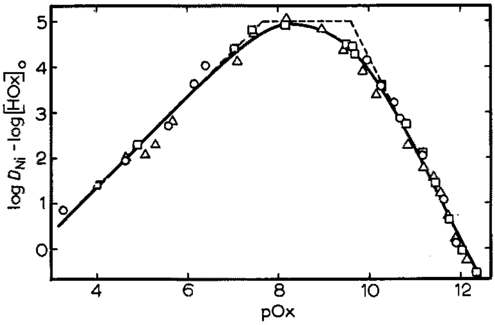


Fig. 3. Distribution of nickel as a function of pH. The initial concentrations of nickel in the aqueous phase: solid symbols, $7.64 \cdot 10^{-5}$ *M*; open symbols, $9.0 \cdot 10^{-7}$ *M*. The initial concentration of oxine in the organic phase: (○, ●) 0.100 *M*, (□) 0.0300 *M*; (△,▲), 0.0100 *M*.

Fig. 4. Distribution of nickel as a function of HOx and pOx. For symbols see Fig. 3. Dotted lines are asymptotes. The full drawn curves:

$X = \log v$, $Y = \log(1 + 2v + v^2)$ for pOx>8;

$X = \log u$, $Y = \log(1 + u)$ for pOx<8.

It is of interest to find that the distribution curves given in Fig. 3 are related to the absorbance–pH curves shown in Fig. 1. Up to pH 6, the distribution ratio for nickel continues to increase with increasing pH while the absorbance has a low constant value; above pH 6, the distribution ratio decreases whereas the absorbance increases up to pH 9.

It can be seen from Fig. 3 that the oxine concentration dependence of the distribution ratio of nickel, $\Delta \log D_{\mathrm{Ni}}/\Delta \log [\mathrm{HOx}]_o$, is close to 3 at about pH 3. This result suggests that nickel is extracted as $\mathrm{NiOx_2HOx}$, and not as $\mathrm{NiOx_2}$ as suggested by STARÝ[7].

It is assumed for the extraction process that nickel combines with oxinate anion to form nickel–oxine complexes in the aqueous phase, among which the 1:2 complex, $\mathrm{NiOx_2}$, is extracted to form the 1:3 complex, $\mathrm{NiOx_2HOx}$, in the organic phase. In such cases, D_{Ni}, could be expressed as:

$$D_{\mathrm{Ni}} = \frac{[\mathrm{NiOx_2HOx}]_o}{[\mathrm{Ni}]+[\mathrm{NiOx}]+[\mathrm{NiOx_2}]} \tag{1}$$

where square brackets with and without subscript "o" denote the concentrations in the organic and aqueous phases, respectively, and charges are neglected in equations for simplicity.

The following are the necessary equations for describing the equilibria. The stability constants of nickel oxine complexes are defined as:

$$\beta_1 = \frac{[\mathrm{NiOx}]}{[\mathrm{Ni}]\,[\mathrm{Ox}]}, \beta_2 = \frac{[\mathrm{NiOx_2}]}{[\mathrm{Ni}]\,[\mathrm{Ox}]^2} \tag{2}$$

The distribution coefficient of $\mathrm{NiOx_2}$, $D_{\mathrm{Ni}}{}^0$, is defined as:

$$D_{\mathrm{Ni}}{}^0 = \frac{[\mathrm{NiOx_2}]_o}{[\mathrm{NiOx_2}]} \tag{3}$$

The formation constant of the 1:3 complex, K, in the organic phase is:

$$K = \frac{[\mathrm{NiOx_2HOx}]_o}{[\mathrm{NiOx_2}]_o\,[\mathrm{HOx}]_o} \tag{4}$$

Combining eqns. (2), (3), and (4), eqn. (1) can be rewritten as:

$$D_{\mathrm{Ni}} = \frac{D_{\mathrm{Ni}}{}^0\,K\beta_2\,[\mathrm{Ox}]^2\,[\mathrm{HOx}]_o}{1+\beta_1[\mathrm{Ox}]+\beta_2[\mathrm{Ox}]^2} \tag{5}$$

or

$$\log D_{\mathrm{Ni}} - \log [\mathrm{HOx}]_o = \log D_{\mathrm{Ni}}{}^0\,K\beta_2 - 2\mathrm{pOx} - \log (1+\beta_1\,[\mathrm{Ox}]+\beta_2\,[\mathrm{Ox}]^2) \tag{6}$$

To test eqn. (6), a plot of $\log D_{\mathrm{Ni}} - \log [\mathrm{HOx}]_o$ *vs.* pOx is given in Fig. 4, in which all the experimental points practically fall on a single curve independent of the initial concentrations of oxine. The pOx at equilibrium was calculated as reported previously[8]. The final concentration of oxine in the organic phase was calculated from eqn. (7).

$$\log [\mathrm{HOx}]_o = \log [\mathrm{HOx}]_i - \log \left(1 + \frac{[\mathrm{H}]}{D_{\mathrm{R}}{}^0 K_1} + \frac{1}{D_{\mathrm{R}}{}^0} + \frac{K_2}{D_{\mathrm{R}}{}^0[\mathrm{H}]}\right) \tag{7}$$

where the subscript "i" refers to the initial concentration, K_1 and K_2 are the acid dissociation constants of the oxinium ion and oxine, respectively, and $D_{\mathrm{R}}{}^0$ is the distribution coefficient of oxine. The values $\mathrm{p}K_1 = 5.14$, $\mathrm{p}K_2 = 9.74$, and $\log D_{\mathrm{R}}{}^0 = 2.64$ are used[8].

It can be expected from eqn. (6) that the plot given in Fig. 4 will have two asymptotes in the higher pOx region ($\mathrm{pOx} > 8$):

$$\log D_{Ni} - \log [HOx]_o = \log D_{Ni}{}^0 K \qquad (8)$$

$$\log D_{Ni} - \log [HOx]_o = \log D_{Ni}{}^0 K\beta_2 - 2pOx \qquad (9)$$

By means of a curve-fitting method[9], the equilibrium constants, $D_{Ni}{}^0 K$, β_1 and β_2 were determined graphically from Fig. 4. The experimental points were compared to the normalized curves:

$$Y = \log(1 + pv + v^2); \qquad X = \log v \qquad (10)$$

where p is a parameter and v is an auxiliary variable:

$$p = \frac{\beta_1}{\sqrt{\beta_2}}; \qquad v = \frac{1}{\sqrt{\beta_2}\,[Ox]} \qquad (11)$$

The calculated curve for $p = 2$ which gives the best fit and the asymptotes are shown in Fig. 4; the following constants were obtained: $\log \beta_1 = 9.90$, $\log \beta_2 = 19.20$ and $\log D_{Ni}{}^0 K = 5.00$. The stability constants obtained in the present paper are in good agreement with reported values which were determined with water as solvent[10].

Distribution of nickel at high pH

As can be seen from Fig. 1, the absorbance of nickel complexes in the organic phase increases over the pH range 6–9*, which suggests that there are at least two or more extractable complexes, some of which increase while others decrease with pH in the alkaline region. The distribution data obtained in the alkaline region for three concentrations of oxine could also be successfully treated by the plot of $\log D_{Ni} - \log [HOx]_o$ *vs.* pOx. These results indicated that the extractable complexes from acidic and alkaline media are isomers which differ clearly in their absorbance spectra, but only slightly in their distribution coefficients. The distribution data were analyzed on this assumption.

The decrease in the distribution ratio with increasing pH in the alkaline region could be regarded as caused by the formation of an anionic complex in the aqueous phase. Because the 1:3 anionic nickel complexes of some oxine derivatives have been reported[12,13], an anionic complex of similar type, $NiOx_3^-$, was assumed. The extractable complex was expected to have the composition, $NiOx_2HOx$, from the unit slope of the distribution curve (given in Fig. 3) in the alkaline region. The fall-off from the unit slope is due to the appearance of $NiOx_2$ in the aqueous phase at about pOx 5.5.

Thus, the distribution ratio may be written as:

$$D_{Ni} = \frac{[NiOx_2HOx]_o}{[NiOx_2] + [NiOx_3]} \qquad (12)$$

$$= \frac{D_{Ni}K\beta_2[HOx]_o}{\beta_2 + \beta_3[Ox]} \qquad (13)$$

or

$$\log D_{Ni} - \log [HOx]_o = \log D_{Ni}{}^0 K\beta_2 - \log(\beta_2 + \beta_3[Ox]) \qquad (14)$$

where β_3 is the stability constant of the 1:3 anionic complex, $NiOx_3^-$, in the aqueous phase.

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* Absorption spectra of the extractable oxine complexes of cobalt(II), scandium, and thorium also change with pH[11].

$$\beta_3 = \frac{[\mathrm{NiOx_3}]}{[\mathrm{Ni}]\,[\mathrm{Ox}]^3} \tag{15}$$

The plot given in Fig. 4 also has another asymptote in the lower pOx region:

$$\log D_{\mathrm{Ni}} - \log\,[\mathrm{HOx}]_o = \log D_{\mathrm{Ni}} K\beta_2/\beta_3 + \mathrm{pOx} \tag{16}$$

The β_3 were determined graphically from Fig. 4, comparing the experimental points to the normalized curve[9]:

$$Y = \log\,(1+u) \qquad X = \log u \tag{17}$$

where

$$u = \frac{\beta_3}{\beta_2}\,[\mathrm{Ox}] \tag{18}$$

With the equilibrium constants determined in the acidic region, log β_3 was found to be 26.80.

Thus, the distribution data indicate the existence of $\mathrm{NiOx_2HOx}$ as the extractable complexes and do not support the existence of $\mathrm{NiOx_22HOx}$[6] or $\mathrm{NiOx_2}$[7] in the organic phase. SEKIDO's data only prove the intimate interactions between simple nickel chelate, $\mathrm{NiOx_2}$, and oxine.

The $\mathrm{pH}_{\frac{1}{2}}$ values determined in the present work for $7.64 \cdot 10^{-5}$ M nickel (2.15 for 0.1 M and 3.13 for 0.01 M oxine) agree quite well with those determined by STARÝ (2.38 for 0.1 M and 3.16 for 0.01 M oxine)[7]. However, the distribution curves given in Fig. 3 become steeper with decreasing pH because oxine is transferred to the aqueous phase as oxinium ions, which do not interact with nickel or its oxine complexes, and a marked decrease in the distribution ratio with decreasing pH occurs. In such a case, it is not reasonable to presume the composition of the extractable complex only from change in the $\mathrm{pH}_{\frac{1}{2}}$ values.

The author wishes to thank Dr. JUN'ICHI KOBAYASHI for his helpful discussions and Miss HIDEKO KOIKE for her experimental aid.

SUMMARY

The equilibrium distribution ratios of nickel between aqueous 0.1 M perchlorate solutions and oxine solutions in chloroform (0.01–0.1 M) have been determined at 20°. The nickel–oxine complex extracted from acidic aqueous solutions and that from alkaline solutions have different absorbance spectra. A plot of log D_{Ni} − log $[\mathrm{HOx}]_o$ *vs.* pOx gave a single curve for three different concentrations of oxine (D_{Ni} = distribution ratio of nickel, $[\mathrm{HOx}]_o$ = equilibrium concentration of oxine in the organic phase, pOx = negative logarithmic concentration of oxinate anion) and it was concluded that nickel was extracted as $\mathrm{NiOx_2HOx}$. The equilibrium constants describing the extraction of nickel with oxine were determined.

RÉSUMÉ

Les coefficients de partage du nickel entre des solutions aqueuses de perchlorate 0.1 M et des solutions d'oxine dans le chloroforme (0.01 à 0.1 M) ont été déterminés à 20°. Le complexe nickel–oxine extrait en solution acide donne un spectre d'absorption différent de celui obtenu en solution alcaline. L'expression log D_{Ni} − log $(HOx)_o$ *vs.* pOx donne une simple courbe pour trois différentes concentrations d'oxine (D_N: coefficient de partage du nickel, $(HOx)_o$: concentration de l'oxine dans la phase organique à l'équilibre, pOx: concentration logarithmique négative de l'anion oxinate). Le nickel est extrait sous forme de $NiOx_2HOx$. On a déterminé les constantes d'équilibre de l'extraction du nickel avec l'oxine.

ZUSAMMENFASSUNG

Die Gleichgewichtsverteilungsverhältnisse von Nickel zwischen wässrigen 0.1 *M* Perchlorat-Lösungen und Oxin-Lösungen in Chloroform (0.01–0.1 *M*) wurden bei 20° bestimmt. Der Nickeloxinkomplex, der aus sauren Lösungen extrahiert wird, hat ein anderes Absorptionsspektrum als der Komplex, der aus alkalischen Lösungen extrahiert wird. Die Auftragung von logD_{Ni} − log $[HOx]_o$ gegen pOx ergab eine einzige Kurve für drei verschiedene Oxinkonzentrationen (D_{Ni}: Verteilungsverhältnis von Nickel, $[HOx]_o$: Gleichgewichtskonzentration des Oxins in der organischen Phase, pOx: negativer Logarithmus der Konzentration des Oxinat-Anions). Es wird angenommen, dass Nickel als $NiOx_2HOx$ extrahiert wird. Die Gleichgewichtskonstanten, die die Extraktion von Nickel mit Oxin beschreiben, wurden bestimmt.

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

THE EXTRACTION OF ZIRCONIUM(IV) FROM HYDROCHLORIC ACID SOLUTIONS BY TRICAPRYLMETHYLAMMONIUM CHLORIDE

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(Received August 19th, 1969)

For the extraction of metal ions from aqueous halide media, high-molecular-weight quaternary ammonium halides are generally more efficient than the corresponding secondary or tertiary amines. This probably results from the extraction mechanism of ion association to produce neutral species by the charge-neutralization of anionic metal complexes, causing an increase in the percentage extraction of metal. This property of the quaternary ammonium halides has recently been used to extract various metal ions from aqueous solutions in many analytical procedures[1]. In particular, WILSON *et al.*[2] have reported the results of studies on the extraction of Co(II), Zn(II), Fe(III), Tl(III), Hf(IV), Ta(V) and Mo(VI) from hydrochloric acid solutions with quaternary ammonium halides in 1,2-dichloroethane, and GOOD *et al.*[3] have carried out the extraction of Co(II), Fe(III), In(III) and Ga(III) from hydrochloric acid solutions with quaternary ammonium halides in toluene and chloroform. However, observations on the extraction of zirconium(IV) are few. The present study was therefore undertaken to obtain further information on the extraction of zirconium(IV) from hydrochloric acid solutions by a suitable high-molecular-weight quaternary ammonium chloride.

EXPERIMENTAL

Reagents

Tricaprylmonomethylammonium chloride (General Mills, Aliquat-336) was used as the quaternary compound. This was purified by washing several times with aqueous 0.05 *M* sodium chloride solution and *n*-hexane, and by heating at 90° and 1 mm Hg. The resulting material had the composition $R_3R'NCl$.

The zirconium chloride solution was prepared by dissolving zirconium chloride in hydrochloric acid solution of the required concentration. The other chemicals were of analytical-reagent grade.

Extraction and analytical procedures

Equal volumes (15 ml) of the quaternary compound in benzene and the aqueous solution containing hydrochloric acid were shaken for 10 min in 50-ml stoppered conical flasks in a water-bath thermostatted at the required temperature. After the separation of the aqueous and organic phases by centrifugation, zirconium in the organic phase was stripped with 0.5 *M* nitric acid, and then the partition coefficient (the ratio of the equilibrium concentration of zirconium in the organic phase to that in the aqueous phase) was obtained. Zirconium concentrations were determined by titration with EDTA and xylenol orange as indicator[4]; the sample solution was boiled with an excess of EDTA for about 15 min, cooled and adjusted to pH 1.6–2.0 with hexamethylenetetramine, and then back-titrated with bismuth nitrate solution. The acidity of the organic phase was determined by adding 2 ml to 25 ml of 75% ethanol and titrating with 0.02 *N* sodium hydroxide solution using a Beckman zeromatic pH meter. The chloride concentration in the organic phase was determined by Volhard's method with nitrobenzene, and the water content of the organic phase by Karl Fischer titration.

Infrared and n.m.r. spectral measurements

For the compounds freed from benzene by drying the organic phase at 90° and 1 mm Hg, the spectra were determined on a Japan Spectroscopic Co., Ltd. Model IR-S equipped with potassium chloride prisms, as a capillary film between thallium halide plates.

Nuclear magnetic resonance (n.m.r.) spectra were obtained in carbon tetrachloride solution on a Hitachi Perkin-Elmer Model R-20 high-resolution n.m.r. spectrometer utilizing a permanent magnet of 14,092 gauss. Tetramethylsilane was used as an internal reference.

RESULTS AND DISCUSSION

Extraction of hydrochloric acid

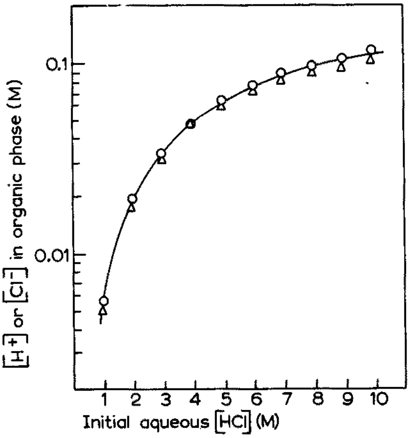
The variation in the acidity and the chloride concentration of the organic phase with the initial acidity of the aqueous phase in the extraction of hydrochloric acid solutions without zirconium by 0.082 *M* quaternary compound in benzene at 20° was examined to investigate the reaction between a benzene solution of the quaternary compound and aqueous hydrochloric acid solution. The results (Fig. 1) for acidity were corrected by subtracting the amount of hydrochloric acid extracted by benzene alone[5], and for chloride by deducting the chloride concentration contained in quaternary compound itself. Figure 1 shows that the acidity of the organic phase corresponding to the chloride concentration of the organic phase initially rises with the acidity of the aqueous phase; it reaches about 0.082 *M* at an initial hydrochloric acid concentration of 7 *M*, and then increases gradually at higher initial acidity. As this curve resembles that in the nitric acid–tributyl phosphate extraction system[6], it is inferred that most or all of the hydrochloric acid dissolves in the organic phase in the form of a 1:1 compound, $HCl \cdot R_3R'NCl$. This explanation is also supported by the following fact. In the extraction of hydrochloric acid from aqueous solutions of varying acidity with a benzene solution of quaternary compound at constant concentration at 20°, the acidity of the organic phase increases linearly with the acidity of the aqueous phase; the slopes of the lines are nearly unity (1.12 at hydrochloric acid concentrations of 6.8 and 10 *M*).

Consequently, it is thought that at low initial acidities, hydrochloric acid is extracted into the solution of the quaternary salt by the following reaction:

$$H^+(a) + Cl^-(a) + R_3R'NCl(o) \rightleftarrows HCl \cdot R_3R'NCl(o) \qquad (1)$$

where (a) and (o) represent aqueous and organic phases respectively.

The organic solution from the extraction at 8 *M* initial aqueous acidity was found to contain hydrochloric acid: quaternary compound: water in the mole ratio 1:1:4, indicating the formation of the compound $HCl \cdot R_3R'NCl \cdot 4H_2O$. However, since the water-saturated quaternary compound showed a mole ratio for $R_3R'NCl$: H_2O of 1:5, it is assumed that the compound $HCl \cdot R_3R'NCl \cdot 4H_2O$ is probably formed by replacing a water molecule in $R_3R'NCl \cdot 5H_2O$ with a molecule of hydrochloric acid.



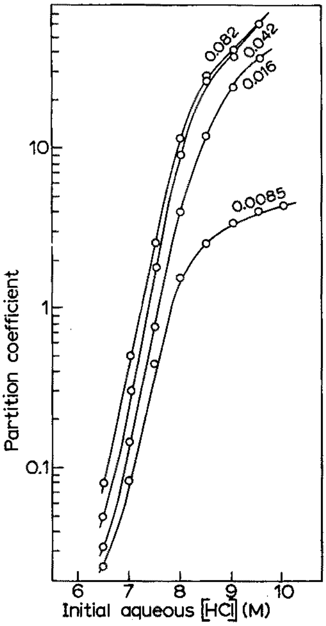


Fig. 1. Variations in acidity and chloride concentration of the organic phase with initial hydrochloric acid concentration in the aqueous phase, for the extraction of hydrochloric acid by 0.082 *M* quaternary compound in benzene. (○)H^+, (△)Cl^-.

Fig. 2. Extraction of zirconium(IV) from hydrochloric acid solutions by quaternary compound in benzene (numbers on curves are quaternary compound concentrations, *M*).

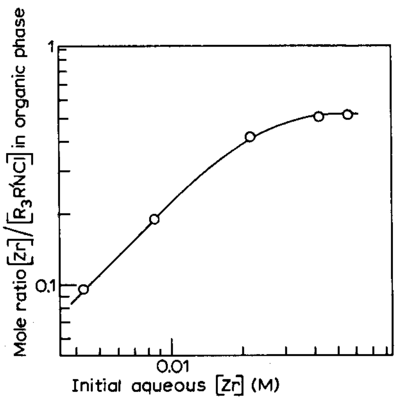
Dependence on hydrochloric acid concentration and extraction in presence of lithium chloride

The extraction of zirconium(IV) from aqueous solutions containing hydrochloric acid at an initial zirconium concentration of 0.0043 *M* with solutions of the quaternary compound in benzene at 20° was examined at different acidities. Figure 2 shows that the partition coefficient for zirconium increases steeply with aqueous acidity at concentrations above about 6 *M*.

The data for 0.082 *M* quaternary compound in benzene were compared with the results for zirconium chloride solutions (0.0043 *M*) containing 0.1 *M* hydrochloric acid and lithium chloride at various concentrations. With increasing initial total chloride concentrations of 7.0, 7.5, 8.0 and 8.5 *M*, the values of the partition coefficient were found to be 0.084, 0.447, 1.53 and 2.55 in the presence of hydrochloric acid only, and 0.043, 0.085, 0.269 and 0.673 in the mixture with lithium chloride. When the hydrochloric acid in the aqueous phase was partly replaced by lithium chloride, the partition coefficient was lower than that in the presence of hydrochloric acid alone at the same chloride concentration, presumably owing to hydrolysis[7], but its value rose with the total chloride concentration. This probably implies that the controlling factor is the total chloride ion concentration.

Dependence on concentration of zirconium

In the extraction of zirconium chloride solution containing 8 *M* hydrochloric acid with 0.042 *M* quaternary compound in benzene at 20°, the mole ratio of the zirconium concentration in the organic phase to the concentration of quaternary compound plotted as a function of the initial aqueous zirconium concentration approached a limiting value of 0.5 (Fig. 3). Furthermore, for those organic phases, the mole ratios of the increase in the chloride concentration and the water content to the concentration of zirconium extracted were determined; the former reached a limiting value of 6 and the latter decreased to zero as illustrated in Table I, suggesting that the zirconium complex formed in the organic phase does not contain water molecules.



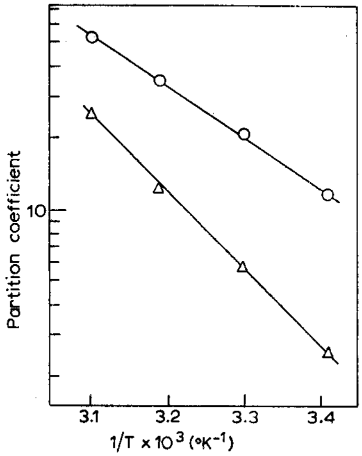


Fig. 3. Variation in zirconium concentration of the organic phase with initial zirconium concentration in the aqueous phase for the extraction of zirconium(IV) from 8.0 *M* hydrochloric acid solution by 0.042 *M* quaternary compound in benzene.

Fig. 4. Temperature dependence of the partition coefficient for the extraction of zirconium(IV) from hydrochloric acid solutions by 0.082 *M* quaternary compound in benzene. (△) and (○) represent 7.5 and 8.0 *M* HCl, respectively.

TABLE I

WATER CONTENT OF ORGANIC SOLUTIONS FROM THE EXTRACTION OF ZIRCONIUM CHLORIDE SOLUTIONS CONTAINING 8.0 *M* HYDROCHLORIC ACID WITH 0.082 *M* QUATERNARY COMPOUND IN BENZENE

Initial $(Zr)_{aq}$ (*M*)	$(H_2O)_{org}$ (*M*)	$(H_2O)_{org}/(Zr)_{org}$
0	0.33	—
0.0043	0.26	61
0.0086	0.22	26
0.022	0.12	6.0
0.043	0.024	0.67
0.056	0.011	0.29

Several investigators[3,8] have reported that in general, the log–log plots of the partition coefficient *vs.* the free quaternary salt concentration do not give reliable predictions for the stoichiometry of the extracted metal chloride–quaternary salt species. According to GOOD AND HOLLAND[9], the concentration of chloride ion greatly affects the slope of the curve since the solution of the quaternary salt has a higher dielectric constant than that of the amine hydrochloride, and in addition, if the amine hydrochlorides react with neutral metal chloride molecules to form the extracted species found in the organic phase, then it may be that the quaternary salts behave truly as liquid anion exchangers. In this extraction system, however, the plotted curves obtained for different initial acidities of 8.0, 8.5 and 9.0 M gave straight lines with slopes of 1.5, 2.1 and 2.4, respectively, at the low concentration of quaternary compound (<0.02 M), which suggests a second-power dependence of the partition coefficient on the solvent concentration.

Hence, the following equilibrium expression is given for the extraction of zirconium(IV) from hydrochloric acid solutions by the quaternary compound:

$$Zr^{4+}(a) + nCl^{-}(a) \rightleftarrows ZrCl_n^{4-n}(a) \qquad (2)$$

$$ZrCl_n^{4-n}(a) + (n-4)R_3R'NCl(o) \rightleftarrows (R_3R'N)_{n-4}ZrCl_n(o) + (n-4)Cl^{-}(a) \qquad (3)$$

It has been reported that in acidic solutions, zirconium(IV) ions are polymeric[10,11]; in 2.8 M hydrochloric acid the main species is a trimer[12], probably $Zr_3(OH)_6Cl_3^{3+}$ but the degree of polymerization increases with decreasing acid strength. Under the present experimental conditions, however, the species $ZrCl_6^{2-}$ in the aqueous phase[12] seems more likely to be the extractable one.

Temperature effect

The extraction of zirconium chloride solutions (0.0043 M) containing 7.5 and 8.0 M hydrochloric acid with 0.082 M quaternary compound in benzene at temperatures between 20 and 50° gave the results shown in Fig. 4, where the logarithm of the partition coefficient is plotted against the reciprocal of the absolute temperature. This shows that the partition coefficient increases with rising temperature, and the heat of reaction (change in enthalpy) in eqn. (3) is estimated to be -14.8 kcal/mole in 8 M hydrochloric acid. As this value is close to that for the energy of the hydrogen bond[13], it is inferred that the nature of the bonding in the organic phase is similar to that for hydrogen bonds.

Infrared study

The infrared spectrum of the compound prepared by drying the organic phase from the extraction of zirconium chloride solution (0.0558 M) containing 8.0 M hydrochloric acid with 0.082 M quaternary compound in benzene at 20° was compared with that from the extraction of 8.0 M HCl alone. The spectrum of the quaternary, water-saturated compound showed the OH-stretching band at 3400 cm^{-1} and the OH-bending band at 1620 cm^{-1}, arising from the composition of $R_3R'NCl\cdot 5H_2O$. For the spectrum of the extract of 8.0 M hydrochloric acid alone, the slight shifts in the lowering of the stretching frequency and the raising of the bending frequency from the corresponding frequencies of the quaternary compound suggest that the combined effect of hydrogen-bonding in the formation of $HCl\cdot R_3R'NCl\cdot 4H_2O$ is stronger than that in the bonding of the water molecules to the quaternary compound. In the zirconium complex, the absorptions caused by the OH-stretching and -bending bands almost disappear, indicating that the complex has no co-ordinated water molecule, in agreement with the result by the Karl Fischer titration (Table I).

N.m.r. spectra

The organic phases from the extraction of zirconium chloride solutions (0.0043 and 0.0086 *M*) containing 8.0 *M* hydrochloric acid with 0.082 *M* tricaprylmethylammonium chloride in carbon tetrachloride at 20° were examined by n.m.r. spectroscopy. Similar experiments were carried out for the extraction of an 8.0 *M* hydrochloric acid solution alone. The spectra are given in Fig. 5.

The n.m.r. spectrum for the quaternary compound shows a peak at 9.12 (τ value) in a triplet from the methyl protons, a strong peak at 8.69, assigned to methylenic protons, a peak at 6.56, from the methylenic and methyl protons attached

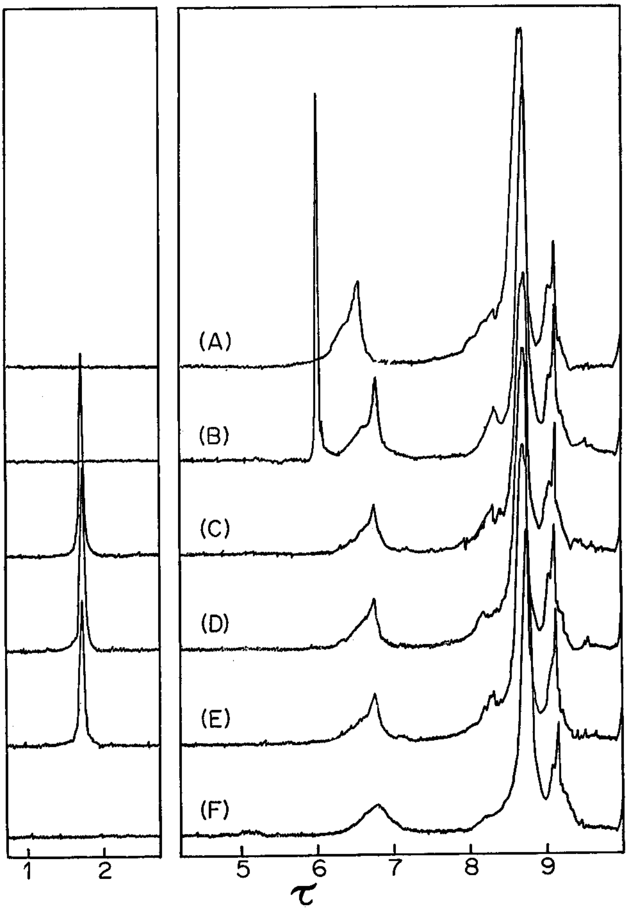


Fig. 5. N.m.r. spectra of the organic phases from the extractions of zirconium chloride solutions containing hydrochloric acid with quaternary compound in carbon tetrachloride. (A) Quaternary compound, (B) quaternary compound solution saturated with water, (C) 8.0 *M* HCl alone, (D) and (E) zirconium chloride solutions of 0.0043 and 0.0086 *M*, respectively, (F) zirconium compound, freed from benzene, dissolved in carbon disulfide.

to the nitrogen atom. For the quaternary compound saturated with water, the water proton resonance appears at 6.01 as a sharp peak, and at the same time the signal from the methylenic and methyl protons attached to nitrogen atom shifts to higher field at 6.77. In the extraction of 8.0 *M* hydrochloric acid alone, the water proton signal at 6.01 is shifted to lower field at 1.71. This may be ascribed to the formation of a stronger hydrogen bond in replacing part of $R_3R'NCl \cdot 5H_2O$ by $HCl \cdot R_3R'NCl \cdot 4H_2O$.

The spectra for the organic solutions from the extractions of zirconium chloride solutions show that the intensities of the water proton signal at 6.01 diminish with increase in the initial aqueous zirconium concentration. This corresponds to the fact that the water content of the organic phase decreases with the amount of zirconium extracted as indicated in Table I. However, since the use of carbon tetrachloride as a diluent for the quaternary compound involved the formation of a third phase in the extraction of aqueous solutions at higher initial zirconium concentrations, the complex prepared by drying the organic phase from the extraction of zirconium chloride solution (0.056 *M*) containing 8.0 *M* hydrochloric acid with 0.082 *M* quaternary compound in benzene was dissolved in carbon disulfide, and then its n.m.r. spectrum was determined. By this method, the water proton signals almost disappear, demonstrating the absence of water in the complex. Thus it is evident that the n.m.r. spectral results are in accord with the infrared data.

Effect of diluent

Table II shows representative results for various quaternary compound–organic solvent systems used in the extraction of zirconium chloride solution (0.0043 *M*) containing 7.5 *M* hydrochloric acid at 20°, in addition to some physical parameters of the solvents (dipole moment and dielectric constant)[14]. The extraction efficiency of the quaternary compound for zirconium is strongly influenced by the diluent, but no simple relationship holds between the extraction efficiency and a physical parameter of the organic solvent, although the extraction efficiency of a quaternary compound for zirconium would be expected to be enhanced by solvents of higher dielectric constant. When the extraction of zirconium(IV) from hydrochloric acid solutions with the quaternary compound was carried out with 1,2-dichloroethane as diluent,

TABLE II

PERCENTAGE OF ZIRCONIUM EXTRACTED FROM 7.5 *M* HYDROCHLORIC ACID SOLUTION WITH 0.082 *M* QUATERNARY COMPOUND IN VARIOUS ORGANIC SOLVENTS

Diluent	*Dipole moment*	*Dielectric constant*[a]	*Percentage extracted*
Benzene	0	2.284	72
Carbon tetrachloride	0.00	2.238	33
Toluene	0.39	2.379	64
Chloroform	1.15	4.806	60
Chlorobenzene	1.56	5.621	91
1,2-Dichloroethane	2.06	10.36	100
o-Dichlorobenzene	2.26	9.93	97
Nitrobenzene	3.99	34.82	99

[a] All values at 25° except for chloroform, carbon tetrachloride and benzene at 20°.

the following result was obtained: the dependence of the percentage extraction on the concentration of hydrochloric acid closely resembled that found with the quaternary compound in benzene; the variation in the composition of the organic phase as a function of the initial zirconium concentration in the aqueous phase suggested that the complex had a mole ratio of zirconium/chloride/quaternary compound of 1:6:2, indicating the stoichiometry $(R_3R'N)_2ZrCl_6$. It is therefore presumed that the mechanism of the extraction of zirconium(IV) does not depend on the kind of diluent.

We wish to thank Mr. F. OZAWA for assistance with n.m.r. measurement, and also would like to thank Professor M. L. GOOD of Louisiana State University in New Orleans for interest in this study.

SUMMARY

The partition of zirconium(IV) between hydrochloric acid solutions and organic solutions of a quaternary ammonium compound was investigated under different conditions. Infrared and high-resolution nuclear magnetic resonance spectroscopy were used to examine the composition of the extracted complex. The effect of organic solvent on the extraction was also examined. The mechanism of zirconium extraction is discussed.

RÉSUMÉ

On a examiné la répartition du zirconium(IV) entre des solutions acide chlorhydrique et des solutions organiques d'un composé ammonium quaternaire, dans diverses conditions. La spectroscopie dans l'infra-rouge et la spectroscopie de résonance magnétique nucléaire ont permis d'examiner la composition du complexe extrait. On a également examiné l'influence du solvant organique sur l'extraction. Une discussion est donnée sur le mécanisme d'extraction du zirconium.

ZUSAMMENFASSUNG

Die Verteilung von Zirkonium(IV) zwischen Salzsäure-Lösungen und organischen Lösungen einer quaternären Ammoniumverbindung wurde unter verschiedenen Bedingungen untersucht. Für die Ermittlung der Zusammensetzung des extrahierten Komplexes wurden Infrarotspektren und Kernmagnetische Resonanzspektren hoher Auflösung untersucht. Der Einfluss des organischen Lösungsmittels auf die Extraktion wurde ebenfalls geprüft. Der Mechanismus der Zirkoniumextraktion wird diskutiert.

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

ANION-EXCHANGE EQUILIBRIA IN ALKALINE MEDIA

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(Received September 29th, 1969)

KRAUS AND NELSON[1] made extensive studies of the absorption of metals from hydrochloric acid solutions by anion exchangers. Since their pioneering work, many other media have been studied, including hydrofluoric acid[2], nitric acid[3], and sulfuric acid[4], as well as mixtures of these acids with organic solvents[5].

Relatively little attention has been paid to anion exchange from alkaline media. A few studies have dealt with the group VIB and group VIIB elements in their highest oxidation states. Methods have been developed based on anion exchange from hydroxide solutions to separate perrhenate and molybdate[6], pertechnetate and molybdate[7], and perrhenate and tungstate[8]. Other work has been concerned with separation of non-metals such as fluoride and phosphate[9], iodide, iodate and periodate[10], borate and silicate[11], and sulfite, selenite and tellurite[12].

A more complete study of anion exchange from hydroxide media has been reported by TAKIURA AND TAKINO[13]. They determined selectivity coefficients for several singly-charged anions into a strongly basic anion exchanger in the hydroxide form. The selectivity coefficients represent the concentration equilibrium constants for the reaction

$$A^-_{\text{ext.soln}} + OH^-_{\text{resin}} = A^-_{\text{resin}} + OH^-_{\text{ext.soln}}$$

This paper reports a comprehensive study of anion exchange of the elements from sodium hydroxide solutions. Common anions and most metal ions which are soluble in highly alkaline solutions were included. Instead of determining selectivity coefficients, the distribution ratios, *D*, were measured

$$D = \frac{[E']_{\text{resin}}}{[E']_{\text{ext.soln}}} \qquad (1)$$

where E represents an element in a particular oxidation state or chemical form and [E′] represents the total analytical concentration of E in the given phase. Distribution ratios are specified for fixed concentrations of sodium hydroxide in the external solution (0.10, 1.00 and 10.0 *F* sodium hydroxide in this study) and therefore may be more useful than selectivity coefficients in devising analytical separation procedures.

EXPERIMENTAL

Equipment

All of the laboratory ware used to store, measure or transfer solutions was made of either polyethylene or polypropylene. Drainage of solutions from these containers

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is complete, since the plastic surfaces are not wetted by aqueous solutions. This allows use of the containers with various sodium hydroxide concentrations without recalibration. A 50-ml graduated cylinder was calibrated for use in all dilutions and volumetric transfers. It was found accurate and reproducible to better than ±0.1 ml.

Dry box

A carbon dioxide-free atmosphere was attained by working inside a dry box, continuously flushed with dry, CO_2-free nitrogen. A pair of small blower fans aimed at a tray filled with indicating soda lime served to insure the absence of carbon dioxide.

Reagents

Boiled, deionized water was used throughout. The sodium hydroxide solutions were prepared from J. T. Baker 50% Reagent, standardized against standard hydrochloric acid solution and stored in polyethylene bottles. All other reagents were of the highest purity available, usually reagent grade.

Resin

Amberlyst A-29 (Rohm and Haas, Philadelphia, Pa.), a macroreticular resin in the chloride form, was chosen because it is reputed to have high resistance to mechanical attrition and excellent stability in highly alkaline solutions, being superior in these respects to conventional gel resins[14]. The beads were unsized but appeared to be mostly in the 20–50 mesh range.

The resin was converted to the hydroxide form by placing a slurry of the material in a column and passing several bed volumes of 1 *F* sodium hydroxide through the beads at a flow rate of two bed volumes per h. The resin was then washed with water until the effluent was neutral, and dried for 3 days in the nitrogen atmosphere. A portion of the product was dried at 110° to determine the moisture content of the resin dried at room temperature.

The exchange capacities and degrees of conversion to the hydroxide form of each batch of anion exchanger were determined by standard methods[15]. The capacity was 2.7–2.8 meq/g resin in all cases. Six bed volumes of the sodium hydroxide solution produced 75% conversion to the hydroxide form, while ten bed volumes were required to reach 90% conversion. However, batches converted to different degrees within the 75–100% range gave similar results for several test ions.

Procedure

Aliquots of a stock solution of the element being studied were diluted with various amounts of sodium hydroxide and water. A 25.0-ml portion of each diluted solution was mixed with a 2-g sample of the resin (weighed exactly) in a capped bottle. The mixture was swirled at frequent intervals for 2 h to ensure that equilibrium was reached.

The solution was then separated from the resin by decantation or filtration through glass wool. This solution, and also a portion of the solution which had not contacted the resin, were then analyzed for the ion under consideration.

Analytical techniques

Radioisotopic tracers[16]. The radioisotopes obtained (New England Nuclear

Corp., Iso-Serve Division of Cambridge Nuclear Corp., Nuclear Science and Engineering Corp., and Baird-Atomic) were all specified by the supplier to be of at least 99% radiochemical purity.

γ-Emitters were assayed in a 5-cm diameter NaI(Tl) crystal well, with a Baird-Atomic Model 135 scaler-timer. Isotopes emitting only β-radiation were assayed by liquid scintillation in a Nuclear-Chicago Model 703P system (the separate standard run at each sodium hydroxide concentration eliminated the need for quench corrections) or by Geiger counting with the Baird-Atomic Model 135 scaler-timer and a thin-window detector tube.

Atomic absorption[17]. A Perkin-Elmer Model 290 spectrophotometer with air–acetylene flame was used for all measurements, except for silicon, which was determined on a Perkin-Elmer Model 303 Spectrophotometer with a nitrous oxide–acetylene flame.

Ion-sensitive electrodes. A Corning Model 10 pH meter was used to measure potentials against a S.C.E. Fluoride ion was determined by direct potentiometry with the Orion Research Model 94-09 Fluoride Electrode[18]. Other direct measurements were made with the Orion Research Model 92-81 Perchlorate Electrode[19,20]. In all cases aliquots of test solutions were neutralized with nitric or acetic acid and made up to a definite volume before the measurement. Separate calibration curves were made up for each ion at each sodium hydroxide concentration. The results can therefore be considered concentration distribution ratios, consistent with the results obtained by using the other measurement techniques.

Titrations[21]. Argentometric titrations were carried out with a standard silver nitrate solution to the potentiometric end-point. Chelometric titrations were carried out with standard EDTA solution to visual indicator end-points; the aluminum determination was a back-titration with zinc. Iodometric titrations were carried out with sodium thiosulfate solutions standardized against potassium iodate. Vanadate was titrated by standard iron(II) sulfate solution[22].

Spectrophotometry. A Beckman DU Spectrophotometer was used. Borate was measured by the carmine method[23], and nitrate by direct spectrophotometry at 220 nm[24].

RESULTS AND DISCUSSION

The distribution ratios (eqn. 1) are calculated from the experimental data by means of eqn. (2):

$$D = \frac{A_r/w}{A_s/V} \qquad (2)$$

where A_r and A_s are the amounts of the given species in the resin and external solution, respectively, w is the net dry weight (corrected for moisture content) of resin taken, and V is the volume of solution contacted by the resin. Since in most cases the concentration of the species in the resin was determined by difference, the calculations are best represented by eqn. (3):

$$D = \frac{(A_i - A_s)/w}{A_s/V} \qquad (3)$$

TABLE I

ANION-EXCHANGE DISTRIBUTION RATIOS FROM AQUEOUS SODIUM HYDROXIDE

Element	*Chemical form*	*Analytical technique*[a]	*Logarithm of distribution ratio in NaOH*		
			0.10 F	*1.00 F*	*10.0 F*
Re	ReO_4^-	ISE	3.96	4.06	2.54[b]
Cl	ClO_4^-	ISE	4.20	3.40	2.76[b]
I	I^-	AgT	3.70	3.34	2.04
Tc	TcO_4^-	GM	3.10	3.28	2.20
N	NO_3^-	Sp	2.54	2.26	2.01
I	IO_4^-	ISE	3.68	2.00	1.56[b]
Br	BrO_3^-	IT	2.24	1.75	1.03
C	CN^-	AgT	2.10	1.54	1.08
Mo	MoO_4^{2-}	AA	3.23	1.49	<0
Cr	CrO_4^{2-}	AA	2.89	1.34	<0
S	S^{2-}	AgT	1.54	1.04	1.23
Br	Br^-	AgT	1.04	1.00	1.20
S	SO_4^{2-}	LS	1.97	0.68	0.78
C	Acetate	LS	1.04	0.53	<0
Tl	Tl(I)	GM	<0	0.18	<0
Cl	Cl^-	AgT	1.00	0.15	<0
Se	SeO_3^{2-}	S	1.28	0.11	0.10
V	VO_3^-	RT	0.56	0.08	<0
Co	Co(II)	S	0.42	0.08	<0
I	IO_3^-	IT	0.75	0.00	<0
F	F^-	ISE	0.32	0.00	0.30
C	CO_3^{2-}	LS	1.25	<0	<0
Zn	Zn(II)	S	0.44	<0	<0
		AA	0.38	<0	<0
Si	SiO_3^{2-}	AA	0.38	<0	<0
Mg	Mg^{2+}	AA	0.23	<0	<0
Al	Al^{3+}	EDTA	<0	<0	0.42
Cu	Cu^{2+}	AA	—[c]	—[c]	0.18
Pb	Pb^{2+}	S	<0	<0	0.08
P	PO_4^{3-}	GM	0.08	<0	<0
As	AsO_2^-	IT	<0	<0	<0
B	Borate	Sp	<0	<0	<0
Ca	Ca^{2+}	EDTA	<0	<0	<0
Cs	Cs^+	S	<0	<0	<0
K	K^+	AA	<0	<0	<0
Mn	Mn(II)	S	—[c]	—[c]	<0

[a] AA = atomic absorption; AgT = argentometric titration; EDTA = EDTA titration; GM = Geiger-Muller counter; ISE = potentiometry with ion-selective electrode; IT = iodometric titration; LS = liquid scintillation counter; RT = direct redox titration; S = NaI(Tl) crystal scintillation counting; Sp = spectrophotometry.

[b] 5.0 *F* NaOH, electrode response unsatisfactory in case of 10.0 *F* NaOH.

[c] Insoluble.

in which A_i is the amount of the species in the external solution before it was brought in contact with the resin.

The results are summarized in Table I. The species are listed in the order of the logarithms of their distribution coefficients in 1.00 *F* sodium hydroxide. Values of log *D* less than 0 are not given as they are lacking in precision and not analytically significant.

The wide range of values of the distribution ratios is similar to that found in other media[1-5]. Several possibilities are suggested for separations of ions or groups of ions: nitrate from phosphate, bromate from iodate, zinc from calcium.

Specific comparisons with previously published data can be made in two instances. The selectivity order indicated by the selectivity coefficients of TAKIURA AND TAKINO[13] can be compared with the selectivities observed in the various sodium hydroxide solutions used in this work. This comparison is presented in Table II. Except for bromate and bromide, the results of the two studies are similar.

TABLE II

SELECTIVITY ORDERS FOR ANION EXCHANGE IN ALKALINE SOLUTIONS

TAKIURA AND TAKINO[13]	$BO_2^- \simeq F^- < AsO_2^- < IO_3^- < BrO_3^- \simeq Cl^- < CN^- < NO_3^- < Br^- < I^-$
This work: 0.1 *F* NaOH	$BO_2^- \simeq AsO_2^- < F^- < IO_3^- < Cl^- < Br^- < CN^- < BrO_3^- < NO_3^- < I^-$
This work: 1.0 *F* NaOH	$BO_2^- \simeq AsO_2^- < F^- \simeq IO_3^- < Cl^- < Br^- < CN^- < BrO_3^- < NO_3^- < I^-$
This work: 10 *F* NaOH	$BO_2^- \simeq AsO_2^- \simeq IO_3^- < Cl^- < F^- < BrO_3^- \simeq CN^- < Br^- < NO_3^- \simeq I^-$

TABLE III

DISTRIBUTION RATIOS FOR PERRHENATE AND MOLYBDATE IN SODIUM HYDROXIDE

$C_{NaOH}(F)$	*log D for perrhenate*		*log D for molybdate*	
	This work	*Literature*[6]	*This work*	*Literature*[6]
0.1	3.96	3.95	3.23	3.00
0.5			2.48	2.90
1.0	4.06	3.78	1.49	2.08
5.0	2.54	2.95	0.38	1.65
10.0		2.00	−0.26	1.65

The data of FISHER AND MELOCHE[6] are shown in Table III. The agreement between the distribution ratios for perrhenate is satisfactory but there is significant disagreement in the case of molybdate. The molybdate distribution data in this work give a straight line when log *D* is plotted against log C_{NaOH}, and the slope of this line is 1.8, which is close to the value of 2 predicted for an "ideal" exchange involving a doubly charged anion in trace concentration and a singly charged anion in macro concentration[25]. The agreement may be fortuitous, however, for the slopes of the log–log plots for most of the other species studied do not fit the prediction. It is possible that the differences between the data obtained in this study and those of the other workers are due to the use of the macroreticular resin in this work.

DISCUSSION

The results may be interpreted by considering the type of species actually present in each case and the extent of interaction between the species and the aqueous solution outside the resin. Ion–water interactions and the effects of the ion on the external water structure have been shown to be of considerable importance in determining selectivity orders for ion-exchange resins[25].

The first type includes those metal cations which do not form anionic complexes regardless of the hydroxide concentration and therefore remain in solution as cations and are not absorbed by the resin. Examples here would be the alkali metals and the alkaline earths.

Type two includes those metal cations forming—at high pH—anionic hydroxide complexes which are not absorbed into the resin to any great extent. Among the members of this group are Al(III), Si(IV), Co(II), As(III), and Zn(II). All precipitate from approximately neutral solutions, but redissolve in highly alkaline media. The neutral hydroxides or oxides are only weakly acidic; thus the anionic complexes are not at all acidic. The reason why these hydroxy anions are not absorbed by the resin, therefore, probably is that the anionic complexes are hydrogen bonded to the water molecules in the external solution. Thus they are not "rejected" by this phase into the resin.

A third type includes the small and medium sized anions of the non-metallic elements, such as fluoride, chloride, sulfide, acetate, and carbonate. The smallest of these ions are hydrated and therefore have small values of D. As the ions increase in size, the extent of hydration decreases and the distribution ratio increases. There is no sharp boundary separating this group from the next one.

The final type includes the anions of the very acidic oxyacids, which are completely dissociated in alkaline solution. They have no chance of hydrogen bonding to the water structure and are completely "rejected" into the ion-exchange resin phase. Examples of this type are perchlorate, perrhenate, periodate, molybdate and chromate. Very large simple anions, such as iodide, also belong in this group because of their size, low charge density, and inability to interact strongly with water.

The authors thank Dr. EUGENE T. MCGUINNESS for his aid with the liquid scintillation counting, Mr. HENRY STOBER for making the atomic absorption measurements on the silicon samples, and the Ion Exchange Department, Rohm and Haas Corporation, for furnishing samples of their macroreticular anion exchangers.

SUMMARY

The distribution ratios of a large number of species are reported for anion exchange from strongly alkaline solutions. The strongly basic macroreticular anion exchanger, Amberlyst A-29, was used. The elements in the oxidation states studied are classified by their ion-exchange behavior. The degree to which a species is absorbed by the resin depends on whether it exists in an anionic form and whether it is hydrated or forms hydrogen bonds with the water in the aqueous solution. While working with hydroxide solutions presents some practical problems, the sizeable differences in distribution coefficients for several groups of ions may be analytically useful.

RÉSUMÉ

On a examiné les coefficients de partage obtenus en solutions fortement alcalines, en utilisant un échangeur d'anions, l'Amberlyst A-29, fortement basique, macroréticulaire. Les éléments aux degrés d'oxydation étudiés sont classés selon leur comportement "échangeur d'ions". Cela dépend de leur forme anionique, s'ils sont hydratés ou s'ils forment des liaisons hydrogène avec l'eau, en solution aqueuse. Les différences dans les coefficients de partage, pour plusieurs groupes d'ions présentent un intérêt du point de vue analytique.

ZUSAMMENFASSUNG

Für eine grosse Anzahl von Spezies werden die Verteilungsverhältnisse für den Anionenaustausch in stark alkalischen Lösungen mitgeteilt. Es wurde der stark basische, hoch vernetzte Anionenaustauscher Amberlyst A-29 verwendet. Die Elemente in den untersuchten Oxidationsstufen werden auf Grund ihres Ionenaustauschverhaltens klassifiziert. Der Grad, mit welchem eine Ionenart vom Ionenaustauscherharz absorbiert wird, hängt davon ab, ob sie in einer Anionenform existiert und ob sie hydratisiert ist oder Wasserstoffbrücken mit dem Wasser in der wässrigen Lösung bildet. Wenn auch das Arbeiten mit Hydroxid-Lösungen einige praktische Probleme stellt, können doch die ziemlich grossen Unterschiede in den Verteilungskoeffizienten für die verschiedenen Ionengruppen analytisch von Nutzen sein.

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

STUDIES IN THE TETRAARYLBORATES

PART V. THE INFLUENCE OF SUBSTITUENTS ON THE STABILITY OF TETRAARYLBORATES

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(Received October 6th, 1969)

The limited stability of the tetraphenylborate anion, especially in acidic solution, is its principal disadvantage as an analytical reagent. This lack of stability prompted us to prepare several tetraarylborates containing substituent groups capable of producing a wide variety of structural effects, and to examine their analytical properties[1-4].

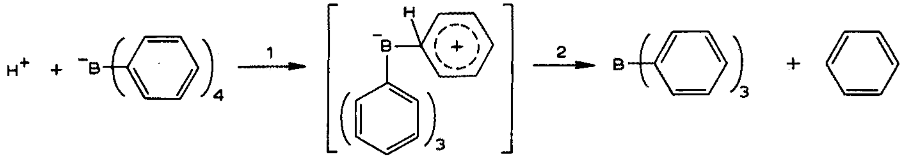
The nature and extent of these structural effects differ somewhat from those usually encountered, because the central atom is boron, a small atom (covalent radius 0.8 Å), which is usually considered a metalloid. The neutral boron atom forms trigonal planar bonds when linked to three similar small groups. However, large groups may sterically hinder each other and lead to non-coplanarity. Three-coordinated boron has a great tendency to acquire electrons and to assume a tetrahedral configuration with a coordination number of four. This tendency is sufficiently great to produce both electron-deficient structures, such as B_2H_6, and singly charged anions with four carbon–boron two-electron bonds, such as found in the tetraarylborates.

It was felt that inductive effects could be used to reduce the nucleophilic nature of the tetraarylborate and hence control the susceptibility to proton attack thereby stabilizing the anion and increasing its usefulness as an analytical reagent.

The tetraarylborates appear capable of decomposition by two general pathways: acid and photolytic processes. Both of these routes have been the subject of previous studies[5-7]. Other mechanisms may also be possible and could play a significant role in some cases.

It has been previously observed that sodium tetraarylborates containing electron-withdrawing substituents on the phenyl rings are relatively more stable than sodium tetraphenylborate in acidic solutions[1-4]; therefore, a more detailed study of the aqueous decompositions of several tetraarylborates seemed warranted.

Sodium tetraphenylborate is believed by some to decompose in acidic solutions according to the following mechanism[5,6]:



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The electrophilic attack by hydrogen ion at a carbon bonded to boron (step 1), is rate-determining and produces an unstable, protonated intermediate which rapidly decomposes into triphenylborane and benzene. Triphenylborane is very susceptible to air oxidation and decomposes further, but hydrogen ion is not involved. The mechanism suggests that electron-withdrawing substituents placed on the phenyl rings should decrease the rate of acid decomposition by making the phenyl rings less susceptible to electrophilic attack.

EXPERIMENTAL

An acidimetric method was developed and used to establish an order of acid stabilities which would be of use to the analytical chemist. The pH of an aqueous sodium tetraarylborate solution was adjusted so that a conveniently measurable decomposition rate would be established. The pH increased as the decomposition progressed. Standard 0.1 *M* hydrochloric acid was added, when the pH had increased 0.1 pH unit, to adjust the pH to its initially selected value. Intermittent addition of hydrochloric acid was continued, as necessary, to maintain a constant pH. Whenever possible, reactions were terminated before all of the tetraarylborate had decomposed. Residual tetraarylborate was precipitated as the cesium or potassium salt.

RESULTS AND DISCUSSION

Williams *et al.*[7] have studied the photolytic decomposition of sodium tetraphenylborate in aqueous solutions. This reaction may occur simultaneously with the acid decomposition; therefore, a comparison of the quantity of tetraarylborate recovered with the quantity of 0.1 *M* hydrochloric acid used in the acid decomposition gives the extent of non-acid decomposition which occurs under the reaction conditions. All decompositions were carried out at 50.0° in air.

The results of the decomposition experiments appear in Table I. The first column lists the sodium tetraarylborates which were studied. The second, the length of time during which the acid decompositions were followed, and the third, the pH at which a decomposition was carried out. The fourth gives the induction period, the length of time between the initial pH adjustment and a 0.1 pH unit rise, requiring the first addition of 0.1 *M* hydrochloric acid. The fifth lists the amount of tetraarylborate which would have been recovered if only acid decomposition had occurred,

TABLE I

ACID DECOMPOSITION RESULTS OF TETRAARYLBORATES

(2.000 mmole of tetraarylborate initially present in each case. All decompositions at 50°)

Compound	*Time (min)*	*pH*	*Induction (min)*	*Theoretically left (mmole)*	*Found (mmole)*	*% Decomposition by non-acid pathways*
$NaB(C_6H_5)_4$	365	3.0	3	0.200	0.125	4.0
$NaB(C_6H_4\textit{p}\text{-}Cl)_4$	20	3.0	7	—	—	—
$NaB(C_6H_4\textit{p}\text{-}CF_3)_4$	525	2.0	235	0.505	0.139	19.7
$NaB(C_6H_4\textit{m}\text{-}CF_3)_4$	588	3.0	227	1.787	1.731	20.8
$NaB(C_6H_4\textit{m}\text{-}F)_4$	(24 h)	2.0	—	2.000	1.207	100.0

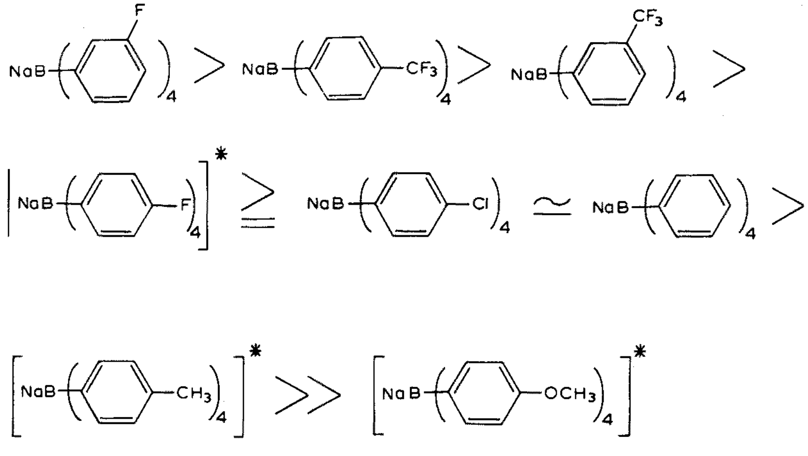
and the sixth is the amount of tetraarylborate actually recovered at the end of an experiment. The last gives the percent decomposition via non-acid pathways, calculated from the equation:

$$\frac{\%\ \text{non-acid}}{\text{decomposition}} = \frac{\text{theoretically left} - \text{actually found}}{\text{total quantity decomposed}} \cdot 100$$

Sodium tetraphenylborate undergoes only 4.0% non-acid decomposition, indicating that pH is the determining factor in any aqueous decomposition. The percentage non-acid decomposition increases for sodium tetraarylborates containing electron-withdrawing substituents at *m*- or *p*-positions on the phenyl rings. This increase is accompanied by a decreased susceptibility to acid attack. Sodium tetrakis(*p*-trifluoromethylphenyl)borate undergoes 19.7% non-acid decomposition, and sodium tetrakis(*m*-trifluoromethylphenyl)borate, 20.8%. These results suggest that tetraarylborates containing electron-withdrawing substituents are increasingly more susceptible to non-acid decompositions, or increased resistance towards acid attack makes the non-acid and acid decomposition rates competitive. Sodium tetrakis(*p*-chlorophenyl)borate has a longer induction period than sodium tetraphenylborate at pH 3.0 and 50.0°, 7 min *versus* 3 min, but decomposition proceeds at a rapid rate beyond this period. No residual sodium tetrakis(*p*-chlorophenyl)borate could be recovered.

The data indicate that sodium tetrakis(*m*-fluorophenyl)borate does not undergo acid decomposition at pH 2.0 and 50.0°. It does undergo non-acid decomposition, and this factor is of importance when considering the suitability of this reagent for a particular analysis.

The sodium tetraarylborates which have been studied can be placed in the following order of decreasing resistance toward acid attack:



Thus sodium tetrakis(*m*-fluorophenyl)borate is the reagent of choice for potassium(I), rubidium(I) or cesium(I) in acidic media.

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[*] These tetraarylborates are categorized in the above scheme according to their stability in acid media in accordance with information gained in previous studies[8,9]. Sodium tetrakis(*p*-methylphenyl)borate and sodium tetrakis(*p*-methoxyphenyl)borate are significantly less stable in acidic media than sodium tetraphenylborate.

The products of the mixed decompositions of sodium tetraarylborates in aqueous solutions were not conveniently isolatable from the complex mixtures; therefore, other approaches were needed to explore the role of substituent effects in the acid decompositions. An alternative consideration to the hydrogen ion attack on a phenyl group in the proposed mechanism would be an attack at the central boron atom. Steric factors appear to make this path improbable because the small boron atom is shielded by four substituted phenyl groups in a tetrahedral arrangement.

It appeared that boron-11 magnetic resonance spectra should yield information on the electron densities in the vicinity of the central boron atom. Boron-11 magnetic resonance spectra were obtained for a series of potassium tetraarylborates and appear to give some relevant information. Effects of the following substituents were studied[8]: *p*-OCH_3, *p*-H, *p*-F, *p*-Cl, *p*-Br, *m*-F and *p*-CF_3. The boron-11 chemical shifts of these compounds varied by only 1.1 p.p.m., from 6.7 to 7.8 p.p.m upfield from the $BF_3 \cdot OEt_2$ external standard. Thus it appears that substituents exhibiting a broad range of inductive effects have only a small influence on the electron density around the central boron atom in a tetraarylborate anion. Tetrahedrally coordinated boron has all sp^3 bonding orbitals occupied, and no other low-lying bonding orbitals are available for overlap with the phenyl ring π-electrons. Resonance effects would, therefore, be small, and electron density could only be shifted inductively via the boron to carbon σ bonds. This inductive effect would appear too small to alter the nucleophilic nature of the boron sufficiently to explain the broad range of acid stabilities displayed by the sodium tetraarylborates. However, substituents of varying electronegativity would vary the nucleophilic nature of the benzene nucleus and thus modify the decomposition pathway initiated by hydrogen ion attack at a phenyl ring and in this way could account for the wide range of stabilities.

The authors wish to express their appreciation to the National Science Foundation for partial support of this work under grant # G.P. 6857, and to Varian Associates for obtaining the boron-11 magnetic resonance spectra.

SUMMARY

The stability of sodium tetraarylborates toward acid attack can be enhanced by placing electron-withdrawing substituents at the *m*- or *p*-positions of the phenyl rings, thus rendering them less susceptible to electrophilic attack. A series of tetraarylborates has been studied, and the following order of decreasing resistance toward acid attack has been established: *m*-fluorophenyl > *p*-trifluoromethylphenyl > *m*-trifluoromethylphenyl > *p*-fluorophenyl ≧ *p*-chlorophenyl ≃ phenyl > *p*-methylphenyl ≫ *p*-methoxyphenyl. Sodium tetrakis(*m*-fluorophenyl)borate does not undergo acid decomposition at pH 2.0 and 50.0°, but it is partially decomposed under these conditions via other pathways.

RÉSUMÉ

On a examiné l'influence de substituants sur la stabilité de tétraarylborates vis-à-vis des acides. Une série de tétraarylborates a été étudiée; l'ordre suivant de résistance décroissante a été établi: *m*-fluorophényl > *p*-trifluorométhylphényl >

m-trifluorométhylphényl > *p*-fluorophényl ≧ *p*-chlorophényl ≃ phényl > *p*-méthylphényl ≫ *p*-méthoxyphényl.

ZUSAMMENFASSUNG

Die Stabilität der Natriumtetraarylborate gegenüber Säureangriff kann dadurch erhöht werden, dass an den *m*- oder *p*-Stellungen der Phenylringe elektronenentziehende Substituenten eingeführt werden, so dass sie weniger einem elektrophilen Angriff ausgesetzt sind. Bei den untersuchten Tetraarylboraten wurde folgende Reihenfolge abnehmender Resistenz gegenüber Säureangriff festgestellt: *m*-Fluorphenyl > *p*-Trifluormethylphenyl > *m*-Trifluormethylphenyl > *p*-Fluorphenyl ≫ *p*-Chlorphenyl ≃ Phenyl > *p*-Methylphenyl ≫ *p*-Methoxyphenyl.

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

INVESTIGATION OF *n*-BUTYL PHOSPHATE AS A SOLVENT FOR VOLTAMMETRY

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(Received October 9th, 1969)

A search of the literature reveals very few investigations in which *n*-butyl phosphate is suggested for use as a solvent in electrochemical studies. This is surprising in view of its wide acceptance as an extraction solvent. The two earliest studies were aimed at the isolation and determination of uranium. In 1956 FISHER AND THOMASON[1], realizing the problems generally associated with solvents of low dielectric constant, diluted their uranium extracts with high-dielectric solvents in order to obtain satisfactory polarographic results. In their paper they referred to some earlier, classified work done by LESTRANGE *et al.*[2], who with *n*-butyl phosphate as an extraction agent, carried out a polarographic study on uranium which had been isolated from solutions which were either 5 *N* in nitric acid or high in aluminum nitrate content. SPLITTGERBER[3] attempted to use *n*-butyl phosphate as a polarographic solvent but he reported no success until dilutions were made with N-methylacetamide. A brief preliminary study of polarography in *n*-butyl phosphate was recently described[4].

The exploratory work described herein includes an examination of the voltammetric behavior of several inorganic depolarizers, plots of the dependence of limiting currents on concentrations, and values of half-wave potentials of a large number of ions. The solvent used was 100% *n*-butyl phosphate. Potentiostatic control of the working electrode was maintained at all times. Conventional d.c., filtered d.c., and first derivative d.c. polarographic techniques were utilized in the study.

EXPERIMENTAL

Apparatus

Conventional and first derivative polarograms were obtained with the Oak Ridge National Laboratory Q-1988ES voltammeter (Indiana Instrument & Chemical Corporation, Bloomington, Ind.). This was modified by the addition of a voltage follower circuit[5] between the reference electrode of the cell and the reference electrode input of the voltammeter. The follower (Fig. 1) was made from a George A. Philbrick P2A operational amplifier and powered by a Philbrick PR-30 regulated power supply. This modification was necessary because of the wave distortion resulting from the

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current which must flow through the high resistance (often 1–10 megohms) of the Luggin capillary probe. This current charges the 1.0-μF capacitor which is necessary to prevent oscillation of the potential control amplifier of the Q-1988ES voltammeter. The purpose of this capacitor is to limit the bandpass or frequency response of the amplifier, thereby preventing the amplifier from attempting to follow the sharp current spike which exists at the moment of drop detachment[6]. In the absence of the high input impedance provided by the auxiliary voltage follower, this charging current can cause severe distortion of the apparent voltage range available.

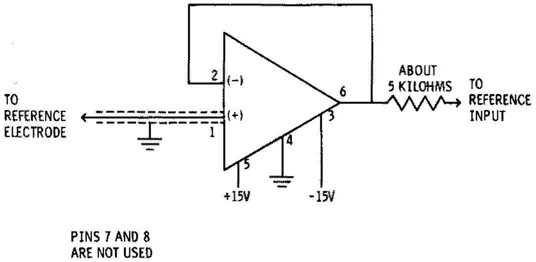


Fig. 1. Voltage follower for use with the ORNL Q-1988ES voltammeter.

Voltages from the scan generator were measured with a Leeds & Northrup Model 7645 potentiometer and monitored with a Non-Linear Systems Model 4312 digital voltmeter. A Sargent SRL recorder with a one-second full-scale pen response was used to record the polarograms.

The electrolysis vessel has been described[6] and incorporated a platinum wire counter electrode, an aqueous saturated calomel reference electrode in a Luggin configuration, and a dropping mercury electrode (d.m.e.). The counter electrode was located on the side of the working electrode opposite to the reference electrode and was maintained at a nominal distance of 4 mm from the d.m.e. Horizontal working electrode–reference electrode distances were measured and monitored with a cathetometer. The minimum distance between these two electrodes was maintained and it was always less than one millimeter.

All measurements were made at room temperature (25°) and time measurements were made with an electric timer.

Reagents

Prepurified nitrogen was used for deaeration and for maintaining an inert atmosphere over the test solution. Thallium(I) nitrate (Fairmount Chemical Co., Inc., Newark, N.J.) was used. All other depolarizers and carrier electrolytes were perchlorate salts (G. Frederick Smith Chemical Company) with the exception of the tetrabutylammonium perchlorate which was synthesized in the laboratory[7]. All salts were dried for 2–10 days over phosphorus pentoxide under vacuum.

The *n*-butyl phosphate was used without purification (Matheson Coleman & Bell, Superior grade, b.p. 143–145° at 5 mm). No reducible impurities were present in the particular lots of solvent chosen for use. However, some bottles of the solvent did contain appreciable amounts of water and other contaminants of an unidentified nature. These bottles of solvent were discarded because completely erratic drop behavior was noted otherwise. Lots containing water gave small reduction waves at about −1.6 V *vs.* aqueous S.C.E. One acceptable lot of solvent was treated by vacuum distillation and the middle one-third was chosen for use in order to determine whether some slight improvement in behavior could be noted. Distillation yielded a solvent judged to be insignificantly different from the original sample, provided that the lot chosen had given acceptable drop behavior before distillation. Unsatisfactory lots of solvent were easily purified by vacuum distillation.

Resistance measurements

Specific resistivities of several electrolyte solutions were measured in a cell with a cell constant of 0.100 cm^{-1} and an Industrial Instruments RC16B2 conductance bridge. Before measurements the cell was washed in acetone, 2 *M* hydrochloric acid and distilled water, and air-dried. The results of the measurements are shown in Table I. Some of the values shown may be approximate since, in a few cases, resistances changed slowly unless the solutions were carefully prepared in a nitrogen-purged dry box and equilibration allowed to proceed for some time. Uptake of atmospheric moisture was rapid in those cases. In all instances, there was good agreement with results obtained from comparative dielectric measurements made with a Sargent-Jensen high-frequency titrator and its 180-ml cell.

TABLE I

SPECIFIC RESISTIVITIES OF SELECTED ELECTROLYTES IN *n*-BUTYL PHOSPHATE

Compound	*Concentration (M)*	*Specific resistivity·10^{-3} (ohm-cm)*
$Ba(ClO_4)_2$	0.10	58
	0.50	5.3
$NaClO_4$	0.10	14
	Satd. (< 0.5)	1.4
$Mg(ClO_4)_2$	0.10	10
	0.50	2.4
NH_4ClO_4	0.10	12
	Satd. (< 0.5)	1.8
$(Bu)_4NClO_4$	0.10	10
$LiClO_4$	0.10	4.9
	0.50	1.1
$Sr(ClO_4)_2$	0.10	15
	0.50	2.8
$KClO_4$	Satd. (< 0.1)	330
$Ca(ClO_4)_2$	0.10	4.4
	Satd. (< 0.5)	3.5
Solvent	—	~16,000

With the high-frequency titrator and by comparisons with various other pure solvents at 25°, a dielectric constant of 8.0 for the samples of *n*-butyl phosphate was obtained by interpolation. This agrees with an earlier reported[8] value of 7.95 obtained at 30°.

RESULTS AND DISCUSSION

Several factors must be considered in the choice of a carrier electrolyte for use in a nonaqueous solvent. The most obvious of these is the bulk solubility of the electrolyte, *i.e.*, physical solubility which leads to a clear solution. A second and more significant factor in a voltammetric investigation is whether or not the bulk solubility is actually accompanied by the generation of a large number of charge carriers in the solvent medium. This is important to insure that the overall rate-controlling step is diffusion. In addition, the avoidance of serious errors in potential measurements depends, to a large extent, on the resistivity exhibited by the solvent–electrolyte system. A third factor of some importance is that of the hygroscopicity of the solvent–electrolyte mixture since the water content must be kept at a minimum during such investigations. Finally, and this factor is always of importance regardless of whether water or some other substance is to be the solvent, the voltage span available for electrolysis is frequently strongly dependent upon the nature of the cation and the anion of the carrier electrolyte.

These requirements suggested a logical order of the investigations necessary to decide on possible carrier electrolytes: bulk solubility, resistivity, behavior towards moisture uptake, and, finally, electrochemical characterization of the salt.

Qualitatively, among the salts chosen for study, the tetraalkylammonium iodides were the least soluble in *n*-butyl phosphate. The Group I metal chlorides exhibited the expected trend with lithium chloride the most soluble. It dissolved to an extent greater than 0.1 *M*. This latter solution and that of calcium chloride, while being soluble, gave cloudy solutions. The perchlorates of Groups I and II decreased in solubility and resistivity with increasing cationic size, with the single exception of calcium(II). The perchlorates of Group II generally gave cloudy solutions.

Lithium perchlorate was the most rapidly soluble salt examined and it yielded clear solutions that were stable indefinitely provided that they were stored under nitrogen. Table I shows the results of resistance measurements made on some of the more soluble salts examined for their potential use as carrier electrolytes. A measurement of the resistivity of the pure solvent is included for comparison only. The actual resistivity is probably much higher but it is out of the range of the conductance bridge and cell combination used for the other measurements. It is interesting to note that the resistivity of saturated potassium perchlorate in *n*-butyl phosphate is similar to that of a sample of good-quality distilled water.

From these observations, it was concluded that lithium perchlorate would be one reasonable choice for a carrier electrolyte. The cathodic decomposition potentials of several possible choices are listed in Table II. The anodic decomposition potential of 0.10 *M* lithium perchlorate solutions in *n*-butyl phosphate was +0.60 V *vs.* aqueous S.C.E. This value, coupled with the cathodic decomposition potential of −2.0 V *vs.* aqueous S.C.E. gives a very satisfactory range of useful electrolysis voltages in this medium.

Because of their expected higher solubility, perchlorate salts of the depolarizers were chosen except in the case of thallium(I). Solubilities were sufficient to allow preparation of millimolar solutions in all cases except for zirconyl and thallium(III). This latter behavior may be attributable to incompletely dried salts whose ions were solvated by water to an appreciable extent before their introduction into the organic solvent. Such a condition could make difficult the necessary ion–dipole interactions between lattice ions and *n*-butyl phosphate molecules so necessary to accomplish bulk solubilization. In the case of thallium(III), the solution turned pale brown while

TABLE II

DECOMPOSITION POTENTIALS OF CARRIER ELECTROLYTES IN *n*-BUTYL PHOSPHATE

Compound[a]	E_d (*V vs. aqueous S.C.E.*)
NH_4ClO_4	−1.59
$Ba(ClO_4)_2$	−1.78
$NaClO_4$	−1.79
$Mg(ClO_4)_2$	−1.82
$Sr(ClO_4)_2$	−1.82
$LiClO_4$	−2.01
$Ca(ClO_4)_2$	−2.03

[a] 0.10 *M* solutions.

stirring to dissolve the salt. This color change was largely reversible, however, on the prolonged passage of dry, pure nitrogen gas through the solution. In addition, in almost every solution examined, regardless of the depolarizer present, the half-wave potential observed initially tended to shift slightly in the positive direction upon prolonged passage of the dry gas. These observations bear out the possibility that even though initially there may have been present surface or bound water on much of the salt introduced, this can slowly be removed by prolonged sparging with the dry nitrogen. The shift observed upon sparging was as great as 100 mV in the case of aluminum(III). Only in the case of cadmium(II) was a small shift in the negative direction noted.

TABLE III

HALF-WAVE POTENTIALS FOR LEAD(II) IN 0.50 *M* $LiClO_4$ IN *n*-BUTYL PHOSPHATE–WATER MIXTURES

Volume % water	$E_{\frac{1}{2}}$ (*V vs. aqueous S.C.E.*)
0.3	−0.30
0.9	−0.28
1.8	−0.26
2.7	−0.25

Table III shows the effect of the addition of water on the recorded half-wave potential of lead(II). The existence of the trend is significant in connection with the previous discussion. The magnitude of the shift is probably too great to attribute solely to changes in uncompensated iR-drop through the solution. This iR-drop occurs through the working electrode-to-reference electrode distance but this distance was at all times maintained at less than 1 mm. It is the iR-drop through this small volume element of the solution that conventional potentiostatic devices cannot control or eliminate. A change of the magnitude observed is not very likely if one considers the reasonably low specific resistivity of the solvent–carrier electrolyte system used. Separate, independent measurements of resistance through the volume element of solution in question virtually rule out the possibility that a bulk resistance effect is totally responsible for the shifts in half-wave potentials encountered upon the addition or removal of water from the system. Since the shifts observed were frequently different for different ions, while the water content of the solvent and changes in the water content brought about by sparging were essentially constant, not all of a given shift can be attributed to changes in junction potential.

The foregoing observations strongly suggest that changes in activities, or double-layer structures, or even significant changes in reaction mechanisms, are operating to bring about the observed shifts in half-wave potentials. They also, therefore, tend to indicate, first, that the traces of water present may be specifically associated with the ion groups present in the system, second, that these associations can have an important influence on the localized interactions between the electrode surface and the ion groups within the applied field, and third, that the passage of dry, inert gas may, through some kind of shift in chemical equilibrium, slowly change the magnitude or mode of interaction between the ion groups and their associated water because of a reduction in the total water content of the system.

The fact that in some cases considerable difficulty was encountered in obtaining reproducible half-wave potentials is understandable in light of the previous discussions. The observations made are also consistent with the solubility of *n*-butyl phosphate in water compared to that of water in *n*-butyl phosphate. The latter is *ca.* 150 times greater than the former when calculated on a molar basis[9]. This suggests that *n*-butyl phosphate molecules cannot readily displace adsorbed or bound water on the crystals in the dissolving process and that the water–water or water–ion interactions are much too strong to be greatly or easily influenced by the bombarding *n*-butyl phosphate molecules. Thus, if a salt is not adequately dried before use, solubilization may be made more difficult than it otherwise would be.

The 150-fold greater solubility of water in *n*-butyl phosphate than of *n*-butyl phosphate in water also partially accounts for the observation that all solutions in this solvent quickly absorbed water from the air if a dry atmosphere was not used. This tendency was, of course, enhanced by the considerable concentration of carrier electrolyte in the solvent and its affinity for water. In the case of 0.10 *M* calcium chloride solutions, the uptake of water from air was so great that a second, aqueous phase was formed shortly after exposure to the air.

The addition of water to the solvent–electrolyte system in the absence of a depolarizer yielded a wave at −1.60 V, which was attributed to the reduction of water. In solutions containing improperly dried salts, this same wave appeared, thus indicating a sensitive test for the presence of small amounts of water in the system.

Observed half-wave potentials of the salts studied are shown in Table IV. Cd(II), Pb(II), Zn(II), Mn(II), Zr(IV), and Tl(I) solutions gave well formed, single waves. The half-wave potential observed for cadmium(II) was shifted to a more

TABLE IV

OBSERVED VALUES OF HALF-WAVE POTENTIALS IN 0.10 *M* $LiClO_4$ IN *n*-BUTYL PHOSPHATE

Depolarizer	$E_{\frac{1}{2}}$ *(V vs. aqueous S.C.E.)*	*Depolarizer*	$E_{\frac{1}{2}}$ *(V vs. aqueous S.C.E.)*
Hg(0)	(+0.60) (anodic)	Cr(III)	−0.61; −1.24
Ag(I)	+0.57	Zn(II)	−0.70
Cu(II)	+0.30	Ni(II)	−1.0
U(VI)	−0.22; −0.50	Fe(III)	See text
Tl(I)	−0.27	In(III)	−1.18
Pb(II)	−0.31	Al(III)	−1.20
Cd(II)	−0.37	Zr(IV)	−1.20
Tl(III)	−0.58; −1.20	Mn(II)	−1.36

negative value, −0.48 V, in 0.50 *M* lithium perchlorate. This was also noted in the cases of zinc(II), nickel(II), and aluminum(III) since the substitution of 0.50 *M* for 0.10 *M* lithium perchlorate resulted in the more negative values of −0.76 V, −1.1 V, and −1.47 V, respectively. These significant shifts can be attributed to normal changes in junction potentials or, more likely in these instances, either complexation between the depolarizer and the carrier electrolyte or a significant change in the charge density of the electroactive species in the vicinity of the electrode. This latter mechanistic effect will be more common in those cases involving irreversible reduction or significant adsorption behavior. Both of these cases can be expected to be of some importance in a low-dielectric solvent such as *n*-butyl phosphate. Complexation cannot be completely ruled out as a contributing effect[10]. Changes in activity of the solvent brought about by increased carrier electrolyte concentrations could result in significant displacement of the complexation equilibria which describe either the depolarizer–solvent or the depolarizer–carrier electrolyte interactions.

The nickel wave was reasonably well formed but the half-wave potential was not very reproducible. The wave appeared to be highly irreversible as evidenced by comparison of the slope of the wave front with that of, say, zinc. The silver wave came very close to that caused by the oxidation of mercury and the value given in Table IV is best described as the decomposition potential. Copper(II) exhibited an occasional maximum of unknown origin.

The uranium(VI) salt gave two closely spaced waves of equal height which suggests reduction first to uranium(V) and then to uranium(IV). The first derivative mode of the voltammeter is useful in the separation of such waves provided that the scan rate is not so great that it introduces significant distortion. The overall reduction process appeared to be adsorption-controlled for uranium(VI), since the limiting current was proportional to the height of the mercury column. Adsorption control was also noted in the case of lead(II).

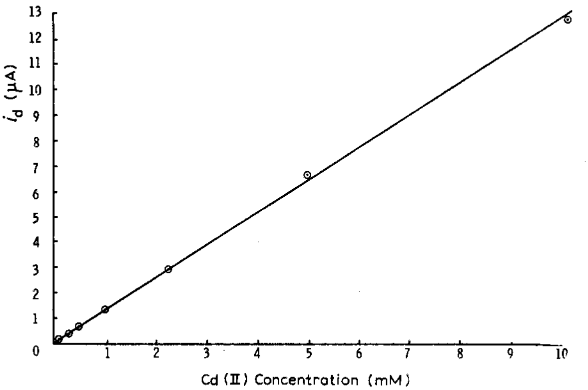
Aluminum(III) gave a wave with a significant maximum which was removed on the addition of 4 drops of a 0.4% solution of Triton X-100 in *n*-butyl phosphate. Small, occasional maxima on the chromium(III) and indium(III) waves were removed in the same manner.

Chromium(III) exhibited two distinct waves. These waves, which appeared at −0.61 V and −1.24 V with a current ratio of 1:2, are due to reductions to the Cr(II) state and the Cr(0) state, respectively.

Traces of thallium(I) present in the thallium(III) salt gave the expected wave at −0.27 V. Also there was always present the principle wave in the thallium(III) solutions at −1.20 V. Occasionally, however, a wave also appeared at −0.58 V. When this wave did appear, it would decrease in height on standing while the wave at −0.27 V would increase until the two waves merged into one. This occurred with no observable change in total limiting current measured at −1.40 V. Although adsorption phenomena can account for such behavior, explanation must await additional experimentation involving both thallium(I) and thallium(III). The value of −1.20 V for the half-wave potential indicates that the normally high oxidizing potential of thallium(III) is very much subdued in this solvent, even to the point of rendering it more difficultly reducible than thallium(I).

The waves obtained from iron(III) solutions are unusual in that it was possible to obtain what looked like one wave at −1.16 V on the conventional d.c. polarogram but which could be separated into three distinct, closely spaced waves of equal height when the filtered d.c. polarogram or the first derivative d.c. polarogram was examined. Such behavior merits further study. The three waves appeared repeatedly at -1.06, -1.22, and -1.31 V. Proposal of an iron(I) state is much too facile and it is more plausible to propose the existence of the iron(III) or iron(II) oxidation state in two different solvation configurations or environments or to suspect adsorption phenomena.

Notice should be made of the fact that $E_{\frac{1}{2}}$ for iron(III) is made much more negative in this solvent than it is in water. This very negative value, along with those which are also apparent in the cases of thallium(III) and aluminum(III), is in agreement with the observation that in water solutions most cations, especially those with greater positive charges, tend to be more difficultly reduced at lower hydrogen ion concentrations. If one assumes that the only source of hydrogen ion in this instance is the trace of water which is inevitably present, then it is understandable that there would be observed in *n*-butyl phosphate a shift of the half-wave potential to a more negative value. These magnitudes of shift almost certainly are not entirely due to changes in liquid junction potential. As in the cases of most organic depolarizers, they can be partly attributed to changes in activity or mechanistic behavior of the depolarizers.



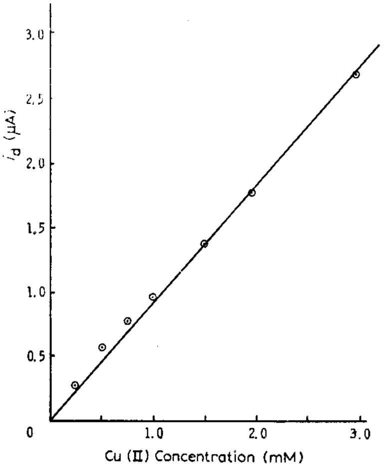


Fig. 2. Influence of cadmium concentration on diffusion current in 0.10 *M* $LiClO_4$ in *n*-butyl phosphate.

Fig. 3. Influence of copper concentration on diffusion current in 0.10 *M* $LiClO_4$ in *n*-butyl phosphate.

Figures 2, 3, and 4 illustrate the kinds of working curves that may be obtained with *n*-butyl phosphate as the solvent. The plots for various concentrations of the perchlorates of cadmium(II), copper(II), and uranium(VI) exhibit satisfactory linearity. The measured diffusion or limiting currents are considerably less than those to be expected from water solutions of the same concentrations owing to the much higher viscosity of *n*-butyl phosphate (3.2 centipoise at 25°).

Figure 5 shows typical electrocapillary curves obtained in *n*-butyl phosphate. The electrocapillary maximum occurs at about -0.20 V in both 0.10 *M* and 0.50 *M* lithium perchlorate. The shape of the curves indicates that no significant adsorption phenomena have occurred in the absence of depolarizers.

The authors are grateful for the support of this work by the National Science Foundation (Grant GY-4090).

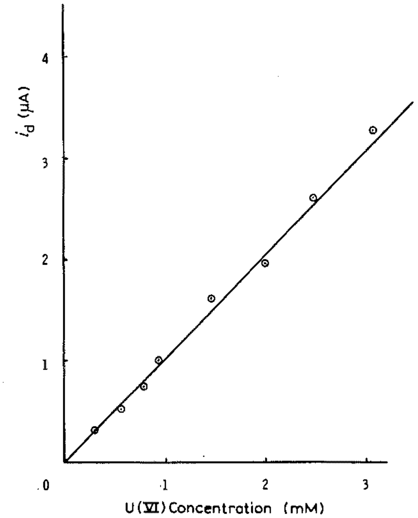


Fig. 4. Influence of uranyl concentration on diffusion current in 0.10 M $LiClO_4$ in n-butyl phosphate.

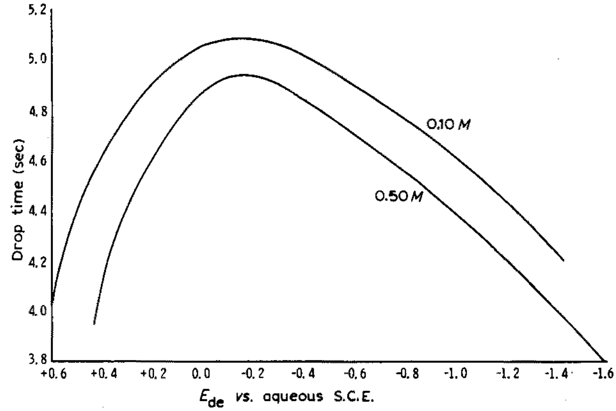


Fig. 5. Electrocapillary curve for mercury in 0.50 M and 0.10 M $LiClO_4$ in n-butyl phosphate.

SUMMARY

Controlled potential voltammetric investigations of several depolarizers and potentially useful carrier electrolytes have been carried out in n-butyl phosphate. Half-wave potentials have been measured and analytical calibration curves have been constructed. Most depolarizers gave well formed waves but adsorption behavior was present in some cases. The influence of water was very significant.

RÉSUMÉ

Une étude est effectuée sur l'utilisation du *n*-butyl phosphate comme solvant en voltammétrie. On a ainsi mesuré les potentiels de demi-vague et tracé des courbes d'étalonnage analytiques. La plupart des dépolarisants ont donné des vagues bien définies, mais parfois avec des adsorptions. L'influence de l'eau est très importante.

ZUSAMMENFASSUNG

Es wurden potentialkontrollierte voltammetrische Untersuchungen verschiedener Depolarisatoren und möglicherweise günstiger Trägerelektrolyte mit *n*-Butylphosphat ausgeführt. Die Halbstufenpotentiale wurden gemessen und analytische Eichkurven erstellt. Die meisten Depolarisatoren gaben gut ausgebildete Stufen, jedoch traten in einigen Fällen Adsorptionseffekte auf. Der Einfluss von Wasser war sehr ausgeprägt.

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

A SPECTROPOLARIMETRIC TITRIMETRIC METHOD FOR THE DETERMINATION OF CADMIUM, MERCURY, LEAD AND BISMUTH

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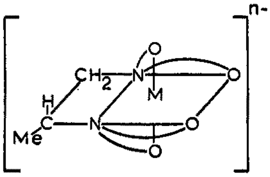
(Received October 6th, 1969)

Spectropolarimetric titrimetry is a new analytical technique first described by KIRSCHNER AND BHATNAGAR[1] in 1963. A photoelectric polarimeter is used to monitor the change in optical rotation of a solution upon the addition of titrant. A recognizable change in optical rotation of the solution must occur at the titration end-point. Applications of this technique to the determination of metal ions have been limited.

Only three metal ion–ligand titrations have been described to date: the titration of L-(+)-histidine monohydrochloride with copper(II) chloride[1], the titration of disodium EDTA with zinc(II) nitrate using L-(+)-histidine as the asymmetric indicator[2], and the titration of D-(−)-1,2-propylenediamine with nickel(II) perchlorate[2].

The titrimetric procedures are rapid, simple, and require no external indicators to mark the end-point. A strong stereospecific chelating agent, D-(−)-1,2-propylenediaminetetraacetic acid (D(−)PDTA), was selected as the titrant. It has been estimated that the free energy difference caused by a methyl-acetate interaction in the D*-isomer (structure II) compared to the L*-isomer (structure I) approaches 3 kcal/mole[3], giving a minimum of 99.9% stereospecific reactions. The greater stability of the L*-isomer assures complete stereospecificity and therefore maximum rotations are obtained for the metal–chelate complexes. Comparisons of the available stability constants indicate larger stability constants for racemic PDTA than EDTA for many metals in solution[4]. The present paper is part of a systematic study of the potentialities and limitations of a spectropolarimetric titrimetric technique with D(−)PDTA, which appears to offer many advantages over present techniques. In a subsequent paper, titrations of aluminum, indium and thallium will be described.



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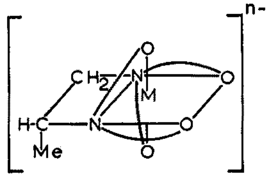

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EXPERIMENTAL

Apparatus

The spectropolarimetric titrations were carried out at room temperature with a Perkin-Elmer model 141 photoelectric polarimeter. This polarimeter has a digital readout of the observed optical rotation to 0.001°. The radiation sources are a sodium vapor lamp and a mercury vapor lamp. These sources, with appropriate filters in a filter wheel, permit the selection of the following wavelengths: 589 nm, 578 nm, 546 nm, 436 nm, and 365 nm. The polarimeter cell used in this study was a 5-ml flow-through cell with optically inactive glass endplates. The polarimeter cell had a path length of 10 cm. The flow-through cell was connected to a stirbar pump, the titration vessel, with two 20-cm portions of Tygon tubing. Mallinckrodt QD connectors were placed in the Tygon tubing to facilitate handling and cleaning. The stirbar pumps were fabricated from 75-ml and 125-ml Erlenmeyer flasks, with two attached glass tubes, one at the bottom center, and the other 1/5 the distance up the side. The titration vessel was positioned over a magnetic stirrer and a magnetic stirbar, placed in the vessel, pumped the solution through the polarimeter cell. With this apparatus, the response time was less than 5 sec. All pH measurements were made with an Orion model 801 digital pH meter and a Sargent combination glass electrode.

Reagents

All solutions were prepared from analytical reagent grade chemicals, with demineralized water, and stored in polyethylene bottles.

D-(−)-1,2-Propylenediaminetetraacetic acid monohydrate was prepared by a modification of the method of DWYER AND GARVAN[5]. A 0.5% aqueous solution of D-(−)-1,2-propylenediaminetetraacetic acid monohydrate gave $[\alpha]_{589}^{22} = -46.9°$. Approximately 0.25 mole of the acid monohydrate and 0.50 mole of sodium hydroxide pellets were dissolved in 500 ml of water. The resultant straw-colored solution was filtered through a fine sintered-glass filter. The Na_2D(−)PDTA solution was then standardized by titrating it against both a standard zinc solution, with eriochrome black T as the indicator[6], and against standard lead solutions, with xylenol orange as the indicator[6]. The titer and optical rotation of the standard Na_2D(−)PDTA solutions remained constant during a 4-month period.

The pH 10 buffer was prepared by dissolving 280 g of ammonium chloride in water, adding 568 ml of concentrated ammonium hydroxide, and diluting the resultant solution to 1 l. The pH 5 buffer was prepared by dissolving 102 g of sodium acetate in 500 ml of a solution containing 28 ml of glacial acetic acid and diluting the resultant solution to 1 l. Solutions titrated below pH 2 were adjusted with concentrated nitric acid.

Standard solutions of EDTA were prepared from G.F. Smith dried primary-standard $Na_2H_2EDTA \cdot 2H_2O$ (G.F. Smith Chemical Company).

The standard cadmium(II) solution was prepared from cadmium perchlorate and standardized by EDTA titrimetry[7]. The standard mercury(II), lead(II) and bismuth(III) solutions were prepared from the nitrate salts, with dilute nitric acid to prevent hydrolysis, and were standardized by EDTA titrimetry[8,9]. The dilute solutions were prepared by volumetric dilutions of the standardized stock solutions. The molar concentration ratio of Na_2D(−)PDTA titrant to metal ion solution was approximately 50:1.

Spectropolarimetric procedure

The flow-through cell was attached to the stirbar pump and aliquots of the standard metal ion solutions were pipetted into the titration vessel. The appropriate volume of water and buffer was then added to the titration vessel. This was done to simplify dilution corrections. With the aid of a magnetic stirrer, the solution was then pumped through the flow-through cell positioned in the polarimeter. The digital readout of the polarimeter was then zeroed with the metal ion–buffer solution serving as a blank. The solution was then titrated with a relatively concentrated solution of Na_2D(−)PDTA, from a 5-ml microburet readable to ± 0.001 ml. After the addition of each increment of titrant, the polarimeter digital readout was allowed to stabilize, which usually required 15 sec. Generally, it was only necessary to obtain five points before and five points after the end-point for each determination. The data points near the end-point were not generally useful, because of slow approaches to equilibrium, and the titration plots were rounded near the equivalence point. The spectropolarimetric end-point was determined graphically by plotting optical rotation *versus* volume of titrant and extrapolating the two straight lines to the end-point on large graph paper readable to 0.001 unit. For greatest accuracy, the rotational readings should be corrected for the change in volume during the course of the spectropolarimetric titration. The corrected optical rotation is obtained as follows: (corrected optical rotation) = (observed optical rotation) $\cdot (V/V_i)$ where V_i is the initial and V is the actual volume of the solution at that titration point. Table I lists the optimum conditions for the spectropolarimetric titrations of these metals with D(−)PDTA.

TABLE I

CONDITIONS FOR SPECTROPOLARIMETRIC TITRATIONS

Metal	*Wavelength (nm)*	*Buffer used*[a]	*Comments*
Cd^{2+}	365	pH 10[a]	pH 5 buffer was used for the titration of the dilute solution of Cd^{2+}.
Hg^{2+}	365	pH 5[a]	A 75-ml titration vessel was used for the most dilute Hg^{2+} solution.
Pb^{2+}	365	pH 5[a]	A 75-ml titration vessel was used for the most dilute Pb^{2+} solution.
Bi^{3+}	365	pH 1[b]	A 75-ml titration vessel was used for the most dilute Bi^{3+} solution.

[a] 25 ml was the optimal amount.
[b] 1–2 ml of nitric acid was optimal.

RESULTS

In order to obtain results of analytical significance, there should be markedly different optical rotations of D(−)PDTA and the metal complex at the wavelength chosen for the spectropolarimetric titration. If the optical rotations are not significantly different, the end-point becomes indistinct and there is a large uncertainty in the value obtained for the extrapolated end-point. Another criterion in the selection of the wavelength used in a spectropolarimetric titration is that the absorbance of the solution should be low. Highly absorbing solutions decrease the sensitivity of the polarimeter, leading to errors in the measured rotation. The optical rotatory dispersion and absorption spectra for the metal complexes and D(−)PDTA were examined to determine the wavelength giving the maximum optical rotational difference with suitable transmittance. The absorption of D(−)PDTA was never the limiting factor in the selection of a suitable wavelength. The molecular rotations for the metal complexes and D(−)PDTA were obtained by preparing 0.01 *M* solutions and adjusting them to the desired pH value with acetic acid–sodium acetate buffer, ammonia–ammonium chloride buffer or concentrated nitric acid. Measurements were made at ambient temperatures in a 10-cm polarimeter cell (Table II). Most of the metal complexes exhibited their maximum rotations at 365 nm, while D(−)PDTA had a relatively small rotation at 365 nm. Consequently, 365 nm was chosen as the analytical wavelength for these titrations.

TABLE II

MOLECULAR ROTATIONS OF THE Cd^{2+}, Hg^{2+}, Pb^{2+} AND Bi^{3+} COMPLEXES OF D(−)PDTA AND D(−)PDTA

Metal complexed	*589 nm*	*578 nm*	*546 nm*	*436 nm*	*365 nm*	*pH*
Cd^{2+}	+392	+410	+470	+832	+1377	9.67
Hg^{2+}	+804	+843	+968	+1757	+3010	2.94
Pb^{2+}	+1530	+1605	+1848	+3404	+5963	5.00
Bi^{3+}	+1171	+1228	+1419	+2668	+4862	0.98
D(−)PDTA	−159	−165	−186	−305	−455	2.01
D(−)PDTA	−117	−122	−138	−230	−354	5.07
D(−)PDTA	−183	−191	−215	−355	−534	10.04

The protonation or deprotonation of D(−)PDTA changes its structure and charge, resulting in optical rotational dependence on pH. A spectropolarimetric titration of D(−)PDTA with standard sodium hydroxide was carried out to determine the effect of pH on the molecular rotations of D(−)PDTA. The molecular rotation of D(−)PDTA increases from pH 2 to pH 3 and remains nearly constant until it increases again to a maximum at pH 7.5. After pH 7.5, the molecular rotation decreases very rapidly. The sharp inflections in this pH–molecular rotation curve occur at the approximate p*K* values for the racemic PDTA. The curve is nearly linear over the pH range of 3–5.5 and, consequently, the use of the acetic acid–sodium acetate buffer is highly advantageous. The maximum buffering capacity of this buffer lies in this range and the acetate ion is a very poor complexing agent. It was found that 25 ml of the acetic acid–sodium acetate buffer, 25 ml of the ammonia–ammonium chloride and 1–2 ml of the nitric acid were satisfactory for titrations at pH values of 5, 10, and 1, respectively.

The relationship between the observed optical rotation of an optically active complex in solution and the concentration and nature of optically inactive ions present is not well known[10]. It was found in this study that ammonium, perchlorate, sulfate, chloride and acetate ion had no effect on the observed end-point.

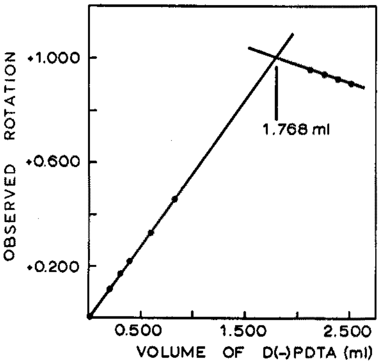
Table III gives the results of the metal ion titrations. Each reported value is the average of at least three individual titrations. The range of the average deviations from visual chelometry for the four metals titrated was 0.05–0.29%. The maximum

TABLE III

RESULTS OF SPECTROPOLARIMETRIC TITRATIONS

Metal	*Metal taken (mg)*	*Metal found (mg)*	*Deviations*	
			(mg)	*(%)*
Cd^{2+}	108.6	108.5 ± 0.1	−0.1	−0.09
	10.86	10.83 ± 0.01	−0.03	−0.28
Hg^{2+}	205.8	205.4 ± 0.1	−0.4	−0.19
	20.58	20.59 ± 0.02	+0.01	+0.05
	2.058	2.054 ± 0.001	+0.004	−0.19
Pb^{2+}	207.8	207.5 ± 0.3	−0.3	−0.14
	20.72	20.78 ± 0.02	+0.06	+0.29
	2.072	2.071 ± 0.005	−0.001	−0.05
Bi^{3+}	208.2	208.1 ± 0.1	−0.1	−0.05
	1.040	1.037 ± 0.005	−0.003	−0.29

time required for the titration and graphical evaluation of the data was in no case greater than 15 min. Typical titration graphs for the spectropolarimetric titrations of the most concentrated cadmium(II) and lead(II) determinations are presented in Figs. 1 and 2. All of the titration graphs for the *ca.* 0.10 *M* stock solutions of cadmium(II), mercury(II), bismuth(III) and lead(II) have the same general shape. From the molecular rotations of the metal complexes at 365 nm in Table II, it can be seen that the observed optical rotational axes for the titration graphs of mercury(II) and bismuth(III) are intermediate between those of cadmium(II) and lead(II). Figure 3 shows the spectropolarimetric titration of the most dilute solution of lead(II) analyzed. It can readily be seen from Fig. 3 and Table II that mercury(II), bismuth(III) and lead(II) can be determined in solutions approximately one order of magnitude more dilute than cadmium(II) at 365 nm. In each graph, the first straight-line portion of the curve corresponds to the formation of the metal complex of D(−)PDTA and the second straight-line section corresponds to the excess D(−)PDTA titrant. The



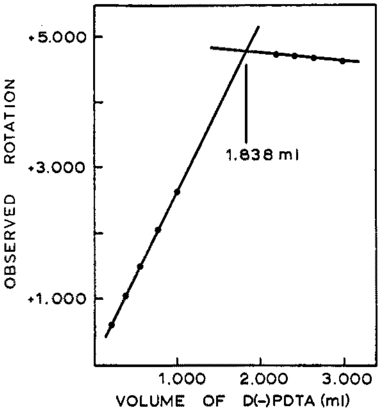


Fig. 1. Spectropolarimetric titration of 0.09664 *M* cadmium(II) at pH = 10 and 365 nm.

Fig. 2. Spectropolarimetric titration of 0.1003 *M* lead(II) at pH = 5 and 365 nm.

intersection of these two straight lines is the end-point of the titration. In the spectropolarimetric titrations of the most dilute solutions of mercury(II), lead(II) and bismuth(III), it was necessary to use a 75-ml titration vessel to increase the rotation of the solution.

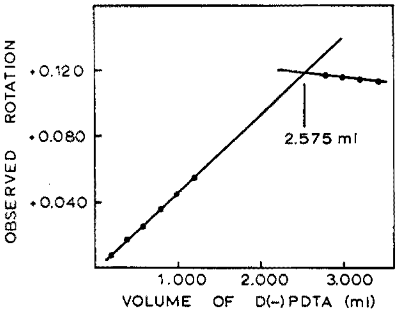


Fig. 3. Spectropolarimetric titration of $5.002 \cdot 10^{-4}$ M lead(II) at pH = 5 and 365 nm.

DISCUSSION

The main advantages of spectropolarimetric titrimetry are its range of accurate analysis, versatility, simplicity, rapidity, and applicability in solutions of high electrolyte concentrations. Moreover, the many exotic indicators and associated buffers to control the pH for sharp indicator color transitions can be eliminated, as can the subjectivity associated with the establishment of various visual end-points.

Since the titrant is stereospecific in its reactions with these metal ions, maximum rotations are obtained. The titrant and complexes formed serve as self-indicators and permit the use of the maximum quantitative pH range for each metal. The determination of the end-point is obtained through relative measurements of optical activity and hence is capable of achieving greater precision than visual methods. In the construction of the titration plots, the best straight line is drawn through a number of experimental points in order to minimize the spectropolarimetric error associated with each point. The extrapolated end-point is not adversely influenced by high electrolyte concentrations; therefore, this technique is suitable for use with many separation schemes, whereas chelometry based on indicator color transitions, whether visually or spectrophotometrically monitored, can give erroneous results in certain solutions of high electrolyte concentrations[11].

The range of accurate spectropolarimetric analyses at 365 nm with the Perkin-Elmer 141 was 10^{-1}–10^{-3} M for cadmium(II) and 10^{-1}–10^{-4} M for lead(II), mercury(II) and bismuth(III).

This work was supported by The Robert A. Welch Foundation Fellowship Grant A-262. The authors wish to thank Paul E. Reinbold for his assistance with illustrations.

SUMMARY

Spectropolarimetric methods of analyses for cadmium(II), mercury(II), lead(II) and bismuth(III) were developed, based on the stereospecific ligand, D-(−)-1,2-propylenediaminetetraacetic acid (D(−)PDTA). The optical rotation of the solution was monitored with a photoelectric polarimeter to determine the end-point of the titration. The titrant and metal complexes formed are optically active and serve as self-indicators. Since D(−)PDTA is stereospecific in its reaction with these metals, maximum utilization of the optical rotation of these complexes is achieved. The observed optical rotation is linear with respect to concentration of the metal complexes, hence straight-line extrapolations to the end-point are possible. The effects of pH, wavelength, and dilution are discussed and the optimum conditions for the determination of each metal are established. The range of accurate spectropolarimetric analyses at 365 nm with the Perkin-Elmer 141 spectropolarimeter was 10^{-1}–10^{-3} M for cadmium(II), and 10^{-1}–10^{-4} M for lead(II), mercury(II) and bismuth(III). The range of the average deviations from visual chelometry for the four metals titrated was 0.05–0.29%.

RÉSUMÉ

On propose des méthodes spectropolarimétriques pour l'analyse du cadmium(II), du mercure(II), du plomb(II) et du bismuth(III), basées sur le ligand stéréospécifique l'acide D-(−)-1,2-propylènediaminotétracétique (D(−)PDTA). Le titrant et les complexes métalliques formés sont optiquement actifs et servent de self-indicateurs. La rotation optique observée est linéaire par rapport à la concentration des complexes métalliques. On a examiné l'influence du pH, de la longueur d'onde et de la dilution; les conditions optima pour le dosage de chaque métal ont été établies. Le domaine pour des analyses spectropolarimétriques précises à 365 nm avec l'appareil Perkin-Elmer, spectropolarimètre 141 est de 10^{-1} à 10^{-3} M pour le cadmium et 10^{-1} à 10^{-4} M pour plomb, mercure et bismuth.

ZUSAMMENFASSUNG

Es wurden spektropolarimetrische Analysenmethoden für Cadmium(II), Quecksilber(II), Blei(II) und Wismut(III) unter Verwendung des stereospezifischen Liganden D-(−)-1,2-Propylendiamintetraessigsäure (D-(−)PDTA) entwickelt. Für die Bestimmung des Endpunktes der Titration wurde die optische Rotation der Lösung mit einem photoelektrischen Polarimeter gemessen. Der Titrant und die gebildeten Metallkomplexe sind optisch aktiv und dienen als Selbstindikatoren. Da D(−)PDTA mit diesen Metallen stereospezifisch reagiert, wird die optische Rotation dieser Komplexe maximal ausgenutzt. Die beobachtete optische Rotation verläuft linear mit der Konzentration der Metallkomplexe; daher sind geradlinige Extrapolationen bis zum Endpunkt möglich. Die Einflüsse von pH-Wert, Wellenlänge und Verdünnung werden diskutiert und die optimalen Bedingungen für die Bestimmung eines jeden Metalls festgestellt. Der Bereich genauer spektropolarimetrischer Analysen, die bei 365 nm mit dem Spektropolarimeter Perkin-Elmer 141 ausgeführt wurden, war 10^{-1}–10^{-3} M bei Cadmium(II) und 10^{-1}–10^{-4} M bei Blei(II), Quecksilber(II) und Wismuth(III). Die durchschnittlichen Abweichungen von der visuellen Chelatometrie lagen bei den vier titrierten Metallen bei 0.05–0.29%.

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Anal. Chim. Acta, 49 (1970) 497–504

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

THE DIRECT SPECTROPOLARIMETRIC TITRATION OF ALUMINUM, INDIUM, AND THALLIUM WITH D-(—)-1,2-PROPYLENEDIAMINETETRAACETIC ACID

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(Received October 13th, 1969)

Spectropolarimetric metal ion–ligand titrimetry has already been described[1,2]. Basic to this new analytical technique is the use of a photoelectric polarimeter to monitor the change in optical rotation of a solution on addition of titrant. The system must be chosen so that a recognizable change in optical rotation occurs near the titration end-point. The spectropolarimetric titrimetric procedures are rapid, simple, and require no external indicators to mark the end-point. In a previous paper[3], methods for the titration of cadmium, mercury, lead and bismuth ions were described, and methods for the spectropolarimetric determination of lanthanide metals have also been developed[4].

For all these titrations the strong stereospecific chelating agent, D-(—)-1,2-propylenediaminetetraacetic acid (D(—)PDTA), was selected as the titrant because of its chelating strength and its intrinsic optical activity[5]. The characteristics and advantages of this chelating agent and its metal chelates have been discussed previously[3]. The present work forms part of a systematic study of the potentialities and limitations of a spectropolarimetric titrimetric technique with D(—)PDTA. In this paper, an extension of the technique to the direct determination of the Group IIIA elements is described.

EXPERIMENTAL

Apparatus

The equipment used was exactly the same as that described previously[3]. All titrations were made at 365 nm.

Reagents

All solutions were prepared from analytical reagent-grade chemicals, with demineralized water, and stored in polyethylene bottles.

D(—)PDTA was prepared as described previously[3] with certain modifications to increase the overall yield[6]. An aqueous 0.5% solution gave $[\alpha]_{589} = -47.2°$, comparing favorably with the literature value of $[\alpha]_{589} = -47.0°$. The standard solution was prepared and standardized as described in the previous paper[3].

EDTA standard solutions were prepared from dried primary-standard disodium dihydrogen ethylenediaminetetraacetate dihydrate (G. F. Smith Chemical Co.).

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* Present address: The Dow Chemical Company, Freeport, Texas.

The aluminum(III), indium(III) and thallium(III) perchlorate solutions were prepared from the hydrated perchlorates (G. F. Smith Chemical Co.). The aluminum(III) solution was standardized by an EDTA back-titration method, with standard zinc chloride solution[7]. The indium(III) solution was standardized with the standard EDTA at a pH of 2.4, with PAN as the indicator[8]. The thallium(III) solution was deep brown in color owing to the presence of colloidal Tl_2O_3. This solution was standardized at 90° at pH 4.5 in acetic acid–sodium acetate buffer (at which point the colloidal Tl_2O_3 dissolves and the brown color disappears) with the standard EDTA, with xylenol orange as the indicator[9].

pH 3.5 and 5.0 buffers were prepared from glacial acetic acid and sodium acetate.

Spectropolarimetric titrimetric procedures

The general technique for the titration and for establishment of the titration curve were the same as those described previously; volume corrections were applied as before[3]. Details of the titration conditions for the different metals are given below.

Indium. Place an aliquot of the metal solution to be determined in the titration vessel, add 25 ml of pH 5.0 buffer solution and dilute the sample with sufficient deionized water to bring the total volume to 100 ml. (A large amount of buffer was required to ensure that the D(−)PDTA complexes or the excess D(−)PDTA did not change coordination states or ionic species during the course of the titration.) Insert the flow-through polarimeter cell into the cell compartment and set the optical digital readout of the polarimeter to zero.

Titrate the solution with a relatively concentrated solution of Na_2D(−)PDTA, from a 5-ml microburet readable to ±0.001 ml. The molar concentration ratio of the Na_2D(−)PDTA titrant to the metal ion solution was *ca.* 50:1.

Aluminum. Proceed as described for indium, but use a pH 3.5 buffer and run the titrations in the jacketed titration cell at 50° to facilitate rapid attainment of equilibrium.

Thallium. Proceed as described for indium, but first treat each aliquot with hot acetic acid to dissolve the suspended Tl_2O_3 and then use pH 3.5 buffer.

RESULTS

The molecular rotations for the metal complexes and D(−)PDTA were obtained by preparing 0.01 M solutions and adjusting them to the desired pH value with acetic acid–sodium acetate buffer. Measurements were made at ambient temperatures in a 10-cm polarimeter cell (Fig. 1). The metal complexes exhibited their maximum rotations at 365 nm, while D(−)PDTA had a relatively small rotation at 365 nm; titrations were therefore carried out at this wavelength.

The protonation or deprotonation of D(−)PDTA changes its structure and charge, resulting in a dependence of optical rotation on pH. Previous studies[3] have shown that the molecular rotation of D(−)PDTA is essentially constant over the pH range 3.0–5.5, hence acetic acid–sodium acetate buffers are suitable, as discussed previously[3].

Figure 2 shows a titration plot for aluminum. This is a typical spectropolarimetric titration plot where both the metal complex and the titrant have negative molecular rotations with the titrant having a smaller negative molecular rotation than the complex. The aluminum determinations were titrated at pH 3–4 and at 50° to facilitate rapid attainment of equilibrium. Aluminum can be determined at ambient temperatures, but equilibrium is reached very slowly. Figure 3 shows a titration plot for thallium. This is a typical spectropolarimetric titration graph where the metal complex has a positive molecular rotation and the titrant has a negative molecular rotation. The titration plots for indium are very similar to those for thallium. In each graph, the first straight-line portion of the curve corresponds to the formation of the metal complex of D(−)PDTA and the second straight-line section corresponds to the excess D(−)PDTA titrant.

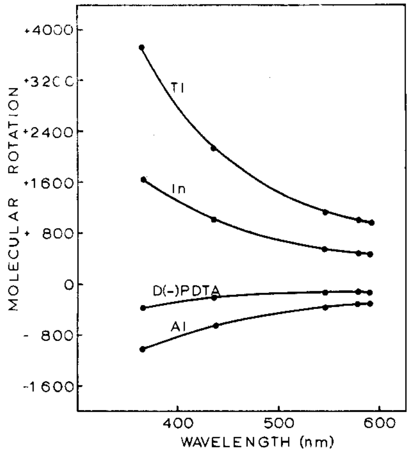
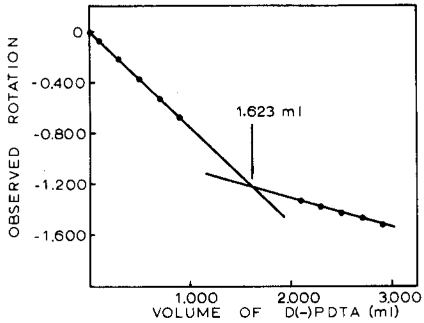


Fig. 1. Optical rotatory dispersion spectra of aluminum, indium, and thallium complexes of D-(−)-1,2-propylenediaminetetraacetic acid.



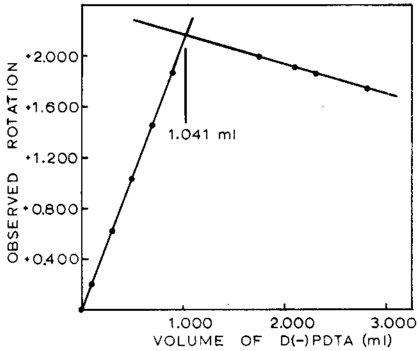


Fig. 2. Spectropolarimetric titration of aluminum at 365 nm.

Fig. 3. Spectropolarimetric titration of thallium at 365 nm.

Table I gives the results of Group IIIA metal ion titrations. Each spectropolarimetric value reported is the average of at least three individual titrations. The range of the average deviations from conventional EDTA titrations for the three metals determined was 0.11 to 0.18%. The maximum time required for a spectropolarimetric titration and the graphical evaluation of the data for that titration was 15 min.

TABLE I

RESULTS OF SPECTROPOLARIMETRIC TITRATIONS

Metal	*Metal taken (mg)*	*Metal found (mg)*	*Deviation*	
			(mg)	*(%)*
Al	26.45	26.42 ± 0.02	−0.03	−0.11
In	109.8	109.6 ± 0.10	−0.2	−0.18
Tl	125.8	125.6 ± 0.76	−0.2	−0.16

DISCUSSION

The spectropolarimetric titration of aluminum was done directly at ambient or slightly elevated temperature, whereas most visual determinations are done by back-titration or under near boiling conditions with exact pH control for direct titrimetry. The direct titrations with acetic acid–sodium acetate buffer at very high temperatures evolve acetic acid fumes which are extremely corrosive to the mucous membranes; also, the handling of these solutions is hazardous. In order to obtain results of analytical significance in the back-titration methods, the pH must be controlled exactly and the titration performed rapidly because of the complex equilibria of these systems, the non-reversibility of many of the visual indicators, and the necessity to observe sharp visual transitions. Many of the visible chelometric methods for indium and thallium have the same disadvantages of slow kinetics near the equivalence point, and usually either back-titration or direct titration in very hot solutions is necessary.

From Figs. 1–3, it can be seen that with the sensitivity of the equipment employed, it should be possible to determine concentrations lower by one order of magnitude.

The results described in the present paper confirm the general advantages of the spectropolarimetric titration method, which were outlined in the previous paper[3]. Particular benefits are gained by its application to the determination of the metals discussed in this present paper, and these further emphasize the usefulness of the method.

This work was supported by The Robert A. Welch Foundation Fellowship Grant A-262. Appreciation is expressed to The Dow Chemical Company for its grant of a leave of absence for the summer of 1968 to D. L. C. This study was presented at the 157th National Meeting of the American Chemical Society on April 18, 1969 at Minneapolis, Minn.

SUMMARY

A direct spectropolarimetric titration method of analysis was developed for aluminum(III), indium(III) and thallium(III), with the stereospecific ligand, D-(−)-1,2-propylenediaminetetraacetic acid (D(−)PDTA). The optical rotation of the solution was monitored with a photoelectric polarimeter to determine the end-point of the titration. The metal complexes and titrant are optically active and serve as self-indicators. Since D(−)PDTA is stereospecific in its reaction with these metals, maximum utilization of the optical rotation of these complexes is achieved. The observed optical rotation is linear with respect to concentration of the metal complexes; consequently, it is possible to perform straight-line extrapolations to the end-point. The effects of some parameters were investigated and optimum conditions were established. The range of the average deviations from visual chelometry for the three metals determined was 0.11–0.18%.

RÉSUMÉ

Une méthode de titrage spectropolarimétrique direct est proposée pour l'analyse de l'aluminium(III), de l'indium(III) et du thallium(III) ay moyen du ligand stéréospécifique acide D-(−)-1,2-propylènediaminotétracétique (D(−)PDTA). Un polarimètre photoélectrique permet de déterminer le point final du titrage. Les complexes métalliques et le titrant sont optiquement actifs et servent de self-indicateurs. On a examiné l'influence de divers paramètres et établi les conditions optima de dosages des déviations moyennes par chelométrie visuelle pour les 3 métaux dosés est de 0.11 à 0.18%.

ZUSAMMENFASSUNG

Es wurde eine direkte spektropolarimetrische Titrationsmethode für die Analyse von Aluminium(III), Indium(III) und Thallium(III) entwickelt unter Verwendung des stereospezifischen Liganden D-(−)-1,2-Propylendiamintetraessigsäure (D(−)PDTA). Für die Bestimmung des Endpunktes der Titration wurde die optische Rotation der Lösung mit einem photoelektrischen Polarimeter gemessen. Die Metallkomplexe und der Titrant sind optisch aktiv und dienen als Selbstindikatoren. Da D(−)PDTA mit diesen Metallen stereospezifisch reagiert, wird die optische Rotation dieser Komplexe maximal ausgenutzt. Die beobachtete optische Rotation verläuft linear mit der Konzentration der Metallkomplexe; daher sind geradlinige Extrapolationen bis zum Endpunkt möglich. Die Einflüsse einiger Parameter wurden untersucht und die optimalen Bedingungen festgestellt. Die durchschnittlichen Abweichungen von der visuellen Chelatometrie betrugen bei den drei bestimmten Metallen 0.11–0.18%.

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

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS IN ALLOY STEELS

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(Received October 24th, 1969)

Phosphorus can be determined in iron and steels by forming phosphovanadomolybdate in perchloric–nitric acid solution and subsequently measuring the extracted yellow colour in isoamyl alcohol[1] or isobutyl methyl ketone[2]. The latter method is limited to steels which do not contain tungsten, niobium or tantalum, and colour development time must be increased to 1 h for samples containing up to 2% of titanium and up to 0.5% of zirconium. A lengthy modification must be made to determine phosphorus when tungsten, niobium or tantalum are present. The B.I.S.R.A. Chemical Analysis Committee[3] has recommended an improved method which allows the determination of phosphorus in steels containing either 7% tungsten or 0.8% niobium, provided that the samples will dissolve in a mixture of concentrated hydrochloric and nitric acids.

This paper describes a method for the spectrophotometric determination of phosphorus in all types of alloy steels. The only interferences are chromium, which must be volatilized as chromyl chloride when more than 2% is present, and tungsten above 10%. The interference of tungsten can be overcome by selecting a smaller sample size. Hydrofluoric acid is used to complex tungsten, niobium, tantalum, titanium and zirconium and prevent their interference in the phosphorus determination, thus removing the need for lengthy modifications required by earlier methods.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer with 2-cm cells was used.

Standard phosphorus solution. Prepare a stock solution containing 0.1 mg P/ml by dissolving 0.4393 g of potassium dihydrogen phosphate in 1 l of water. Prepare a working solution (0.04 mg P/ml) by diluting 100 ml of stock solution to 250 ml.

Ammonium molybdate solution (15%). Prepare from $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$ and store in a polythene bottle.

Ammonium vanadate solution (0.25%). Dissolve 2.5 g of ammonium metavanadate in 500 ml of warm water. Cool and dilute to 1 l.

Recommended procedure for samples containing less than 10% W and less than 0.08% P

Weigh 0.5 g of sample into a 125-ml conical beaker and add 7 ml of water, 7 ml of 15 *M* nitric acid, 7 ml of 10 *M* hydrochloric acid and 0.5 ml of 40% hydrofluoric acid. After dissolution add 12 ml of 70% perchloric acid (use 14 ml when chromium is higher than 2%) and evaporate to fumes. Continue fuming for 2 min at a temperature such that the perchloric acid is refluxing down the sides of the beaker.

If the chromium content is higher than 2%, add 3 ml of hydrochloric acid to the fuming solution, then continue fuming until the remaining chromium is again fully oxidized. Repeat this procedure twice.

Cool, add 15 ml of water and transfer to a 250-ml Teflon beaker, using 5 ml of water for washing. Add 3 ml of 40% hydrofluoric acid and boil for 30 sec. Cool below the ambient temperature and add 12.5 ml of 6 *N* sulphuric acid. Add 10 ml of ammonium vanadate solution and 65 ml of ammonium molybdate solution, and then allow to stand for 7 min. Add 25 ml of water. Transfer the solution to a 250-ml separating funnel and dilute to 150 ml with water.

Add 15 ml of 50% citric acid solution, mix, immediately add 40 ml of isobutyl methyl ketone (IBMK) and shake for 30 sec. Allow the two layers to separate and discard the aqueous layer. Filter the ketone layer through a double-layer rapid filter paper into a small dry beaker and measure the absorbance immediately in 2-cm cells at a wavelength of 425 nm against water. Subtract the blank value.

To prepare a blank and a standard curve in the range 0–400 μg P, add 8 ml of 70% perchloric acid to aliquots of the standard phosphorus solutions and evaporate to fumes. Cool and continue as in the recommended procedure.

DISCUSSION

Dissolution of sample

Samples were dissolved in a dilute nitric–hydrochloric acid mixture containing 0.5 ml of 40% hydrofluoric acid. Hydrofluoric acid is used to volatilize silicon and to prevent the precipitation of tungsten, niobium and other oxides during the initial dissolution step. Steel samples (0.25 g) containing 18% tungsten were dissolved in a mixture of 10 ml of water, 7 ml of 15 *M* nitric acid and 0.5 ml of 40% hydrofluoric acid, followed by 7 ml of 10 *M* hydrochloric acid after the initial reaction has ceased. All samples were fumed with perchloric acid to oxidize any insoluble carbides, precipitated tungsten and niobium oxides remaining in the solution. Boiling with 3 ml of 40% hydrofluoric acid renders niobium oxide and mixtures of niobium and tungsten oxides soluble. Tungsten oxide is not dissolved completely, but does not interfere with the phosphorus determination.

Sensitivity and stability of the method

The absorbance of the phosphovanadomolybdate can be measured in the region between 400 and 480 nm. The absorbance of the complex and blanks increases with decreasing wavelength. The 2-cm cells and the wavelength of 425 nm were selected to determine phosphorus in alloy steels containing phosphorus up to 0.08% P, for a 0.5-g sample. For steels containing larger amounts of phosphorus, a wavelength of 460 nm is recommended, where the sensitivity is only half that obtained at 425 nm. The molar absorptivity of the complex in IBMK is 1750 and 750 for 425 nm and 460 nm, respectively. Beer's law is obeyed to at least 38 μg P/ml.

The colour of the complex and blank in the organic phase increases slightly on standing, but the absorbance of the complex is constant for at least 1 h, when measured against the reagent blank. The absorbance of the phosphovanadomolybdate does not change in the investigated temperature range of 19–25°.

Choice of acidity and effect of varying reagent concentrations

About 3.5 ml of perchloric acid (42 meq) is used when 0.5 g of iron is dissolved and the iron perchlorate solution fumed as directed by the recommended procedure. The effect of concentration of various acids on the absorbance was determined by a modified procedure that can also be used to determine phosphorus in steels containing less than 1% of tungsten and less than 0.08% of phosphorus.

Modified procedure. Dissolve the sample, evaporate to fumes and volatilize chromium as in the recommended procedure. Cool, add 25 ml of 3 *N* sulphuric acid and transfer to a 250-ml Teflon beaker using 5 ml of water for washing. Add 3 ml of 40% hydrofluoric acid and boil for 30 sec. Cool. Add 10 ml of ammonium vanadate solution and 65 ml of ammonium molybdate solution, and continue as in the recommended procedure.

The amounts of perchloric and other acids were varied to determine the effect of total free acid on the absorbance. The minimum amount of perchloric acid that had to be added to the sample to obtain satisfactory dissolution was 5 ml. The amount of hydrochloric, nitric and sulphuric acids added to hydrolyse pyrophosphates formed after fuming with perchloric acid was 25 ml, and varied in acidity between 1 and 4 *N* (Table I).

TABLE I

THE EFFECT OF VARYING AMOUNTS OF ACIDS ON ABSORBANCE

(Volume 115 ml)

Initial $HClO_4$ 11.6 M (ml)	*Other acids added 1–4 N 25 ml*	*Total free acid at colour development (meq)*[a]	*Absorbance 2-cm cells 425 nm*
8–18	(H_2O 25 ml)	50–170	0.570
6–20	H_2SO_4	50–220	0.565
6–18	HCl	50–200	0.575
6–24	HNO_3	50–255	0.580

[a] Acidity does not include HF.

The addition of 25 ml of 3 *N* sulphuric acid was used because sulphate ions form complexes with, and prevent the hydrolysis of, titanium, zirconium, niobium and tantalum. Addition of nitric and hydrochloric acids to solutions containing titanium, zirconium and niobium and 3 ml of 40% hydrofluoric acid, produced results low by 2–4%.

To overcome the interference of tungsten, the perchloric acid concentration must be kept to a minimum (12 ml used to dissolve sample) and pyrophosphates must be hydrolysed in a small volume containing no sulphate ions. The volume of 40% hydrofluoric acid must be maintained at 3 ml. This amount of hydrofluoric acid is also sufficient to complex other alloying elements, which may interfere by forming either hydrated oxides or strong complexes with phosphorus.

The concentration of ammonium molybdate was increased from 15 to 65 ml to compensate for the added fluoride. It was necessary to add 17 ml of 15% ammonium molybdate for each ml of 40% hydrofluoric acid, otherwise the maximum colour development of phosphovanadomolybdate was not obtained. The concentration of ammonium vanadate was left unchanged[2] because addition of larger amounts of reagent did not affect the results.

Reagent blank and standard curve

The absorbance of the reagent blank is low (0.040 abs. units *vs.* water). Blanks are affected by perchloric acid concentration which gives slightly higher blanks. A hydrochloric–perchloric acid system gives the highest blanks, and the blank increases with increase in the hydrochloric acid concentration (Fig. 1).

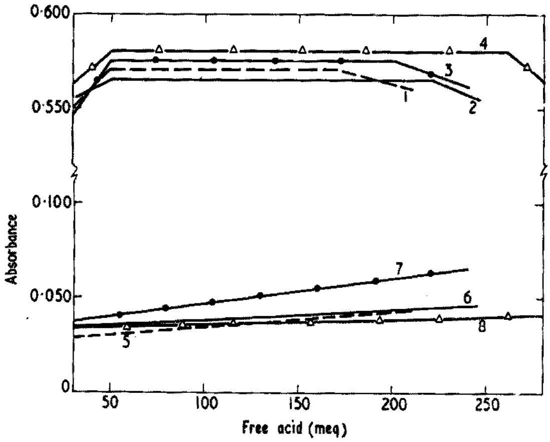

Fig. 1. Effect of free acid in 115-ml volume on the absorbance (200 µg P, 2-cm cells, 425 nm). Absorbance *vs.* blank: (1) $HClO_4$, (2) H_2SO_4–$HClO_4$, (3) HCl–$HClO_4$, (4) HNO_3–$HClO_4$. Blank *vs.* water: (5) $HClO_4$, (6) H_2SO_4–$HClO_4$, (7) HCl–$HClO_4$, (8) HNO_3–$HClO_4$.

Although standard methods recommend[2] the use of high-purity iron containing less than 0.001% phosphorus for the preparation of standard curves, it is impossible to find any standard iron samples low in phosphorus; high-purity iron BCS 149/2 contains 0.006% phosphorus. It was established by using an iron(III) chloride solution containing 5 p.p.m. phosphorus[4], that iron(III) has no effect on the absorbance and therefore the standard curve may be prepared by omitting iron from the procedure.

Extraction

The volume of solution before extraction was increased because extraction of the yellow complex from a 120-ml volume led to unstable absorbance readings. Some precipitation occurred in the filtered organic phase after a short standing time, which required an additional filtration step. By diluting the aqueous phase to 150 ml the salt concentration in the aqueous phase was decreased, and addition of reagents to a cool solution produced more stable organic extracts. The filtered organic solution is stable for 15 min, but to overcome any possible errors caused by the formation of precipitates in the blank, water should be used as a reference solution. Provided that the correct amount of free acid is present for the formation of the phosphovanadomolybdate, dilution before the extraction has no effect on the absorbance.

Study of interferences

No interference was observed from the following concentrations of alloying elements: 25% Co and Ni, 10% Cu, Mn, Mo and W, 5% Ti, Zr, Nb and V, 1% Sn and 0.1% As.

TABLE II

INTERFERENCE BY CHROMIUM

(0.5-g sample, 200 μg P, 2-cm cells, 425 nm)

Chromium added		*Cr*	*Absorbance*	*Error*
as	*(mg)*	*(%)*		*(%)*
Nil	—	—	0.565	—
Cr^{3+}	10	2	0.560	−1
Cr^{3+}	25	5	0.550	−3
Cr^{3+}	50	10	0.535	−6
Cr(VI)	25	5	0.575	+2
Cr(VI)	50	10	0.585	+4
Cr(VI)	100	20	0.605	+7

TABLE III

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS IN VARIOUS MATERIALS

Sample	*Certified P (%)*	*P found (%)*	*Other methods (%)*
BCS 149/2 (pure iron)	0.0060	0.0048	0.0050[b]
BCS 225/1 (Ni–Cr–Mo steel)	0.019	0.0182	0.0180[b]
BCS 225/2 (Ni–Cr–Mo steel)	0.019	0.0179	
BCS 224 (Cr–V steel)	0.012	0.0104	0.0106[b]
BCS 312 (13Ni–24Co–Ti–Nb steel)	—	0.0120	
BCS 220/1 (7W–5Mo steel)	0.029 (0.027–0.031)	0.0305	
BCS 241 (Cr–V–W–Co–Mo steel)	0.021 (0.019–0.023)	0.0250[a]	
BCS 233 (11Ni–24Co–Ti steel)	—	0.0125	0.0137[b]
BCS 246 (Nb–Mo 18/12 steel)	0.027 (0.025–0.029)	0.0294	
BCS 235/1 (18/8–Ti steel)	0.020	0.0206	0.0196[b]
BCS 231/2 (Ferro-molybdenum)	0.08	0.0930[a]	0.0960[b]
SRM 467 (Low alloy steel)	0.033	0.0315	
SRM 50 (18W–4Cr–1V steel)	0.027	0.0270[a]	
SRM 50a (18W–4Cr–1V steel)	0.020	0.0192[a]	0.019[c]
SRM 50b (18W–4Cr–1V steel)	0.029	0.0306[a]	0.030[c]
SRM 50c (18W–4Cr–1V steel)	0.022 (0.019–0.025)	0.0250[a]	0.024[c]
SAA 101 (6W–5Mo steel)	—	0.0386	0.0375[c]
SAA 115 (20W–5Co steel)	—	0.0358[a]	0.0366[c]
SAA 125 (13Ni–13Cr–12Co–3Nb–3W–3Mo steel)	—	0.0344	0.033[c]

[a] 0.25-g sample.

[b] Extraction method, Ref. 4.

[c] Gravimetric, Ref. 5.

Chromium is the only element which interferes in the procedure. The maximum amount of chromium which can be tolerated is 2%, equivalent to 10 mg of chromium per sample. Larger amounts of chromium must be volatilized as chromyl chloride. Although it is recommended that volatilization of chromium should be repeated twice, one repeat is sufficient for steels containing less than 10% chromium. In the presence of hydrofluoric acid, the interference by chromium(III) is greater than that by chromium(VI), and therefore it is more advantageous to leave chromium in the oxidized state (Table II).

Tungsten is limited to 50 mg per sample because larger amounts cause bumping. For steels containing tungsten above 10%, smaller sample weights must be selected to keep the tungsten below 50 mg.

Reproducibility of the method

Readings on a series of 10 standards showed the relative standard deviation at the 5 μg P/ml level (in isobutyl methyl ketone) to be ± 0.5%.

Comparison with standard samples

The results obtained for a variety of materials are shown in Table III and are in good agreement with certified values.

It is a pleasure to acknowledge the assistance given by Mrs. B. McAllister with the experimental work.

SUMMARY

A general method based on the extraction of phosphovanadomolybdate by isobutyl methyl ketone is presented for the spectrophotometric determination of 0–0.08% phosphorus in high-alloy steels. No interference is caused by less than 2% of chromium; larger amounts can be volatilized as chromyl chloride. The molar absorptivity is 1750 at 425 nm for the extracted phosphovanadomolybdate, with a standard deviation of ±0.5%.

RÉSUMÉ

Une méthode générale basée sur l'extraction de phosphovanadomolybdate par l'isobutylméthylcétone est proposée pour le dosage spectrophotométrique de 0 à 0.08% de phosphore dans des aciers. Le chrome en quantité inférieure à 2% ne gène pas. Pour des teneurs plus élevées, on peut procéder à une volatilisation sous forme de chlorure de chromyle. L'absorption molaire est de 1750 à 425 nm pour le phosphovanadomolybdate extrait, avec une déviation standard de ±0.5%.

ZUSAMMENFASSUNG

Für die spektrophotometrische Bestimmung von 0–0.08% Phosphor in hochlegierten Stählen wird eine allgemeine Methode beschrieben, die auf der Extraktion von Molybdatovanadatophosphat mit Isobutylmethylketon beruht. Bei weniger als 2% Chrom tritt keine Störung auf; grössere Mengen können als Chromylchlorid

verflüchtigt werden. Der molare Extinktionskoeffizient für das extrahierte Molybdatovanadatophosphat beträgt 1750 bei 425 nm mit einer Standardabweichung von ±0.5%.

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

RAPID COMBUSTION METHODS FOR DETERMINING SULFUR IN ROCKS, ORES AND STONY METEORITES

A COMPARATIVE STUDY OF THE USEFULNESS OF RESISTANCE-TYPE AND INDUCTION FURNACES

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(Received October 13th, 1969)

The combustion method of determining sulfur is popular in both rock analysis and metallurgical laboratories. In spite of its widespread use, the method suffers from the drawback that no universal technique is available for different kinds of samples; modifications are needed, depending on the nature of the sample and its sulfur content. The degree of recovery of sulfur also varies considerably (70–100%) between laboratories and even between operators.

The low-temperature (900–950°) combustion technique involving the use of vanadium pentoxide as a flux is applicable to a variety of materials[1–4], but is unsuitable for most samples containing about 1% or more sulfur, owing to low recoveries. Combustion at high temperatures (varying between 1050° and 1450°) in a resistance-type furnace has been used to determine sulfur in ores, concentrates and metallurgical samples[5], sedimentary rocks[6], blister and refined copper[7], and steels[8–10]. Induction heating has been employed for the determination of sulfur in various types of steel, ferro-alloys and metals[11–18], synthetic glass[19] and soil[20]; but this method does not seem to have been applied to meteorites, various kinds of naturally occurring rocks, or sulfide ores.

In this paper, a satisfactory procedure is described for the determination of total sulfur in rocks, ores and stony meteorites by means of a Leco induction furnace. Suitable fluxes for effective coupling in the induction heating, and the time for complete evolution of sulfur dioxide after heating for different kinds of samples are discussed.

The results obtained by using three different combustion methods for sulfur in a variety of geological materials have been compared with gravimetric data. These results indicate that induction heating is superior to resistance heating in the determination of total sulfur in most samples containing 0–20% total sulfur.

EXPERIMENTAL

Equipment

Resistance-type furnace, combustion tube and boat. The furnace and combustion tube were the same as described by SEN GUPTA[4]. A Leco sulfur-free boat with cover, and pure tin accelerator, were used.

Furnace and parts for induction heating. A Leco high-frequency induction furnace model 522 (220 V) equipped with a two-combustion tube unit (both sides capable of independent operation) was used. A Leco silica combustion tube (#550–120) was joined with a polyethylene tube to the "right-angle bend" (part #550–119). Leco heavy-duty crucibles (#528–120), covers (#528–42) and iron chips (#501–77 or 501–077), or iron powder (#501–78) were required.

Starch–iodide solution

Prepare a 0.45% (w/v) solution of soluble starch in the usual way. Add 4.5 g of potassium iodide per 100 ml and mix well. Transfer to a stoppered bottle and store in a refrigerator. The solution should be discarded at the first sign of blue coloration.

High-temperature (1450°) combustion involving the resistance-type furnace

The procedure developed by the present author has appeared in detail in a recent book[21] where it is included as one of the methods used at the Geological Survey of Canada for rock analysis. Briefly, the method involves ignition of the sample premixed with 1 g of tin in a ZIRCUM combustion tube (Burrell Corporation) at 1450° in a current of oxygen and absorption of the sulfur dioxide in two receivers[4] containing acidified iodate–iodide–starch solution; the determination is finished by titrating the excess of iodine with sodium thiosulfate solution. This method is also applicable to ores and stony meteorites. Because the above reference[21] does not give any data to support the validity of the high-temperature combustion method for various kinds of samples, they are included here (see Table I).

High-temperature combustion in the induction furnace

By means of polyethylene tubing, connect the tapered end of the combustion tube to the wide end of the right-angle bend and join the other end of the latter to the two receivers (these are similar to those used previously[4] except that the teflon stopcocks are now used) through a guard tube which has been narrowed at the center and packed with a small amount of cotton wool. Seal all connections by means of Krönig cement. Connect the oxygen gas supply (through a regulator) in series with a sulfuric acid bubbler, a tube packed with ascarite and magnesium perchlorate, and finally to the gas inlet at the bottom of the combustion assembly.

It was observed that in order to obtain tight seals, the silicone ring should be placed on the bottom part of the combustion tube in such a way that 3 mm of the ring remains outside the tube.

Weigh the sample (200 mg for 0–1%, 100 mg for 1–5%, 50 mg for 5–12% and 10–25 mg for >12% sulfur) and transfer it to a crucible. Add 1.5 g of iron chips or iron powder (2 g of either material for more than 6% sulfur), mix with a long narrow nickel spatula and brush off any adhering particles from the spatula into the crucible. Cover the crucible and place it on the pedestal of the furnace. Introduce the crucible into the combustion tube by raising the locking mechanism handle. At this point care should be taken to see that the bottom of the crucible is near the geometric center of the inductor coil, otherwise the sample will not heat up to the desired temperature (1450°) during the combustion of the sample and recovery of sulfur will be low.

For up to 12% sulfur, place 25 ml of 0.2 *M* hydrochloric acid in each of the two receivers, and, depending on the sulfur content, add 2–6 ml of starch–iodide solution to the first receiver and 1 ml to the second receiver. For more than 12% sulfur, place 50 ml and 25 ml of 0.2 *M* hydrochloric acid in the first and the second receivers, respectively, and add 6–10 ml of starch–iodide solution to the first receiver and 1 ml to the second. Depending on the amount of sulfur dioxide to be expected, add 2–20 ml of standard 0.005 *M* potassium iodate solution to the first receiver and 1 ml to the second receiver. In all cases add a known excess (equivalent to 0.5–1.0% more sulfur than will actually be present in the sample being analyzed) of standard potassium iodate solution to the first receiver.

Decrease the flow of oxygen through the combustion tube to 1 bubble per sec and connect the receivers to the combustion tube assembly, that containing larger amount of potassium iodate being connected first. Increase the flow of oxygen through the system and turn on the furnace. To overcome the back-pressure developed, quickly increase the flow of oxygen (1–1.5 l/min) until the products of combustion bubble smoothly through the receivers.

It has been found that for satisfactory results the maximum plate current reading should be between 350 and 450 mA.

The completion of combustion will take about 5–25 min depending on the sulfur content of the sample (5–8 min for 0–1%, 10 min for 1–5%, 15 min for 5–12% and 15–25 min for >12% sulfur). Adjust the oxygen flow rate constantly during the combustion period so that at no time does it become too vigorous. At steady state the flow rate should be about 5–7 bubbles/sec. After combustion, transfer the contents of the receivers to a 250-ml flask by washing with water and titrate with standard 0.006 *M* sodium thiosulfate solution to a colorless end-point. Run a blank for the crucible with its cover and iron accelerator. Calculate the total sulfur as described previously[4,21].

RESULTS AND DISCUSSION

The results obtained with different furnaces, temperatures and fluxes are given in Table I. Unless otherwise stated, the results are the average of two or more determinations. Calculations were based on direct stoichiometric relationships between the reactants, and no empirical correction factor, as used by some authors[5,14,18] was employed. However, during the analysis of a batch of unknown samples, one or more suitable standard samples having similar sulfur contents should be run simultaneously with the unknowns. If necessary, a correction factor with respect to the recovery of the standards should be applied to the unknown to bring the recovery to 100%.

Although the low-temperature method[4] works well with rock samples containing less than 1% sulfur, it generally gives low results when the sulfur content exceeds 1% (see Table I) because the temperature (900–950°) is not high enough to release all sulfur from these samples. By increasing the time of combustion to 1–2 h the yield of sulfur dioxide can be improved, but this is time-consuming.

The high-temperature technique with resistance heating gives better results for samples containing up to 6% sulfur, but the method gives low results for sulfide ores (see Table I). The results are much improved when the induction heating furnace is used (*cf.* Table I).

TABLE I

COMPARISON OF THE SULFUR RESULTS (AS % S) OF SOME ROCKS, ORES AND STONY METEORITES OBTAINED BY DIFFERENT PROCEDURES

Sample	*Found by combustion with*			*Gravimetric value*
	V_2O_5 (resistance heating at 950°)	*Tin (resistance heating at 1450°)*	*Iron (induction heating)*	
NBS 1A (Limestone)	0.27	0.27	0.27	0.27
NBS 97 (Flint clay)	0.02	n.d.[a]	0.02	0.02
Pyrite-impregnated sandstone 1	0.71	1.10	1.14	1.17[f]
Pyrite-impregnated sandstone 2	2.30	2.56	2.70	2.83[f]
Pyrite-impregnated sandstone 3	4.66	6.00	6.15	6.27[f]
Benton (stony meteorite)	1.90	2.48	2.51	2.58[f]
Dresden (stony meteorite)	2.10	2.10	2.19	2.19[f]
Belly River (stony meteorite)	1.72	2.08	2.00	2.17[f]
				1.60[b]
Peace River (stony meteorite)	n.d.[a]	n.d.[a]	2.36	2.35[c]
Bruderheim (stony meteorite)	n.d.[a]	n.d.[a]	2.26	2.33[d]
CAAS sulfide ore-1	n.d.[a]	11.2	11.9	Range 11.77–12.2[e]
		11.2	11.9	
Bronson sulfide ore	n.d.[a]	20.2	21.9	22.18
		19.0	21.6	
Chalcopyrite	n.d.[a]	30.5	31.7	32.8
		30.0	32.0	

[a] Not determined.
[b] Mason and Wiik[22].
[c] Baadsgaard *et al.*[23].
[d] Baadsgaard *et al.*[24].
[e] Webber[25].
[f] Independent operator.

A comparison of the last two columns of Table I shows that there is slight negative error for sulfur for some samples. Gravimetric values for sulfur obtained by conventional barium sulfate precipitation method are also subject to positive error owing to coprecipitation of silica and barium chromate. This error can be reduced by removal of silica with hydrofluoric acid, and by fusion and reprecipitation of barium sulfate. But this is very time-consuming, and may not remove any interference of chromium. On the other hand, the recovery of total sulfur as sulfur dioxide from a sample by any high-temperature combustion method may be slightly less than 100%.

Several authors[5,8,10,14] have given reasons for incomplete and variable recoveries of sulfur in the high-temperature process. For complete decomposition of the sample and expulsion of all the sulfur, a high temperature is essential. Although the American Society for Testing and Materials[26] recommends a temperature of 1425–1550° for complete recovery of sulfur as sulfur dioxide, some authors[6,7] have used temperatures varying from 1150° to 1320° in the resistance-type furnace and have claimed complete recovery of the sulfur dioxide. Rice-Jones[5] has shown from theoretical consideration that conversion of sulfur trioxide to sulfur dioxide is complete only at 1450°. At lower temperatures, sulfur dioxide recombines with oxygen to form sulfur trioxide. It is our experience that the combination of a temperature of 1450° and a clean combustion tube gives the best recovery of sulfur. A lower temperature may give incomplete recovery, and a higher temperature can lead to complications such as breakage of the combustion tube (resistance heating) or blocking of the pedestal by molten iron (induction heating), owing to escape of the molten material through the boat or the crucible bottom.

FULTON AND FRYXELL[14] have shown by radiochemical studies that most of the sulfur losses are due to adsorption on the glasswares and connecting tubes between the crucible and the absorption vessel. They, therefore, rinsed the delivery and the combustion tubes after each combustion to recover this adsorbed sulfur. The present author has observed that the loss of sulfur dioxide can be serious if the sample contains a high percentage of water which is evolved and deposited on the walls of the delivery tubes; sulfur dioxide is trapped in this water. However, rinsing of the delivery tubes as done by FULTON AND FRYXELL[14] is unsuitable for routine determinations as it necessitates redrying and increases the determination time. The difficulty can be overcome and quantitative recovery can be obtained for these samples containing much water if the combustion time is increased until all micro water droplets disappear from the connecting tubes by the action of the flow of hot oxygen gas.

Other sources of error could arise from the loss of sulfur in the slag[14], reconversion of sulfur dioxide to sulfur trioxide by oxygen, and the improper choice of flux. Loss of sulfur in the slag can be reduced to 1% by using high-temperature (1550°) induction heating[14]. But there is a danger of crucible leakage and blocking of the pedestal by the molten material as previously noted.

Table I shows that in the high-temperature (1450°) resistance heating procedure, tin works well as a flux for samples with up to 6% sulfur. In the present work, when tin (up to 2 g) was used as a flux in the induction-heating procedure, the recovery of sulfur was either nil or very low; satisfactory recoveries were obtained in most cases when tin was replaced as flux by iron chips or iron powder (*cf.* Table I).

BURKE[18] has claimed that the use of a mixture of iron powder (1 g) and treated vanadium pentoxide (1 g) in the induction heating improves the yield of sulfur dioxide to 90 ± 10%. To test whether results superior to those given in Table I for the induction-heating procedure can be obtained with this mixture, experiments were carried out with two of the samples listed in Table I. The results (Table II) show that the yield is lower than that obtained by using 2 g of iron only as the flux; this may be due to the fact that vanadium pentoxide tends to oxidize sulfur dioxide to sulfur trioxide when a large amount of sulfur dioxide is present. Another possible reason is that a sufficiently high temperature is not attained in the induction heating when a mixture of 1 g of iron and 1 g of vanadium pentoxide is employed as a flux.

TABLE II

RECOVERY OF SULFUR (AS % S) BY INDUCTION HEATING WITH A MIXTURE OF 1 g OF IRON POWDER AND 1 g OF TREATED VANADIUM PENTOXIDE AS A FLUX

Sample	*Found*	*Gravimetric value*
Pyrite-impregnated sandstone 3	6.08	6.27
	6.08	
CAAS sulfide ore-1	11.5	Range 11.77–12.2[a]
	11.6	

[a] WEBBER[25].

Duplicate tests on pyrite-impregnated sandstone 3 with a mixture of 2 g of iron chips and 1 g of tin as flux showed no improvement in results compared with those given in Table I. Moreover, during heating with this mixture explosions occurred in both cases followed by flash fire and intense glow around the crucible. The crucible cover was thrown out and the melt spilled onto the silica combustion tube. After cooling, the crucible remained firmly attached to the wall of the combustion tube and the silica of the tube at the point of contact was attacked, rendering the tube unsuitable for further use. A combination of iron chips and tin as flux is therefore not recommended.

To determine whether an absence of oxygen in the combustion system would improve the yield of sulfur dioxide (by diminishing the possibility of its re-oxidation), tests were carried out with the same two samples of Table II. The sample was mixed with up to 3 g of iron powder and 1 g of vanadium pentoxide and heated in an induction furnace in a current of prepurified nitrogen gas. However, the plate current was then quite insufficient even to heat the sample to glowing and the yield of sulfur dioxide was either nil or very low.

After 3–4 weeks of continuous use, the combustion tube (induction heating) becomes coated with some dust and little sulfuric acid. This should be cleaned with cloth followed by heating of the tube on a burner until sulfur trioxide fumes are expelled. The cotton wool should also be changed periodically.

SUMMARY

A satisfactory procedure for determining total sulfur in rocks, ores and stony meteorites with a Leco induction furnace is described. Suitable fluxes, time for complete evolution of sulfur dioxide, and suitable absorption solutions for sulfur dioxide are discussed. A comparative study of three different combustion methods for determining sulfur in a variety of geological materials has also been made. The results indicate that induction heating is superior to resistance heating for most samples containing up to 20% total sulfur.

RÉSUMÉ

On décrit un procédé pour le dosage du soufre total dans les roches, les minerais et les météorites pierreux à l'aide d'un four à induction Leco. On indique les flux appropriés, la durée de dégagement total de l'anhydride sulfureux et les solutions qui conviennent pour l'absorption de SO_2. On a également effectué une étude comparative de trois différentes méthodes de combustion pour le dosage du soufre dans diverses substances géologiques. Les résultats montrent que le chauffage par induction est supérieur au chauffage par résistance pour la plupart des échantillons renfermant jusqu'à 20% de soufre total.

ZUSAMMENFASSUNG

Ein befriedigendes Verfahren zur Bestimmung des Gesamt-Schwefels in Gesteinen, Erzen und Steinmeteoriten mit Hilfe eines Leco-Induktionsofens wird beschrieben. Geeignete Flussmittel, die zur vollständigen Entwicklung von Schwefeldioxid erforderliche Zeit und für das Schwefeldioxid geeignete Absorptionsflüssigkeiten werden diskutiert. Eine vergleichende Untersuchung dreier verschiedener Verbrennungsmethoden für die Bestimmung von Schwefel in einer Auswahl geologischer Materialien ist ebenfalls durchgeführt worden. Die Ergebnisse zeigen, dass für die meisten Proben, die bis zu 20% Gesamt-Schwefel enthalten, die Induktionsheizung der Widerstandsheizung überlegen ist.

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

THE DETERMINATION OF NICOTINIC ACID AND NICOTINAMIDE BY THIN-LAYER CHROMATOGRAPHY AND *IN SITU* FLUORIMETRY

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(Received October 13th, 1969)

Reflectance spectroscopy *in situ* has been found suitable for the analysis of nucleic acid derivatives and related compounds in biological systems[1-4]. The determination of nicotinic acid and nicotinamide in these systems by the same method has met with some difficulties: (*a*) because of the low concentration in which they are present in systems of interest, and (*b*) because of the poor resolution of the two, after two-dimensional chromatography according to the previously described methods[5].

Both compounds can be rendered fluorescent in a fairly selective manner by the KÖNIG reaction[6]. This offers a possibility of developing a rapid method for the specific and highly sensitive determination of these two clinically important substances. In the present work the fluorescence properties of the derivatives of nicotinamide and nicotinic acid are studied for quantitative and qualitative analytical purposes. The applicability of the method to biological systems is tested on organ extracts.

EXPERIMENTAL

Rumalon samples (Robapharm, Ltd., Basle) were prepared by freeze-drying the native extract and redissolving in water in a five times more concentrated form. Of this solution, 4 × 5 μl were spotted on the chromatogram with a 5-μl capillary (Microcaps, Drummond Scientific Co. Ltd., Broomall, Pa., U.S.A.).

Rubiron (Robapharm, Ltd., Basle), a solid powder, was extracted with distilled water (50 ml per 5 g of material) and 5 μl of the resulting solution was spotted on the same plate.

Stock solutions of nicotinic acid (Hoffman la Roche, Basle, Switzerland) and nicotinamide (Mann Chemicals Ltd., New York) were prepared (2 g per liter in 10% isopropanol in water mixture) and then diluted to suitable standard concentrations.

One-dimensional thin-layer chromatography was carried out on purified cellulose[5] with butanol saturated with a 3% ammonia solution as eluent. Complete separation of the two compounds was effected in 45–60 minutes. This was followed by a 30-min drying period in a cold air stream.

The KÖNIG reaction[6] was rigidly standardized. A saturated bromine solution (ice-cooled) was mixed in a petri dish in a chamber with an aqueous 10% sodium cyanide solution until the color of the bromine disappeared. The chromatograms were exposed to the saturated atmosphere of bromine cyanide in the chromatography chamber for 1 h. The plates were then sprayed uniformly with compressed air with a spray reagent consisting of 2 g of *p*-aminobenzoic acid (analytical grade, Merck, Darmstadt) dissolved in 75 ml of 0.75 *M* hydrochloric acid and filled to the 100-ml mark with 96% (v/v) ethanol. After spraying, a 1-h drying period in a cold air stream was used. At higher concentrations brownish yellow-colored spots were seen. Visual detection of the spots was also carried out under an ultraviolet lamp (Camag, Muttenz, Switzerland) at 254 nm.

Fluorescence spectra were measured directly on the chromatogram with a Zeiss chromatogram-spectrophotometer (set-up Pr-M[7]). Quantitative measurements were carried out on the Zeiss and on the Camag-Turner 111 instruments. Optimum filter combinations are discussed later. Chromatographic plates were evaluated with a planimeter (Ott Ltd., Kempten, Bavaria).

RESULTS AND DISCUSSION

Fluorescence spectra

A number of primary filters (Zeiss, Oberkochen, Germany) were tested with the Zeiss instrument to obtain the best analytical conditions. The use of the 436-nm filter is recommended for both compounds when adsorbed on cellulose (see Figs. 1 and 2). The maxima of the emission spectra are found at 545 nm for nicotinamide and 530 nm for nicotinic acid. Background interference from the spray reagent is only slightly above

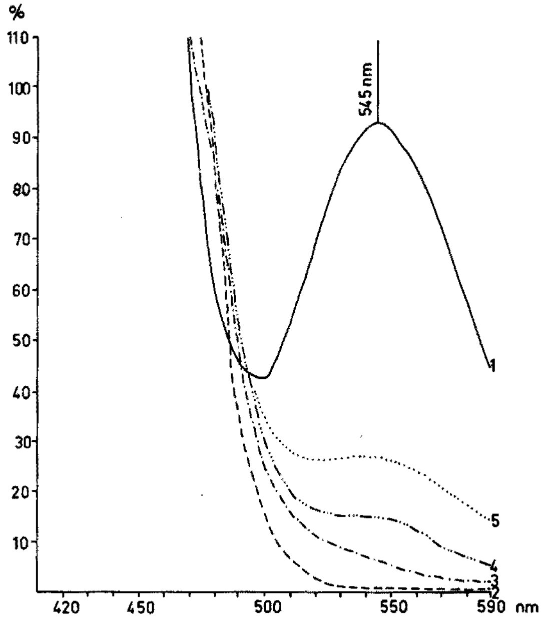

Fig. 1. Fluorescence emission spectrum of nicotinamide excited at 436 nm. (1) Nicotinamide, (2) pure cellulose background, (3) spray reagent background immediately after drying, (4) background after 24 h, (5) background after 96 h.

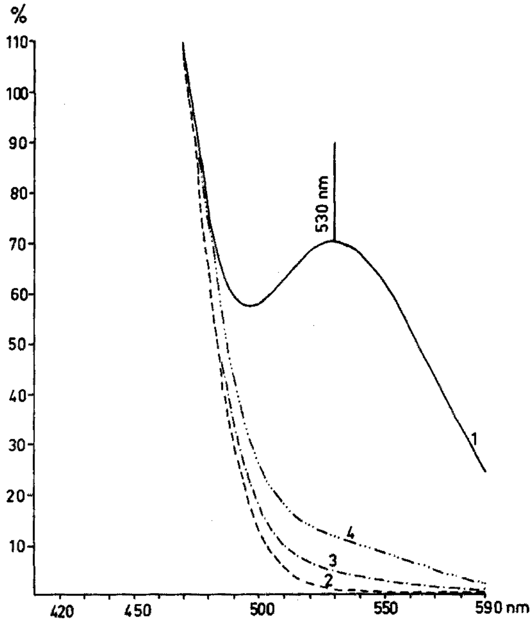

Fig. 2. Fluorescence emission spectrum of nicotinic acid excited at 436 nm. (1) Nicotinic acid, (2) pure cellulose background, (3) spray reagent background immediately after drying, (4) background after 24 h.

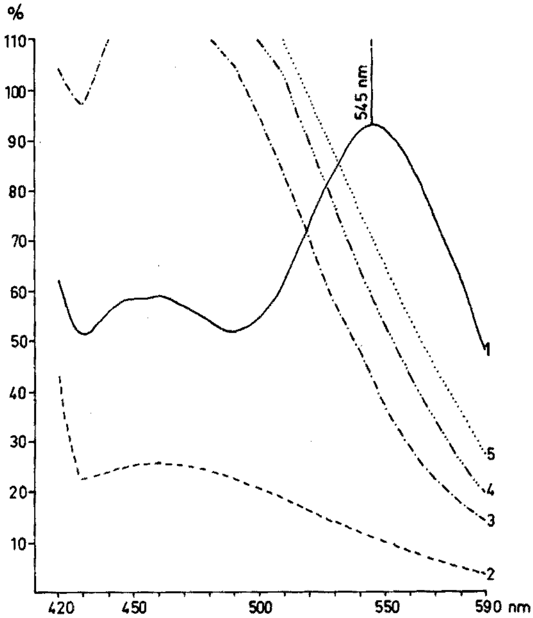

Fig. 3. Fluorescence emission spectrum of nicotinamide excited at 365 nm. (1) Nicotinamide, (2) pure cellulose background, (3) spray reagent background immediately after drying, (4) background after 24 h, (5) background after 96 h.

that of pure cellulose (see Figs. 1 and 2) and at the wavelengths which are of analytical importance, *i.e.* 545 and 530 nm, the background fluorescence is about 5% of the total fluorescence. A time study of the system over a period of 96 h revealed a small increase of the background to about 10% after 24 h and about 20% after 96 h. The intensity of the actual maxima varied only 2–3% over this period; some decrease in fluorescence may have been compensated for by the increase in background fluorescence with time. No shift of maxima was observed.

The choice of the proper primary filter is important, as can be seen from Fig. 3, where a spectrum of nicotinamide is shown with the 365-nm filter. In this case, background interference is so serious that an analysis of the compound would be virtually impossible. The maximum remains the same. The second maximum at 455 nm is not a true maximum for nicotinamide, but is believed to appear because of an excess of reagent.

Chromatography

The separation pattern obtained with the solvent system *n*-butanol saturated with a 3% ammonia solution is depicted in Fig. 4, after a separation time of 3 h. Corresponding R_F values were determined: for nicotinamide 0.62 and for nicotinic acid 0.30. Since no interfering substances were noticed in the organ extracts, the chromatography could be stopped as soon as the two spots were separated, which reduced the time for the chromatographic step to less than 60 min. The separation is also possible on unpurified cellulose MN-300 as obtained from the manufacturer (Macherey + Nagel, Düren, Western Germany). If this is done, a small decrease in accuracy because of some tailing of the nicotinic acid and a decrease in sensitivity because of a quenching effect of some impurities have to be taken into account. They are, however, not very serious, and the time saved by the elimination of the purification step is considerable.

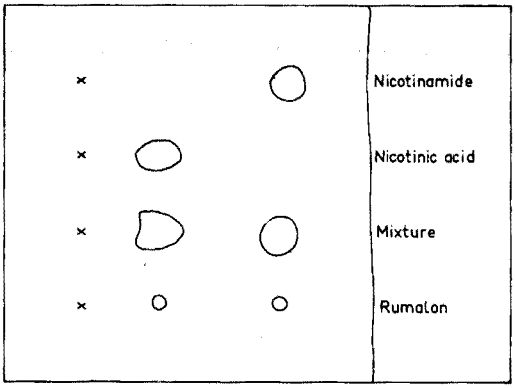

Fig. 4. Chromatogram of nicotinamide and nicotinic acid developed in one dimension on a cellulose layer for 3 h with *n*-butanol saturated with a 3% ammonia solution.

Detection limits

Instrumental detection limits were determined for optimum filter combinations. For the Zeiss instrument only a primary filter was needed and as mentioned earlier, a filter passing mercury lines at 436 nm was used. For the Camag-Turner instrument filters from the deluxe filter set (Turner Ltd., Palo Alto, Calif.) were tested. The best filter combination for both compounds consisted of primary filter 110-813 and secondary filter 110–818. Detection limits for both instruments when used for fluorescence measurements were about the same. Both instrumental and visual detection limits are given in Table I. The increase in sensitivity measured instrumentally for the fluorescence technique is about one hundred-fold in comparison with reflectance and quenching methods. The visual detection limit in daylight is based on the brown-yellow color formation of nicotinic acid and nicotinamide after the spraying step. Detection limits under UV were obtained visually under an ultraviolet lamp at 254 nm.

TABLE I

DETECTION LIMITS OF NICOTINIC ACID AND NICOTINAMIDE ON CELLULOSE LAYERS

	Nicotinic acid (μg/spot)	*Nicotinamide (μg/spot)*
Visual, daylight	0.04	0.02
Visual, UV	0.005	0.002_5
Fluorescence	0.001	0.002
Reflectance	0.1	0.1
Fluorescence quenching	0.2	0.2

Reproducibility

Data obtained by direct scanning on the Zeiss instrument after one-dimensional separation of nicotinic acid and nicotinamide on six different plates resulted in about 8% relative standard deviation for both. On the Turner instrument the reproducibility was about 1% better.

The factor which limits the reproducibility of this method is the spraying procedure, which is hard to standardize. Reflectance spectroscopy in the ultraviolet gives better reproducibility, since no spraying step is needed. For dansyl amino acids the reproducibility is of about the same order.

Calibration curves

Calibration curves for nicotinamide were recorded with the Zeiss instrument for reflectance spectroscopy, fluorescence quenching and fluorescence spectroscopy (see Fig. 5). For UV reflectance and quenching, the same shape of calibration curve was obtained, thus supporting the assumption that both methods work on the same principle, mainly the ultraviolet absorption of the compound of interest. Both curves can be rendered linear over a useful concentration range by plotting (peak area)^2, which is essentially reflectance $(R)^2$ *versus* concentration; this would be a rough approximation of the KUBELKA–MUNK function[7]. In the case of reflectance spectroscopy this UV absorption is measured directly. In the quenching method the compound acts as a UV filter and as a result the degree of excitation of the fluorescent background is lowered and a dark spot appears where the substance is adsorbed. This darkening effect (called quenching of fluorescence even though it is not a quenching phenomenon in the true sense) is again an indirect measure of the concentration of this UV filter (in this case, nicotinamide). The somewhat lower sensitivity of the quenching method can be attributed to the fact that with the available instrumental setup it is more difficult to choose optimum conditions. Fluorescence quenching offers therefore no advantage over reflectance spectroscopy. It suffers from poorer reproducibility owing to higher background fluctuations, and is less specific. If, however, one possesses only the Turner instrument, which does not permit reflectance measurements, then the quenching method offers in most cases a reasonable alternative for the analysis of UV-active substances which do not fluoresce or cannot be rendered fluorescent very easily. The major advantage of true fluorescence spectroscopy is its high sensitivity, which is usually between ten and a hundred times greater than that of reflectance spectroscopy (see also Fig. 5). For compounds which exhibit a stable and natural fluorescence, without necessitating a spraying procedure, the reproducibility is similar to that of reflectance spectroscopy. The calibration plot, fluorescence (plotted as peak area) *versus* concentration, is linear at lower concentration, *e.g.* up to 0.3 μg/spot (Fig. 5), and then so smoothly curved that it can easily be used for analytical purposes. The deviation from linearity at higher concentrations can be attributed to a partial absorption of the emitted fluorescence by the substrate.

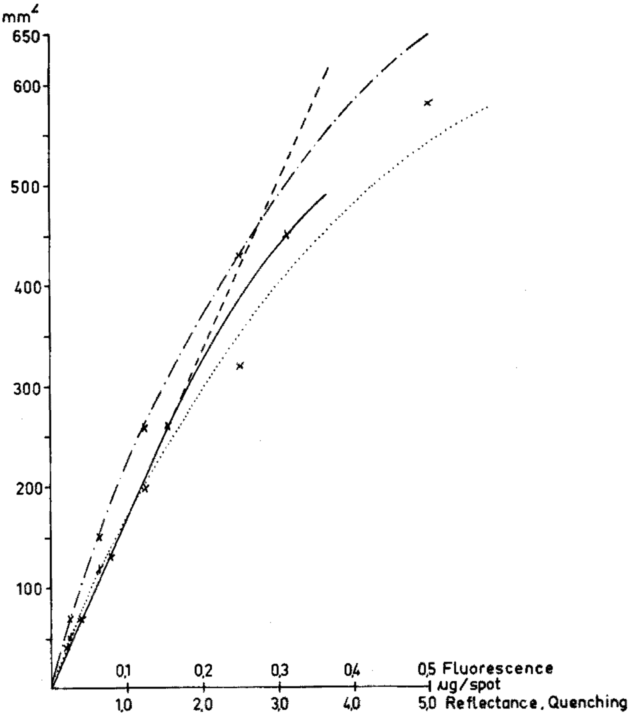

Fig. 5. Calibration curves for nicotinamide obtained by (----) fluorescence spectroscopy (theoretical), (——) fluorescence spectroscopy (experimental), (-.-) reflectance spectroscopy, (...) fluorescence quenching.

ANALYSIS OF SAMPLES

Analysis of an artificial mixture

An artificial mixture containing several other nucleo-derivatives and known

TABLE II

ANALYSIS OF AN ARTIFICIAL MIXTURE OF NUCLEO-DERIVATIVES CONTAINING KNOWN AMOUNTS OF NICOTINIC ACID AND NICOTINAMIDE

Analysis	*Nicotinamide*		*Nicotinic acid*	
	Amount found (µg/spot)	*% deviation from true value*[a]	*Amount found (µg/spot)*	*% deviation from true value*[b]
1	0.096	4.9	0.098	6.4
2	0.097	4.0	0.097	7.6
3	0.089	11.9	0.095	9.5
4	0.118	16.8	0.109	3.8
5	0.099	2.0	0.119	13.3
6	0.110	8.9	0.110	4.8
		Av. 8.1		Av. 7.6

[a] Amount present 0.101 µg/spot.
[b] Amount present 0.105 µg/spot.

TABLE III

ANALYSIS OF ORGAN EXTRACTS

	Nicotinamide	*Nicotinic acid*
Rubiron (batch 634)	$0.075 \pm 0.007_6$ µg/spot[a] 10.1% rel. s. d.[b]	$0.039 \pm 0.004_7$ µg/spot 12.1% rel. s. d.
Rumalon (batch MK 4087)	$0.092_5 \pm 0.012_8$ µg/spot 13.8% rel. s. d.	$0.109_7 \pm 0.009_7$ µg/spot 8.8% rel. s. d.

[a] Average of six determinations each.
[b] Relative standard deviation $s = \sqrt{\Sigma(M-\bar{M})^2/(n-1)}$

amounts of nicotinamide and nicotinic acid was analyzed. The results (Table II) were obtained with six standards and three spots of the "unknown", all spotted on the same plate and evaluated with the Zeiss instrument. The total analysis time with the Zeiss instrument was 5–6 h including chromatographic separation of about 1 h. The actual working time was 2 h. With the Turner instrument, accuracy is slightly better (≃7%), but the analysis takes 8 h and actual working time is about 5 h.

Analysis of biological samples

Cartilage red bone marrow extract (Rumalon, Robapharm Ltd., Basle, Switzerland) and a combination of several organ extracts in solid form (Rubiron, Robapharm Ltd.) were analysed for the two components (Table III). The content of nicotinamide and nicotinic acid in Rubiron was determined from an aqueous extract of this solid product only. The reproducibility of data in these biological samples was slightly poorer than in the synthetic mixture because of some tailing of spots.

The method discussed is suitable for routine analysis of nicotinamide and nicotinic acid in complex biological systems.

R. W. F. is thankful to Robapharm Ltd., Basle, Switzerland for financial support and available facilities to carry out this research. Part of this project was supported by a grant of the National Research Council of Canada.

SUMMARY

The specific determination of traces of nicotinamide and nicotinic acid by a combination of thin-layer chromatography and direct fluorescence spectroscopy is described. Two instruments are compared for performance. Instrumental detection limits of 0.001–0.002 µg/spot are reported. For an artificial mixture an average error of about 8% was found. The relative standard deviation for biological samples was between 8 and 14%. The method can be used for routine analysis and compares favourably with reflectance spectroscopic and fluorescence quenching techniques. The total time of analysis is 5–6 h with an actual working time of 2 h.

RÉSUMÉ

On décrit une méthode spécifique pour le dosage de traces de nicotinamide et d'acide nicotinique en combinant chromatographie sur couche mince et spectroscopie de fluorescence. Les limites de détection instrumentales sont 0.001–0.002 µg/tache. On arrive à une erreur moyenne d'environ 8% pour un mélange artificiel. La déviation standard relative est de 8 à 14% pour des échantillons biologiques. Cette méthode peut s'appliquer à des analyses de routine; les résultats concordent avec ceux obtenus par d'autres techniques de spectroscopie et de fluorescence.

ZUSAMMENFASSUNG

Die spezifische Bestimmung von Spuren von Nicotinamid und Nicotinsäure durch eine Kombination von Dünnschichtchromatographie und direkter Fluoreszenz-Spektroskopie wird beschrieben. Zwei Instrumente für die Ausführung werden verglichen. Es werden instrumentelle Nachweisgrenzen von 0.001–0.002 µg/Fleck mitgeteilt. Bei einer selbst angesetzten Mischung wurde ein mittlerer Fehler von etwa 8% gefunden. Die relative Standardabweichung bei biologischen Proben betrug zwischen 8 und 14%. Die Methode kann für Routineanalysen angewendet werden und ist günstig im Vergleich zur Anwendung der Reflexionsspektroskopie und des Fluoreszenz-Quench-Effektes. Der gesamte Zeitbedarf einer Analyse beträgt 5–6 h mit einer tatsächlichen Arbeitszeit von 2 h.

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

THE COLORIMETRIC DETERMINATION OF TERTIARY ALCOHOLS WITH AN ALDEHYDE-ACID REAGENT

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(Received October 13th, 1969)

The most widely used colorimetric procedure for determining alcohols is that based on the so-called KOMAROWSKY reaction[1]. The reagent is an aromatic aldehyde in the presence of acid. Its chief application has been to the determination of higher alcohols ("fusel oil", made up mainly of isobutanol and isopentanol) in spirits and alcoholic beverages[2-14]. Work has been published on the determination also of sugar alcohols[15] and polyalcohols[16-18] and of some other compound classes such as olefines and related compounds (*e.g.* sorbic[19] and laevulinic[20] acids and terpenes[21,22]). There has, however, been surprisingly little reference to detection or determination of tertiary alcohols. DAL NOGARE AND MITCHELL[16] and ROSENTHALER[23] quoted tertiary butanol as yielding colour with a typical aldehyde-acid reagent. Only KOLESNIKOV[24] appears to have developed a quantitative method, namely for tertiary (and secondary) alcohols in plant material. In the present work, an attempt is made to fill up this gap.

Parameters demanding study are: nature and concentration of aldehyde, acid and alcohol; solvent or diluent; the order of mixing of these components; and reaction temperature and time. A wide range of acids and especially of aldehydes has been employed in previous work. Acids include the common mineral acids, sulphuric, hydrochloric, phosphoric and perchloric as well as acetic and *p*-toluenesulphonic acids. Benzaldehyde or a substituted ($-OH$, $-OR$, $-NR_2$, also $-NO_2$, $-Cl$, $-SO_3H$) benzaldehyde has nearly always been the aldehyde component; cinnamaldehyde and furfuraldehyde (that used originally by KOMAROWSKY) appear only occasionally. The principal solvents used are water, ethanol and acetic acid.

Preliminary studies led us to choose as the most suitable components of the reaction mixture: sulphuric acid, *p*-dimethylamino- or *p*-hydroxybenzaldehyde, and water or acetic acid.

EXPERIMENTAL

Reagents

Sulphuric acid (96%) and glacial acetic acid (analytical grade, Merck) were used.

p-Dimethylamino- and *p*-hydroxybenzaldehydes (reagent grade Merck) were purified further by crystallisation from water; the purity was checked by thin-layer chromatography.

Various reagent-grade alcohols were purified by distillation or recrystallisation;

the purities were checked by gas chromatography. *Tert*-butanol was dried with sodium sulphate, frozen out and finally distilled.

Solutions

The aldehydes were dissolved cautiously in the sulphuric acid at 0°; this reagent could be stored in an amber bottle for several weeks without sensible deterioration.

Solutions of alcohols were prepared in water or glacial acetic acid.

Apparatus

Unicam SP800, with 1-cm cuvettes.

Procedure

Mixtures of the aldehyde reagent in sulphuric acid and the alcohol solution in water or acetic acid were heated in glass stoppered tubes for various times at temperatures ranging from 50 to 100°. After rapid cooling in ice water, the contents of the tubes were transferred to cuvettes. Absorbances were measured against blank solutions without alcohol which had been similarly treated, or spectra were recorded.

RESULTS

Dimethylaminobenzaldehyde

Solutions containing 2 or 3 mg of this aldehyde per 3 ml of 96% sulphuric acid were used; 2.96 ml of this were mixed with 0.04 ml of alcohol solution. Colour development with *tert*-butanol attained a maximum after about 5 min, after which the colour intensity slowly declined. This reaction time was chosen for quantitative work and absorbances were measured at 498 nm, the spectral maximum.

Essentially straight lines relating the absorbance and the amount of *tert*-butanol were found. An absorbance of unity was obtained with about 8 μg of alcohol for the more concentrated aldehyde reagent, and with about 6 μg of alcohol for the more dilute reagent.

This procedure suffered from comparatively high sensitivity to changes in the concentration of water in the mixture, increase of which suppressed colour formation. Moreover, it was difficult to mix the small sample efficiently into the viscous concentrated acid. The procedure was subsequently abandoned in favour of that described immediately below.

p-*Hydroxybenzaldehyde*

Mixtures of *tert*-butanol with *p*-hydroxybenzaldehyde in 90–95% sulphuric acid gave solutions on heating which possess an absorption maximum at 437 nm. This maximum is also suppressed by increase in the water concentration, giving way to another maximum at 575 nm (violet solution). Figure 1 shows the influence of water content on the absorbance at 575 nm. The highest absorbance value, whether after 15 or 30 min at 50°, corresponds roughly to the medium 96% sulphuric acid–water (2+1). This mixture is still rather viscous and evolves considerable heat on mixing with water. For quantitative work, sulphuric acid–water (1+1) was therefore employed, so that these two disadvantages were mitigated, yet not at the expense of a serious slump in absorbance from the highest value.

Absorbance values were then obtained for different amounts of *tert*-butanol by means of the same procedure as that described for dimethylaminobenzaldehyde. The aldehyde reagent contained 5 mg of aldehyde per ml of 96% sulphuric acid–water (1+1); 2.96 ml of this and 0.04 ml of alcohol sample were heated for 10 min at 100° and absorbances were measured at 575 nm against blanks treated in the same way. A satisfactory linear relation was found, with data reproducible to within 1%.

This procedure was tested on some other tertiary alcohols; the results are

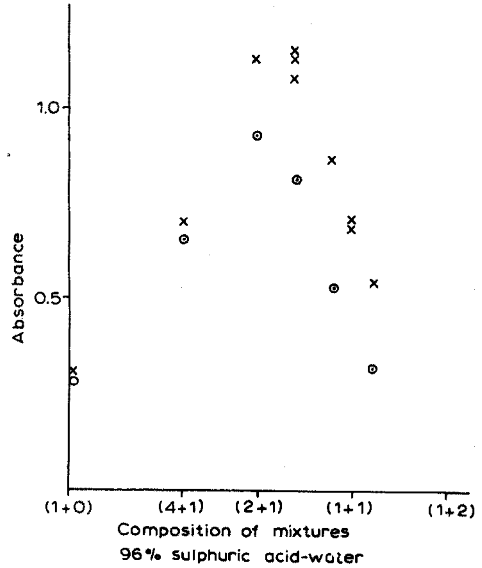


Fig. 1. Influence of water content on absorbance at 575 nm. 2 μg of *tert*-butanol and 0.5 mg of *p*-hydroxybenzaldehyde in 1.5 ml of solution. Reaction time at 50°: (⊙) 15 min, (×) 30 min.

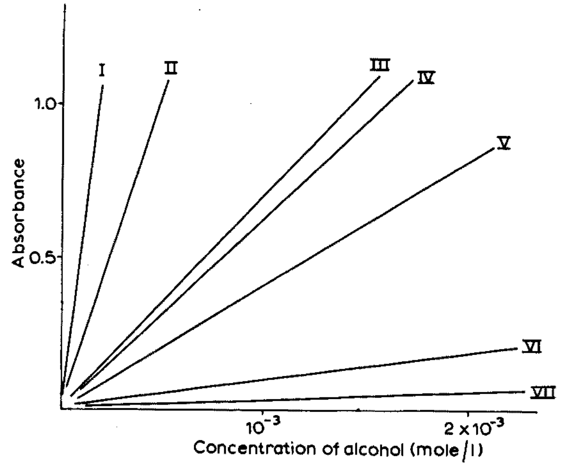


Fig. 2. Calibration curves for tertiary alcohols. 15 mg of aldehyde in 3 ml of 96% sulphuric acid–water (1 + 1). Alcohols: (I) Me_3C–OH, (II) $Me_2C(tBu)$–OH, (III) $Me_2C(Et)$–OH, (IV) $MeC(Et)_2$–OH, (V) Et_3C–OH, (VI) *n*-Pr_3C–OH, (VII) *n*-Bu_3C–OH.

TABLE I

COLORIMETRIC DETERMINATION OF TERTIARY ALCOHOLS WITH *p*-HYDROXYBENZALDEHYDE/SULPHURIC ACID[a]

Tertiary alcohol	*Wavelength of maximum (nm)*	*Molar absorptivity* ($cm^2/mmole$)	*Smallest determinable amounts* (μg)
Me_3C–OH	575	$4.8 \cdot 10^4$	0.1–0.2
$Me_2C(tBu)$–OH	569	$1.9 \cdot 10^4$	0.5–1.0
$Me_2C(Et)$–OH	556	$6.4 \cdot 10^3$	2.0–5.0
$MeC(Et)_2$–OH	558	$5.0 \cdot 10^3$	2.0–5.0
Et_3C–OH	552	$3.7 \cdot 10^3$	5.0–10
n-Pr_3C–OH	556	$7.6 \cdot 10^2$	20
n-Bu_3C–OH	556	$2.1 \cdot 10^2$	50

[a] 5 mg of aldehyde per ml of 96% sulphuric acid–water (1+1).

given in Fig. 2 and Table I. The 200-fold diminution in sensitivity from *tert*-butanol to tri-*n*-butylcarbinol is striking.

No colour was yielded under these conditions by various primary alcohols from C_5 up to C_{18}. Secondary alcohols yield colour but less sensitively. For example, 10–100 times as much isopropanol as *tert*-butanol is required to give the same absorbance.

Water has a similar influence on results with some other hydroxy- and alkoxyaldehydes, such as anisaldehyde, vanillin and ethyl vanillin. *m*-Hydroxybenzaldehyde resembles *p*-dimethylaminobenzaldehyde more in that water suppresses colour formation without yielding another maximum; *o*-hydroxybenzaldehyde, salicylaldehyde, evidently yields too intense a colour without alcohol.

DISCUSSION

DUKE[25] described the isolation of dibenzalacetone from mixtures of isopropanol and benzaldehyde in 9 *M* sulphuric acid or 12 *M* hydrochloric acid after having heated under reflux for 4 h. In the present work, the same product was obtained from this mixture (sulphuric acid also *ca.* 9 *M*) after it had stood for some 10 days. It could be isolated from the red precipitate formed and also from the filtrate from this precipitate. The filtrate also contained monobenzalacetone. Solutions of dibenzalacetone in concentrated sulphuric acid showed the same spectrum with maximum absorbance at 460 nm, as the isopropanol/benzaldehyde/sulphuric acid mixtures.

The protonisation yielding a light-absorbing species may be formulated:

$$(C_6H_5{-}CH{=}CH{-})_2C{=}O \xrightarrow{H^+} (C_6H_5{-}CH{=}CH{-})_2\overset{+}{C}{-}OH \leftrightarrow$$

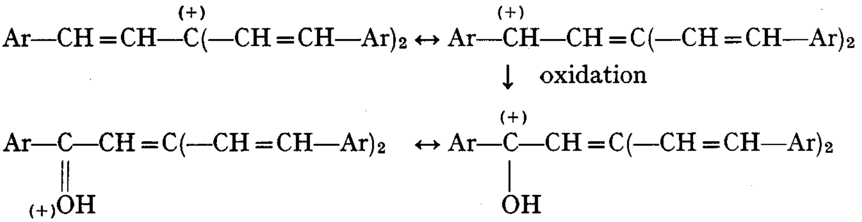
$$(C_6H_5{-}CH{=}CH{-})_2C{=}\overset{+}{O}H$$

Dibenzalacetone could be reduced with sodium borohydride to distyrylcarbinol, $(C_6H_5{-}CH{=}CH{-})_2CHOH$. This carbinol dissolved in concentrated sulphuric acid to yield a solution with an absorbance maximum at 560 nm. Within some minutes, however, this maximum disappeared and was replaced by that at 460 nm, found for solutions of benzalacetone in the acid. The carbinol was presumably formed in an initial reaction between isopropanol and benzaldehyde and was subsequently oxidised to the ketone. The species absorbing at 560 nm may be a carbonium ion of which one resonance form is $(C_6H_5{-}CH{=}CH{-})_2\overset{+}{C}H$. It is evidently so rapidly converted into that absorbing at 460 nm that it does not show in the absorbance spectrum of the isopropanol/benzaldehyde/sulphuric acid mixture. However, the corresponding absorbance maximum of solutions in sulphuric acid of *p,p'*-dimethoxydistyrylcarbinol could be recognised in the absorbance spectrum of mixtures of isopropanol with anisaldehyde in sulphuric acid shortly after mixing. It, too, disappeared swiftly, giving way to the same maximum as that yielded by *p,p'*-dimethoxydibenzalacetone in sulphuric acid. This supports the hypothesis that carbinol is formed before oxidation, as opposed to DUKE's proposal of oxidation of alcohol to ketone, followed by formation of unsaturated ketone through reaction with the aromatic aldehyde.

So far, it has not been possible to identify any individual compounds resulting from reaction of *tert*-butanol with an aromatic aldehyde in acid solution. The infrared absorbance spectrum of the solid coloured product formed in the mixture of *tert*-butanol, *p*-hydroxybenzaldehyde and sulphuric acid (or hydrochloric acid or aluminium chloride) indicated that C—O links had disappeared and that C=C links had been formed. One possibility is that tristyrylcarbinol is yielded, analogously to the formation of distyrylcarbinol from isopropanol:

$$3\ ArCHO + (CH_3)_3C{-}OH \rightarrow (Ar{-}CH{=}CH{-})_3C{-}OH$$

This may then give the tristyrylcarbonium ion as coloured species. In further analogy to the scheme suggested above, oxidation could take place:



$$Ar{-}CH{=}CH{-}\overset{(+)}{C}({-}CH{=}CH{-}Ar)_2 \leftrightarrow Ar{-}\overset{(+)}{C}H{-}CH{=}C({-}CH{=}CH{-}Ar)_2$$

$$\downarrow \text{ oxidation}$$

$$Ar{-}\underset{\underset{{}^{(+)}OH}{\|}}{C}{-}CH{=}C({-}CH{=}CH{-}Ar)_2 \leftrightarrow Ar{-}\underset{\underset{OH}{|}}{\overset{(+)}{C}}{-}CH{=}C({-}CH{=}CH{-}Ar)_2$$

Attempts are being made to prepare and study tristyrylcarbinol (preparation through reaction of dibenzalacetone with styryl magnesium halide). Preliminary indications are that the tristyrylcarbinol does in fact yield the same spectrum in sulphuric acid as that obtained from mixtures of *tert*-butanol, benzaldehyde and sulphuric acid. It is hoped to report later, with more experimental detail, all those results concerned with elucidation of the nature of the coloured species.

One of us (I.V.) wishes to thank the Fonds der Chemischen Industrie, Düsseldorf, for a scholarship, during the tenure of which much of this work was carried out.

SUMMARY

A colorimetric determination of several tertiary alcohols with a reagent consisting of an aromatic aldehyde and sulphuric acid is described. The nature of the coloured reaction product(s) is briefly discussed.

RÉSUMÉ

On décrit un dosage colorimétrique de plusieurs alcools tertiaires à l'aide d'un réactif constitué d'un aldéhyde aromatique en milieu acide sulfurique. On discute brièvement le mécanisme de la réaction.

ZUSAMMENFASSUNG

Es wurde eine kolorimetrische Bestimmung einiger tertiären Alkohole beschrieben. Sie beruht auf der Reaktion mit einem aromatischen Aldehyd in schwefelsaurem Milieu. Der Chemismus der Farbreaktion wurde kurz diskutiert.

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Anal. Chim. Acta, 49 (1970) 535–540

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

SOME KINETIC DATA ON THE OXIDATION OF THE COBALT(II)–BIPYRIDYL COMPLEX BY COPPER(II) AND IRON(III) PERCHLORATES IN ANHYDROUS ACETONITRILE

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(Received October 23rd, 1969)

The use of non-aqueous solvents is a modern trend in titrimetric analysis. Acetonitrile especially seems to be a very promising medium for acid–base titrations as well as for redox titrations. In connection with the latter category, investigations with cerium(IV)[1], iron(III)[2] and copper(II)[3–5] should be mentioned. However, the literature does not appear to provide information on the kinetics of redox reactions in anhydrous acetonitrile, hence the present investigation was started.

The method consisted in observing the time-dependence of the limiting current of the cobalt(II)–bipyridyl complex, $[Co(bipy)_3]^{2+}$, after addition of the oxidant. A similar method has been reported for investigations in aqueous solutions[6–8].

First, the polarographic behaviour of the cobalt(II)– and cobalt(III)–bipyridyl complexes and of the perchlorates of copper(II) and iron(III) was studied at the rotating platinum electrode. The experimental conditions for the kinetic measurements followed from the polarographic results.

EXPERIMENTAL

Reagents

Acetonitrile. Reagent-grade acetonitrile (Merck) was used after purification by the method proposed by FORCIER AND OLVER[9] (three distillations: first from sodium hydride, then from phosphorus pentoxide). The solvent was kept in the dark and protected against humidity by P_2O_5.

Sodium perchlorate. This was prepared from reagent-grade sodium carbonate by adding reagent-grade perchloric acid[10]. It was dried at 150° for 24 h. A 0.1 M solution in acetonitrile was used as supporting electrolyte.

Silver nitrate. The reagent-grade salt was dried at 120°.

Copper(II)tetra(cyanomethane) perchlorate $[Cu(II)(CH_3CN)_4(ClO_4)_2]$. This was prepared from copper(II) perchlorate as described in the literature[3]. The copper content was checked by titration with EDTA with murexide as indicator. 10^{-2} and $5 \cdot 10^{-2}$ M solutions in acetonitrile were used.

Cobalt(III)tris(bipyridyl) perchlorate trihydrate. This was prepared by the method of BURSTALL AND NYHOLM[12]. The cobalt content was determined after potentiostatic reduction, by titration with iron(III) sulfate in the presence of an excess

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of 2,2'-bipyridyl, with biamperometric indication (a similar potentiometric titration is described in the literature[13]).

Iron(III) perchlorate dihydrate. This was prepared from the commercial product (Alfa Inorganics, Inc.) by drying *in vacuo* at 70°[14]. $1 \cdot 10^{-2}$ and $5 \cdot 10^{-2}$ *M* solutions in acetonitrile were used. The iron content was checked after addition of water by titration with EDTA, with thiocyanate as an indicator.

Bipyridyl. The Analar-grade product was dried *in vacuo* at 40°. All solids were stored over P_2O_5.

Apparatus (Fig. 1)

For all experiments, a multipurpose vessel was used. For controlled potential electrolysis, a mercury pool electrode or a rotating platinum spiral electrode served as working electrode. With 0.1 *M* sodium perchlorate as supporting electrolyte the resistance between working electrode and counter electrode was *ca.* 1000 ohms. For controlled potential electrolysis the Wadsworth Controlled Potential Electro-Depositor was used, the sheet electrode serving as counter electrode. Polarographic measurements were carried out with the PO4 Polariter (Radiometer), the sheet electrode then acting as a reference electrode. The characteristics of the dropping mercury electrode (D.M.E.) were: $m = 5.39$ mg sec^{-1}, $t_d = 2.34$ sec in a 0.1 *M* solution of sodium perchlorate at a mercury head of 60 cm with the D.M.E. and reference

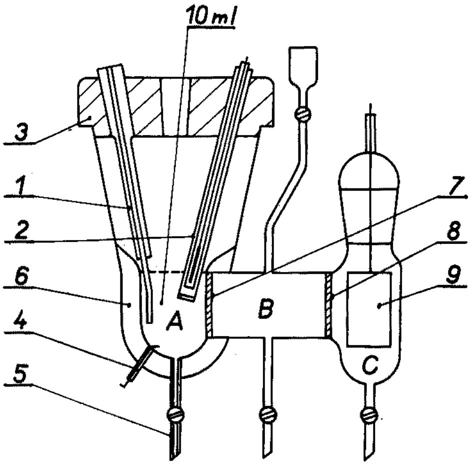

Fig. 1. Multipurpose vessel. (A) Working space, (B) intermediate space filled with 1.0 *M* $NaClO_4$ in acetonitrile, (C) space for Ag sheet electrode filled with 0.01 *M* $AgNO_3$ and 1.0 *M* $NaClO_4$ in acetonitrile, (1) inlet for nitrogen for passing through the solution or above the solution, (2) Ag-wire reference electrode for controlled potential electrolysis consisting of two tubes, the outer filled with 1.0 *M* $NaClO_4$ solution in acetonitrile and the inner one containing Ag wire and filled with 1.0 *M* $NaClO_4$ and 0.01 *M* $AgNO_3$ solution in acetonitrile, (3) cover from a Metrohm polarographic vessel with five openings—central opening for a rotating platinum electrode, a dropping mercury electrode, a rotating platinum spiral electrode or for a stirring rod (for controlled potential electrolysis). Other openings served for the Ag-wire reference electrode, for inlet and outlet of nitrogen and for the addition of solutions, (4) contact for the Hg pool electrode, (5) capillary for removing mercury after controlled potential electrolysis and for emptying the working space, (6) thermostatted jacket, (7) sinter plate, porosity no. 2, (8) sinter plate, porosity no. 1, (9) Ag sheet electrode.

electrode short-circuited. The rotating platinum electrode (Metrohm) was rotated at 750 r.p.m. The rotating platinum spiral electrode (for controlled potential electrolysis) was obtained by turning a spiralized platinum wire (length 42 cm and diameter 0.05 cm) over the shaft of the rotating platinum electrode.

The solutions of $[Co(bipy)_3]^{3+}$, copper(II) and iron(III) were delivered from a microburette (Metrohm E 374; total volume 1 ml) and for kinetic measurement a syringe (volume 0.5 ml) with a Kel-F cannula (Hamilton) was used.

A Varian recorder with chart speed 16 in/min or a Honeywell Electronik 19 recorder with chart speeds variable between 1 in/sec and 1 in/40 sec was used for recording the limiting current during the reaction. The half-wave potentials were assessed from polarograms and corrected for iR drop. The curves were recorded with a potential sweep of 200 mV/min (for the D.M.E.) and 400 mV/min (for the rotating platinum electrode). All measurements were made at a temperature of $20.0° \pm 0.1°$.

Procedure for kinetic measurements

To a cell containing 10.0 ml of 0.1 M sodium perchlorate solution in acetonitrile a known quantity of cobalt(III)–bipyridyl solution was added from a microburette. After de-aeration of the solution a polarogram of the cobalt(III) complex was recorded at the D.M.E. Cobalt(II)–bipyridyl complex was prepared by controlled potential electrolysis at -0.4 V and the limiting current corresponding to traces of unreduced cobalt(III) complex, necessary for the exact estimation of the initial concentration of the cobalt(II) complex, was recorded. The mercury electrode and the reference electrode were then removed and the limiting current was recorded at a suitable constant potential against time. (Before every run the rotating platinum electrode was polarised at $+ 1.5$ V in 0.1 M sodium perchlorate in acetonitrile for 10 min.) Subsequently, a known quantity of the oxidant dissolved in acetonitrile was added from the syringe, the oxidant concentration being in excess over the concentration of the cobalt(II)–bipyridyl complex. Addition and mixing were sufficiently rapid (the time involved was about 0.2 sec) to give reproducible results at the concentration levels used.

RESULTS

Polarographic behaviour of bipyridyl complexes of cobalt in acetonitrile

There are no references* in the literature about the behaviour of these complexes in acetonitrile. The cobalt(III)–bipyridyl complex gave a well-developed wave at a rotating platinum electrode in acetonitrile; the height of the wave was proportional to the concentration. The $E_{\frac{1}{2}}$ value was 0.025 V and was almost independent of the concentration.

The plots of log $i/(i_d - i)$ *vs.* E (corrected for iR drop) showed a mean reciprocal slope of 0.067 V for the rotating platinum electrode and of 0.060 V for the D.M.E. The average half-wave potential of the cathodic wave at the D.M.E. was -0.005 V.

During controlled potential electrolysis at a potential of -0.4 V the polarographic wave shifted downward. After about 20 min, more than 98% of the cobalt(III) was reduced. Cobalt(II)–bipyridyl complex prepared in this way showed an anodic

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* During the present investigations there appeared an article dealing with the polarographic behaviour at a D.M.E. of bipyridyl complexes of cobalt in acetonitrile[15].

wave at the D.M.E. at the same $E_{\frac{1}{2}}$ value and with the same reciprocal slope as the corresponding cathodic wave. With a rotating platinum electrode, the cobalt(II) complex did not produce such a well-developed wave as was the case with the cobalt(III) complex. The half-wave potential shifted about 50 mV in a positive direction, but the limiting current remained proportional to the concentration of the cobalt(II) complex. If, before every run, the rotating platinum electrode was polarized in acetonitrile at a potential of +1.5 V during a few minutes, the limiting current became reproducible.

Polarographic behaviour of copper in acetonitrile

From the literature it is known that a solution of copper(II) perchlorate hexahydrate in acetonitrile gives two reduction waves[16-18]. If a D.M.E. is used, the first wave corresponding to the reduction of copper(II) to copper(I) is influenced by the dissolution effect of the mercury in this medium; the second wave, corresponding to the reduction of copper(I) to copper metal, is reversible with a half-wave potential of about −0.4 V *vs.* S.C.E. At a rotating platinum electrode KOLTHOFF AND COETZEE[17] obtained two waves of equal heights for the reduction of copper(II) with $E_{\frac{1}{2}} = +1.0$ V (for Cu(II) → Cu(I)) and $E_{\frac{1}{2}} = -0.5$ V (for Cu(I) → Cu(0)). For the oxidation of copper(I) they obtained a wave with $E_{\frac{1}{2}} = +1.0$ V. From these results they concluded that the Cu(II)/(I) couple behaves reversibly in acetonitrile. Comparison of the polarographic behaviour of copper in acetonitrile with that in water, leads to the conclusion[17,18] that the solvation energy of copper(I) ion in acetonitrile is much greater than that in water and that the solvation energy of copper(II) is smaller in acetonitrile than in water.

The behaviour of copper(II)cyanomethane perchlorate in acetonitrile at a rotating platinum electrode was quite different. An elongated wave was obtained, corresponding to the reduction of copper(II) to copper(I), the half-wave potential being irreproducible (about 0.4 V).

After controlled potential electrolysis at a potential of about −0.1 V (which corresponded to the limiting current), the wave decreased, but no anodic wave was obtained in the same voltage range; only above +0.8 V did an elongated oxidation wave appear. When the hydrated copper(II) perchlorate, $Cu(H_2O)_6(ClO_4)_2$, was studied in acetonitrile (as was done by KOLTHOFF AND COETZEE), nearly the same results were obtained as in the case of $Cu(CH_3CN)_4(ClO_4)_2$. Even when the rotating platinum electrode was treated in different ways (polarisation at positive potentials, action of cold or hot nitric acid, etc.), well developed and reproducible anodic waves could not be achieved.

Polarographic behaviour of iron in acetonitrile

It was shown by KOLTHOFF AND COETZEE[17] that iron(III) gives at the D.M.E. two reduction waves in acetonitrile, corresponding to the formation of iron(II) and metallic iron, respectively. The first wave rises from the potential at which dissolution of mercury occurs; the second has a half-wave potential of −1.0 V *vs.* S.C.E. These authors obtained for the reduction of iron(III) to iron(II) at a rotating platinum electrode an irreversible wave with $E_{\frac{1}{2}} \sim +1.1$ V and for the oxidation of iron(II) to iron(III) an irreversible wave with $E_{\frac{1}{2}} \sim +1.6$ V. KOLTHOFF AND COETZEE[17] concluded from these values that iron(III) is a much stronger oxidizing agent in acetonitrile than in water. In this work the behaviour of $Fe(H_2O)_2(ClO_4)_3$ was reexamined. The results of this study showed that iron(III) is irreversibly reduced to iron(II) at a rotating platinum electrode at a half-wave potential ∼ +0.5 V (against Ag/0.01 *M* Ag^+ electrode) and the height of corresponding wave is proportional to the iron(III) concentration.

After controlled potential electrolysis (at the rotating platinum spiral electrode) at a potential of about +0.1 V, the cathodic wave height decreased; at the same time an anodic wave starting at +1.0 V appeared, showing too small a slope. Even after treatment of the electrode in different ways, reproducible and well developed waves corresponding to the oxidation of iron(II) to iron(III) could not be achieved.

Some notes on the polarographic behaviour of iron and bipyridyl complexes of cobalt in acetonitrile in the presence of bipyridyl

The above study of iron(III) in acetonitrile showed that an irreversible cathodic wave was obtained with an $E_{\frac{1}{2}}$ of ∼ +0.5 V. After the addition of an excess of bipyridyl (30-fold or higher excess with respect to iron(III)), the wave shifted in a negative direction and its half-wave potential became −0.42 V. The wave height was proportional to the iron(III) concentration, and the shape of the wave was better than it was in the absence of bipyridyl.

Nevertheless, the plot of log $i/(i_d-i)$ *vs.* E was not linear. After controlled potential electrolysis of this solution at a potential of about −0.6 V, the iron(II) generated gave a reversible anodic wave with $E_{\frac{1}{2}} = +0.75$ V. The shape of this wave and its half-wave potential were the same as those of the solution of $Fe(bipy)_3(ClO_4)_2$ in acetonitrile[19].

For the polarographic reduction of cobalt(III) at the rotated platinum electrode, exactly the same results were obtained whether bipyridyl was present in excess or not. On the other hand, the cobalt(II)–bipyridyl complex gave a better developed wave when bipyridyl was present in excess. Its half-wave potential, 0.00 V, was independent of the cobalt concentration, and the wave height was proportional to the cobalt(II) concentration.

When the D.M.E. was used instead of the rotated platinum electrode, only an elongated wave could be obtained for the reduction of iron(III), the current arising at −0.1 V from the anodic current. In all cases where the D.M.E. was used in the presence of free bipyridyl, an anodic wave was observed with a half-wave potential of +0.05 V. This wave is probably due to the formation of a complex between mercury and bipyridyl. For the same reason the wave corresponding to the oxidation of $Co(II)(bipy)_3$ was indistinguishable, and the foot of the cathodic wave of $Co(III)(bipy)_3$ directly coalesced with the anodic wave of bipyridyl.

KINETIC MEASUREMENTS

Reaction between $Co(II)(bipy)_3$ and $Cu(CH_3CN)_4(ClO_4)_2$ in acetonitrile

An attempt was made to obtain some information about the reaction between the cobalt(II)–bipyridyl complex and copper(II) perchlorate in acetonitrile. Data on the stoichiometric ratio, the order and the reaction rate constant of this reaction were required. The stoichiometry of the reaction was determined by the following titration method: to a known quantity of the cobalt(II)–bipyridyl complex in acetonitrile a two-fold excess of a copper(II) perchlorate solution in acetonitrile was added. After a few seconds the solution was acidified with aqueous 5 *M* acetic acid and the excess of copper(II) was determined by iodometry. It was shown that the stoichiometric ratio is 1:1, so that the reaction may be expressed by the equation:

$$\text{Co(II) (bipy)}_3 + \text{Cu(II)} \rightarrow \text{Co(III) (bipy)}_3 + \text{Cu(I)}$$

From polarization curves it was evident that in the potential region from +0.6 V to +0.8 V, the current flowing through the rotated platinum electrode corresponds only to the oxidation of the cobalt(II)–bipyridyl complex. A half life of about 1.9 sec was found for a $9 \cdot 10^{-5}$ M solution of the cobalt(II)–bipyridyl complex and a ten-fold excess of copper(II).

The rate of the reaction can be related to the concentration of the reactants by the equation

$$v = k[\text{Co(II) (bipy)}_3]^m\ [\text{Cu(II)}]^n$$

where v is the reaction rate, k the rate constant, and m and n are orders with regard to the cobalt(II) and copper(II) concentration, respectively. Taking common logarithms, $\log v = \log k + m \log [\text{Co(II) (bipy)}_3] + n \log [\text{Cu(II)}]$. If the initial concentration of copper(II) is very large compared to that of cobalt, the copper(II) concentration can be assumed constant during the run and

$$\log v = m \log [\text{Co(II) (bipy)}_3] + \log k'$$

If, therefore, the reaction rate is measured at various values of instantaneous Co(II) (bipy)$_3$ concentration, a double-logarithmic plot of the reaction rate *vs.* the concentration should give a straight line of slope m (see Table I and Fig. 2). From Fig. 2 the slope m was found to be 0.995.

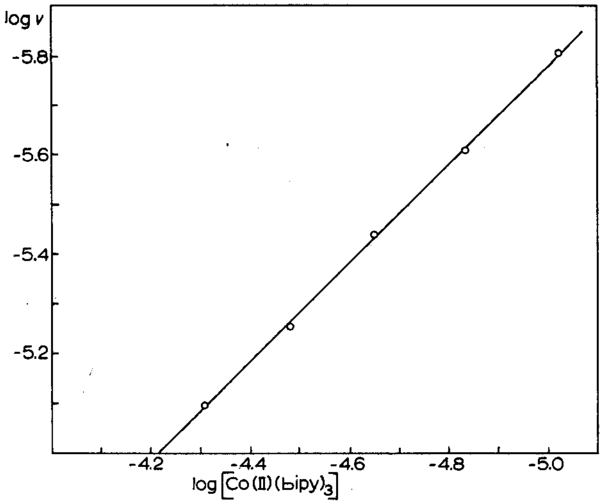

Fig. 2. Log–log plot of the reaction rate v against the concentration of [Co(II) (bipy)$_3$]. $[\text{Cu(II)}]_0 = 9.71 \cdot 10^{-4}$ M, $[\text{Co(II) (bipy)}_3]_0 = 8.82 \cdot 10^{-5}$ M.

The order n was calculated by means of the expression

$$n = \frac{\log k'_{\text{II}} - \log k'_{\text{I}}}{\log [\text{Cu(II)}]_{0,\text{II}} - \log [\text{Cu(II)}]_{0,\text{I}}}$$

where k'_{II} and k'_{I} are the pseudo first-order rate constants and $[Cu(II)]_{0,I}$, $[Cu(II)]_{0,II}$ are the respective initial concentrations. The double-logarithmic plot of the pseudo first-order rate constant against the initial copper(II) concentration gives a straight line with slope n (see Table II and Fig. 3). From Fig. 3 the slope n was found to be 0.492.

TABLE I

DATA FOR THE CALCULATION OF THE ORDER m

($[Cu(II)]_0 = 9.71 \cdot 10^{-4}$ M, $[Co(II)\ (bipy)_3]_0 = 8.82 \cdot 10^{-5}$ M; v was calculated from the slope of the current–time curve)

t (sec)	$v \cdot 10^6$ (mole l^{-1} sec^{-1})	log v	$[Co(II)\ (bipy)_3] \cdot 10^5$ (mole l^{-1})	log $[Co(II)\ (bipy)_3]$
1.3	8.03	−5.095	4.92	−4.308
3.8	5.59	−5.253	3.29	−4.483
6.3	3.58	−5.446	2.24	−4.650
8.8	2.47	−5.607	1.46	−4.836
11.3	1.57	−5.804	0.951	−5.022

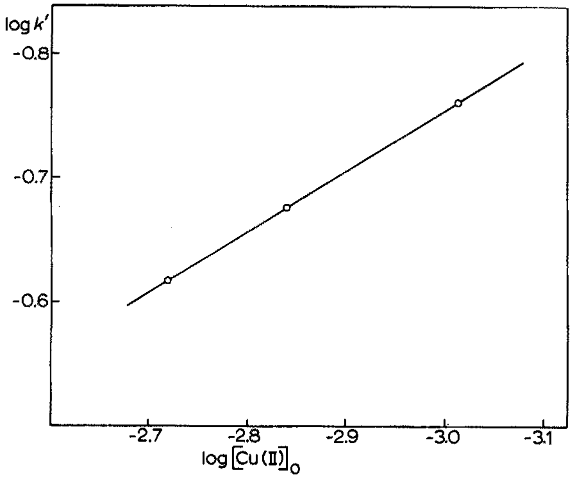

Fig. 3. Log–plot of the pseudo first-order rate constant k' against the initial copper(II) concentration $[Cu(II)]_0$.

TABLE II

DATA FOR THE CALCULATION OF THE ORDER n

$[Co(II)\ (bipy)_3]_0 \cdot 10^5$ (mole l^{-1})	$[Cu(II)]_0 \cdot 10^4$ (mole l^{-1})	log $[Cu(II)]_0$	Pseudo first-order rate constant $k' \cdot 10$ (sec^{-1})	log k'
8.82	9.71	−3.013	1.742	−0.759
8.89	14.40	−2.841	2.110	−0.676
8.85	19.05	−2.720	2.413	−0.617

From the values of m and n obtained it is evident that the reaction rate should be expressed as follows:

$$-\frac{\mathrm{d}\,[\mathrm{Co(II)}\,(\mathrm{bipy})_3]}{\mathrm{d}t} = k\,[\mathrm{Co(II)}\,(\mathrm{bipy})_3]\,[\mathrm{Cu(II)}]^{\frac{1}{2}}$$

The rate constant k was calculated from this rate equation. For every run, the reaction rate v was calculated from the slope of the current–time curve and k was calculated from v and the instantaneous concentrations of Co(II) $(\mathrm{bipy})_3$ and copper(II). Table III gives the results together with the initial concentrations of the two species; each k represents the average value for a single run but derived from measurements at different times (for 3–5 points of the reaction curve).

TABLE III

RATE CONSTANTS CALCULATED FROM $-\frac{\mathrm{d}[\mathrm{Co(II)}\,(\mathrm{bipy})_3]}{\mathrm{d}t} = k\,[\mathrm{Co(II)}\,(\mathrm{bipy})_3]\,[\mathrm{Cu(II)}]^{\frac{1}{2}}$

$[\mathrm{Co(II)}\,(\mathrm{bipy})_3]_0 \cdot 10^4$ (mole l^{-1})	$[\mathrm{Cu(II)}]_0 \cdot 10^4$ (mole l^{-1})	k (mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$ sec^{-1})
0.907	1.46	5.1
0.901	1.94	5.2
0.877	2.42	4.9
0.868	4.91	4.5
0.882	9.72	5.4
1.78	1.93	5.2
1.74	3.78	4.9
1.79	4.80	4.3
1.78	9.62	4.6
1.76	18.9	5.3
		$\bar{k} = 4.9 \pm 0.37$

Reaction between Co(II)(bipy)$_3$ and Fe(III)(ClO$_4$)$_3$ · 2H$_2$O in acetonitrile

As in the former case, the stoichiometric ratio, the order and the rate constant of the reaction between the cobalt(II)–bipyridyl complex and iron(III) perchlorate were determined. The stoichiometry of the reaction was determined by the following titrimetric method: to a known quantity of cobalt(II)–bipyridyl complex in acetonitrile, a two-fold excess of an iron(III) perchlorate solution in acetonitrile was added. After a few seconds, the solution was diluted with aqueous 2 M sulfuric acid and the iron(II) formed was determined by titration with dichromate solution. It was shown that the stoichiometric ratio is 1:1 so that the reaction may be expressed by the equation:

$$\mathrm{Co(II)}\,(\mathrm{bipy})_3 + \mathrm{Fe(III)} \rightarrow \mathrm{Co(III)}\,(\mathrm{bipy})_3 + \mathrm{Fe(II)}.$$

It was evident from polarization curves that within the potential range +0.7–+1.0 V, the current flowing through a rotated platinum electrode corresponded only to the oxidation of the cobalt(II)–bipyridyl complex. The most suitable potential for recording the limiting current of this complex was +0.8 V. A half life of about 0.6 sec was found for an initial $9 \cdot 10^{-5}$ M concentration of the cobalt(II) complex and a two-fold excess of iron(III).

When the overall order of the reaction is two, the integrated form of the rate equation may be expressed by

$$\log\frac{[\mathrm{Fe(III)}]}{[\mathrm{Co(II)\ (bipy)_3}]} = \frac{[\mathrm{Fe(III)}]_0-[\mathrm{Co(II)\ (bipy_3)}]_0}{2.303}\cdot k\cdot t+\log\frac{[\mathrm{Fe(III)}]_0}{[\mathrm{Co(II)\ (bipy)_3}]_0}$$

and the plot log $[\mathrm{Fe(III)}]/[\mathrm{Co(II)\ (bipy)_3}]$ against t should give a straight line for different values of $[\mathrm{Fe(III)}]_0$ and $[\mathrm{Co(II)\ (bipy)_3}]_0$. The rate constant k was calculated from the slope of this plot (Fig. 4). Table IV gives the rate constants together with the initial concentrations of the cobalt(II) complex and iron(III).

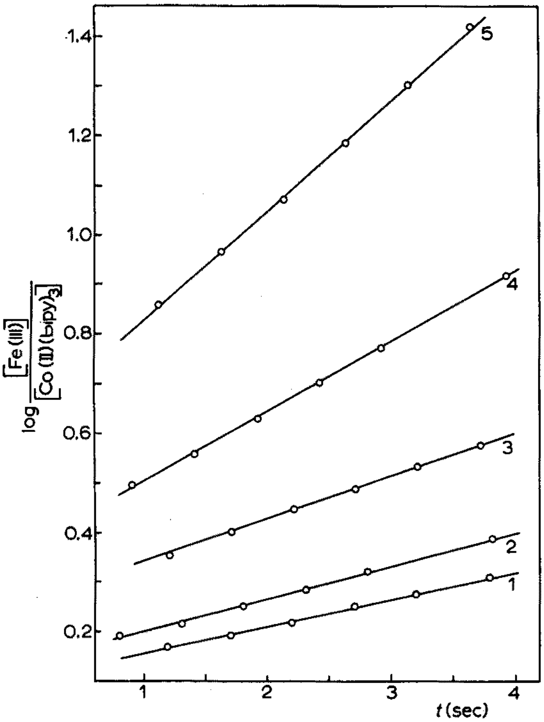

Fig. 4. Second-order plot log $[\mathrm{Fe(III)}]/[\mathrm{Co(II)\ (bipy)_3}]$ against time.

Straight line	*$[\mathrm{Co(II)\ (bipy)_3}]_0\cdot 10^4$ (mole l^{-1})*	*$[\mathrm{Fe(III)}]_0\cdot 10^4$ (mole l^{-1})*
1	1.76	2.17
2	1.35	1.76
3	0.87	1.35
4	0.92	1.80
5	0.86	2.23

Reaction between $\mathrm{Co(II)\ (bipy)_3}$ and $\mathrm{Fe(III)\ (ClO_4)_3\cdot 2H_2O}$ in acetonitrile in the presence of bipyridyl

An initial attempt was made to establish the stoichiometry of the reaction of the cobalt(II)–bipyridyl complex with iron(III) in the presence of an excess of

TABLE IV

RATE CONSTANTS FOR THE SECOND-ORDER RATE LAW

$$-\frac{d[Co(II)\,(bipy)_3]}{dt} = k\,[Co(II)\,(bipy)_3]\,[Fe(III)]$$

$[Co(II)\,(bipy)_3]_0 \cdot 10^4$ (mole l^{-1})	$[Fe(III)]_0 \cdot 10^4$ (mole l^{-1})	$k \cdot 10^{-3}$ (mole^{-1} l sec^{-1})
0.91	1.35	4.1
0.87	1.35	4.2
0.92	1.80	3.8
0.82	1.80	2.9
0.86	2.23	3.8
0.83	2.19	3.4
1.31	1.79	3.5
1.26	1.79	3.4
1.35	1.76	3.7
1.32	2.22	2.6
1.30	2.22	2.8
1.73	2.21	3.2
1.76	2.17	3.1
		$\bar{k} = (3.4 \pm 0.5) \cdot 10^3$

bipyridyl by the following method. A 10-fold excess of iron(III) was added to a $2 \cdot 10^{-4}$ M solution of the cobalt(II) complex containing a 200-fold excess of bipyridyl at the same time. After 1 min the solution was diluted with aqueous 2 M sulfuric acid and the iron(II)–bipyridyl complex formed was determined by titration with cerium-(IV) solution. The stoichiometric ratio was found to be 1:1.

It was evident from the polarization curves that in the potential range -0.2–$+0.6$ V, the current flowing through the rotated platinum electrode corresponded only to Co(II) $(bipy)_3$. The most suitable potential for recording the limiting current of this complex was about $+0.3$ V. The procedure for the kinetic runs was generally the same as in former cases, except that the cobalt(II)–bipyridyl complex was prepared by controlled potential electrolysis at a rotating platinum spiral electrode instead of at a mercury pool electrode, thus preventing the spontaneous reaction between the cobalt(III)–bipyridyl complex and mercury in combination with bipyridyl. The rate of the reaction was found to depend on the bipyridyl concentration; *e.g.*, with $1.81 \cdot 10^{-4}$ M cobalt(II)–bipyridyl complex, $4.74 \cdot 10^{-3}$ M iron(III) and $1.9 \cdot 10^{-2}$ M bipyridyl, the half life of the reaction was about 1 sec; for $4 \cdot 10^{-1}$ M bipyridyl it was about 40 sec.

The determination of the order of the individual components was carried out as described for the reaction of the cobalt(II) complex with copper(II). The order m of the cobalt(II) complex was calculated from the double-logarithmic plot of the reaction rate v against the complex concentration. The order n of iron(III) was calculated from the changes of the pseudo first-order rate constants according to the relationship

$$n = \frac{\log k'_{II} - \log k'_{I}}{\log\,[Fe(III)]_{0,II} - \log\,[Fe(III)]_{0,I}}$$

For a constant concentration of the cobalt(II)–bipyridyl complex and a constant amount (excess) of bipyridyl, the amount of iron(III) was changed in individual cases. The reaction rate was found to be first order with respect to the cobalt(II) concentration and second order with respect to iron(III) concentration provided that at least a 5-fold excess of bipyridyl was present. Moreover, it was shown that the reaction rate was inversely proportional to a power x of the bipyridyl concentration so that the rate equation may be expressed by

$$-\frac{\mathrm{d}\,[\mathrm{Co(II)\,(bipy)_3}]}{\mathrm{d}t} = \frac{k\,[\mathrm{Co(II)\,(bipy)_3}]\,[\mathrm{Fe(III)}]^2}{[\mathrm{bipy}]^x}$$

The order x was calculated from pseudo first-order rate constants from the relationship

$$x = \frac{\log k'_{\mathrm{II}} - \log k'_{\mathrm{I}}}{\log\,[\mathrm{bipy}]_{0,\mathrm{II}} - \log\,[\mathrm{bipy}]_{0,\mathrm{I}}}$$

and was found to depend on the bipyridyl concentration. Thus, for $1.79 \cdot 10^{-4}$ M $[\mathrm{Co(II)\,(bipy)_3}]_0$ and $3.32 \cdot 10^{-3}$ M iron(III), x was 1.57 within the bipyridyl range

TABLE V

RATE CONSTANTS k FOR THE RATE LAW $-\frac{\mathrm{d}[\mathrm{Co(II)\,(bipy)_3}]}{\mathrm{d}t} = k\,[\mathrm{Co(II)\,(bipy)_3}]\,[\mathrm{Fe(III)}]^2$

$[Co(II)\,(bipy)_3]_0 \cdot 10^4$ (mole l^{-1})	$[Fe(III)]_0 \cdot 10^3$ (mole l^{-1})	$[bipy] \cdot 10^2$ (mole l^{-1})	k (mole^{-2} l^2 sec^{-1})
1.79	3.32	1.9	$1.09 \cdot 10^4$
1.74	3.05	4.5	$3.54 \cdot 10^3$
1.64	4.21	8.6	$1.30 \cdot 10^3$
1.85	4.74	15	$8.45 \cdot 10^2$
1.81	4.74	25	$6.32 \cdot 10^2$
1.81	4.74	40	$4.74 \cdot 10^2$

TABLE VI

RATE CONSTANTS k FOR THE RATE LAW $-\frac{\mathrm{d}[\mathrm{Co(II)\,(bipy)_3}]}{\mathrm{d}t} = k\,[\mathrm{Co(II)\,(bipy)_3}]\,[\mathrm{Fe(III)}]^2$

FOR $[\mathrm{bipy}] = 8.6 \cdot 10^{-2}$ M

$[Co(II)\,(bipy)_3]_0 \cdot 10^4$ (mole l^{-1})	$[Fe(III)]_0 \cdot 10^3$ (mole l^{-1})	$k \cdot 10^{-3}$ (mole^{-2} l^2 sec^{-1})
0.83	3.21	1.33
0.83	4.24	1.45
1.66	3.98	1.28
1.65	3.18	1.31
1.67	2.92	1.52
1.64	4.21	1.30
1.65	4.33	1.46
1.67	2.14	1.27
1.67	2.92	1.54
2.48	2.89	1.52
2.46	4.29	1.26
2.44	5.68	1.31
		$\bar{k} = (1.38 \pm 0.11) \cdot 10^3$

$1.9 \cdot 10^{-2}$–$4.6 \cdot 10^{-2}$ *M*; 1.33 in the range $4.6 \cdot 10^{-2}$–$8.8 \cdot 10^{-2}$ *M*, and 0.6 in the range $1.5 \cdot 10^{-1}$–$4.0 \cdot 10^{-1}$ *M*. The rate constant k was calculated from the rate equation on the basis of reaction rate, v, and the instantaneous concentrations of the cobalt(II)–pyridyl complex and iron(III). Since the rate constant k depends on the bipyridyl concentration, Table V contains rate constants for different bipyridyl concentrations. The reproducibility of the rate constant for different initial concentrations of reactants at constant bipyridyl concentrations is evident from Table VI.

DISCUSSION

The polarographic behaviour of the appropriate systems showed that the kinetics of oxidation of the cobalt(II)–bipyridyl complex by copper(II) or iron(III) in acetonitrile could be followed by the rotating platinum electrode method.

The oxidation of the cobalt(II)–bipyridyl complex by iron(III) followed the simplest course; in acetonitrile, the reaction occurred rapidly and went to completion, with a simple reaction rate equation. When this reaction was followed in the presence of an excess of bipyridyl, one would have expected an accelerated reaction, as in aqueous media[13]. However, the oxidation was found to proceed more slowly, and, moreover, in a complicated way.

From the shift of the polarographic wave when iron(III) was reduced at the rotating platinum electrode ($E_{\frac{1}{2}} = +0.5$ V in the absence of bipyridyl and $E_{\frac{1}{2}} = -0.4$ V in its presence), the formation of some iron(III)–bipyridyl complexes of different composition might be inferred, as well as a decrease of oxidation capacity of the iron(III).

It can be assumed that the predominant form of iron(III) in a solution of iron(III) perchlorate in acetonitrile is the solvated cation $[\mathrm{Fe(AN)_6}]^{3+}$ [20,21]. The kinetic results indicate that in presence of an excess of bipyridyl a binuclear complex is formed. The reaction mechanism of the oxidation of the cobalt(II)–bipyridyl complex by iron(III) in the presence of bipyridyl can then be expressed in two steps: a fast reaction

$$2\ \mathrm{Fe(III)} + x\ \mathrm{bipy\ (excess)} \overset{K}{\rightleftharpoons} \mathrm{Fe(III)\text{-}(bipy)}_x\mathrm{\text{-}Fe(III)} \qquad \text{(I)}$$

followed by the rate-determining step

$$\mathrm{Fe(III)\text{-}(bipy)}_x\mathrm{\text{-}Fe(III)} + \mathrm{Co(II)\ (bipy)_3} \xrightarrow{k'} \mathrm{Fe(II)\ (bipy)_3} + \mathrm{Co(III)\ (bipy)_3} + \mathrm{Fe(III)} + (x-3)\ \mathrm{bipy} \qquad \text{(II)}$$

The rate of reaction is:

$$-\frac{\mathrm{d}\,[\mathrm{Co(II)\ (bipy)_3}]}{\mathrm{d}t} = k'\,[\mathrm{Fe(III)\text{-}(bipy)}_x\mathrm{\text{-}Fe(III)}]\,[\mathrm{Co(II)\ (bipy)_3}]$$

and after the $[\mathrm{Fe(III)\text{-}(bipy)}_x\mathrm{\text{-}Fe(III)}]$ concentration from (I) is substituted, the following equation is obtained:

$$-\frac{\mathrm{d}\,[\mathrm{Co(II)\ (bipy)_3}]}{\mathrm{d}t} = k' \cdot K\,[\mathrm{Co(II)\ (bipy)_3}]\,[\mathrm{Fe(III)}]^2$$

A direct proof of the presence of a binuclear complex of iron(III) in acetonitrile was not obtained. Nevertheless, the second order obtained with respect to iron(III) gave reasonable evidence for it. Similarly, the presence of cobalt(II) in a binuclear form in the reaction between cobalt(II) and lead(IV) in anhydrous acetic acid[22] and of binuclear cobalt(III) after hydration in aqueous solution[23] have been assumed. The formation of binuclear complexes of iron(III) with bipyridyl and phenanthroline in weakly acidic aqueous solutions has been proved by ANDEREGG[24]. Binuclear complexes of copper(II) and some organic acids have been shown to be stable in dioxane solutions[25], dimerisation of copper(II)–bipyridyl complexes has been found in aqueous solutions, and the equilibrium constant between the mononuclear and the binuclear form has been calculated[26,27].

No explanation for the influence of the concentration of bipyridyl on the reaction rate is apparent. The reduction of the reaction rate by bipyridyl may be due to the partial dissociation of bipyridyl molecules from the binuclear iron(III)–bipyridyl complex. To summarize, it can be stated, that iron(III) in solutions of iron(III) perchlorate in acetonitrile behaves as a strong oxidation agent. However, in the presence of bipyridyl its oxidation capacity is decreased and the redox reaction is complicated.

With regard to the reaction between the cobalt(II)–bipyridyl complex and copper(II), the overall order of the reaction is 1.5. A possible explanation for this fractional order is a sequence of elementary reactions with comparable rates. In this case, the more complicated mode of oxidation might be due to the partial dissociation of the cobalt(II)–bipyridyl complex and to formation of bipyridyl complexes of copper(II)[26].

Two of the authors (I.N. and I.N.) are grateful to the University of Technology, Delft, for temporary assistantships which allowed this work to be carried out.

SUMMARY

On the basis of the polarographic behaviour of Co(II)–Co(III) bipyridyl complexes, Cu(II)–Cu(I) and Fe(III)–Fe(II) perchlorates in anhydrous acetonitrile at a rotating platinum electrode, kinetic data for the oxidation of the cobalt(II)–bipyridyl complex in acetonitrile were obtained. The rotating platinum electrode method was used to study the oxidation of the cobalt(II) complex by copper(II) and iron(III) in 0.1 *M* sodium perchlorate in anhydrous acetonitrile. The reactions follow the rate laws:

$$-\frac{d\,[\mathrm{Co(II)\,(bipy)_3}]}{dt} = k_1\,[\mathrm{Co(II)\,(bipy)_3}]\,[\mathrm{Cu(II)}]^{\frac{1}{2}}$$

$$-\frac{d\,[\mathrm{Co(II)\,(bipy)_3}]}{dt} = k_2\,[(\mathrm{Co(II)\,(bipy)_3}]\,[\mathrm{Fe(III)}]$$

where $k_1 = 4.9 \pm 0.37$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ sec^{-1}, $k_2 = (3.4 \pm 0.5) \cdot 10^3$ mole^{-1} l sec^{-1} at 20°. The oxidation of the cobalt(II) complex by iron(III) in the presence of an excess of bipyridyl follows the rate law:

$$-\frac{d\,[\mathrm{Co(II)\,(bipy)_3}]}{dt} = k\,\frac{[\mathrm{Co(II)\,(bipy)_3}]\,[\mathrm{Fe(III)}]^2}{[\mathrm{bipy}]^x}$$

where order x changes from 1.6 to 0.6 for the range $1.9 \cdot 10^{-2}\ M$–$4.0 \cdot 10^{-1}\ M$ bipyridyl. The data for this oxidation are interpreted in terms of a reaction between a mononuclear cobalt(II) complex and a binuclear iron(III)–bipyridyl complex.

RÉSUMÉ

On a déterminé les valeurs cinétiques de l'oxydation du complexe cobalt(II)–bipyridyle, en examinant le comportement polarographique avec électrode de platine tournante. On a ainsi pu étudier l'oxydation par le cuivre(II) et le fer(III) en milieu perchlorate de sodium 0.1 M, en milieu acétonitrile anhydre; de même que l'oxydation par le fer(III), en présence d'un excès de bipyridyle.

ZUSAMMENFASSUNG

Auf Grund des polarographischen Verhaltens von Co(II)–Co(III)–Bipyridyl-Komplexen, Cu(II)–Cu(I)- und Fe(III)–Fe(II)-Perchlorat in wasserfreiem Acetonitril an einer rotierenden Platinelektrode wurden kinetische Daten für die Oxidation des Kobalt(II)–Bipyridyl-Komplexes in Acetonitril erhalten. Die Methode der rotierenden Platinelektrode wurde angewendet um die Oxidation des Kobalt(II)-Komplexes durch Kupfer(II) und Eisen(III) in einer Lösung von 0.1 M Natriumperchlorat in wasserfreiem Acetonitril zu untersuchen. Die Reaktionen gehorchen folgenden Geschwindigkeitsgesetzen:

$$-\frac{\mathrm{d}\,[\mathrm{Co(II)\,(Bipy)_3}]}{\mathrm{d}t} = k_1\,[\mathrm{Co(II)\,(Bipy)_3}]\,[\mathrm{Cu(II)}]^{\frac{1}{2}},$$

$$-\frac{\mathrm{d}\,[\mathrm{Co(II)\,(Bipy)_3}]}{\mathrm{d}t} = k_2\,[(\mathrm{Co(II)\,(Bipy)_3}]\,[\mathrm{Fe(III)}]^2.$$

Die Werte bei 20° sind $k_1 = 4.9 \pm 0.37\ \mathrm{mol^{-\frac{1}{2}}\,l^{\frac{1}{2}}\,sec^{-1}}$, $k_2 = (3.4 \pm 0.5) \cdot 10^3\ \mathrm{mol^{-1}\,l\ sec^{-1}}$. Die Oxidation des Kobalt(II)-Komplexes durch Eisen(III) in Gegenwart eines Bipyridyl-Überschusses gehorcht folgendem Geschwindigkeitsgesetz:

$$-\frac{\mathrm{d}\,[\mathrm{Co(II)\,(Bipy)_3}]}{\mathrm{d}t} = k\,\frac{[\mathrm{Co(II)\,(Bipy)_3}]\,[\mathrm{Fe(III)}]^2}{[\mathrm{Bipy}]^x}$$

x variiert hierbei zwischen 1.6 und 0.6 im Konzentrationsbereich $1.9 \cdot 10^{-2}\ M$–$4.0 \cdot 10^{-1}\ M$ Bipyridyl. Die Ergebnisse für diese Oxidation werden gedeutet als Reaktion zwischen einem einkernigen Kobalt(II)-Komplex und einem zweikernigen Eisen(III)-Bipyridyl-Komplex.

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

TITRATION CURVES OF COMPLEXIMETRIC BACK-TITRATIONS

PART III. CONDITIONS FOR SHARP END-POINTS WITH INDICATION BY MEANS OF AN INDICATOR ION

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(Received October 10th, 1969)

In previous papers, some mathematical expressions for compleximetric back-titrations of mixtures of metals have been derived[1] and conditions for the possibility of sharp potentiometric end-point indication in the case of indication by means of the titrant have been discussed[2].

Another method of potentiometric end-point indication is the method based on the addition of an indicator ion, *e.g.* mercury(II) or silver(I). Conditions for sharp end-points with this indication method are derived in the present paper, and some experimental applications are presented.

CONDITIONS FOR SHARP END-POINTS

The conditions for sharp end-points in the back-titration of a mixture of two metals N and P, to which a ligand Y has been added in excess, with the titrant metal M may be obtained from the equation

$$f = \left(1 + \frac{[\mathrm{P}]}{c_\mathrm{P} - [\mathrm{P}]}\frac{K_\mathrm{PY}}{K_\mathrm{MY}}\right)$$

$$\left(1 - \frac{c_\mathrm{N}}{c_\mathrm{Y}}\left(\frac{[\mathrm{P}]}{c_\mathrm{P} - [\mathrm{P}]}\frac{K_\mathrm{PY}}{K_\mathrm{NY}} + 1\right)^{-1} - \frac{c_\mathrm{P}}{c_\mathrm{Y}}\frac{1 + [\mathrm{P}]K_\mathrm{PY}}{[\mathrm{P}]K_\mathrm{PY}}\frac{c_\mathrm{P} - [\mathrm{P}]}{c_\mathrm{P}}\right) \qquad (1)$$

which was derived previously[1]. P is considered as the indicator metal; therefore, f has been expressed in terms of the concentration of P.

It is convenient to abbreviate eqn. (1) by

$$f = f_\mathrm{M}(1 + f_\mathrm{N} + f_\mathrm{P}) \qquad (1a)$$

Some remarks have to be made in advance concerning the concentrations of P, N and Y. It will be assumed that the concentrations c_Y and c_N, as well as the excess of Y, *i.e.*, $c_\mathrm{Y} - c_\mathrm{N} - c_\mathrm{P}$, are of the same order of magnitude in all cases. As to c_P the situation may be different. It may happen that P is present in the original sample so that in fact the problem is the analysis of a mixture of N and P. However, in most applications of the indication method under consideration, the metal P will not be present in the sample. In those cases, P will be added in trace amounts so that we may consider $c_\mathrm{P} \ll c_\mathrm{N}$.

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Therefore, in this paper two extreme cases will be dealt with: either P may be present as a major constituent in which case c_P is of the same order of magnitude as c_N and c_Y, or P is added as indicator ion in trace amounts, c_P being very small with respect to c_Y and c_N.

As the titration curves also depend on the values of the conditional stability constants K_{MY}, K_{NY} and K_{PY}, many different cases could be considered. The present discussion is limited to a series of extreme cases in which these stability constants are largely different, but the conditions for sharp end-points have been derived in all these cases. In this paper the detailed calculations are given only for some of the cases, but the results of these and all other calculations are summarized so that some general conclusions may be drawn.

$c_N \approx c_P;\ K_{MY} \gg K_{NY} \gg K_{PY}$

A theoretical titration curve of this type is shown in Fig. 1. Only one pP jump occurs at $f = 1 - c_N/c_Y - c_P/c_Y$, when the excess ligand has been titrated. After this equivalence point, the titrant breaks up the complex PY, and a normal S-shaped titration curve results.

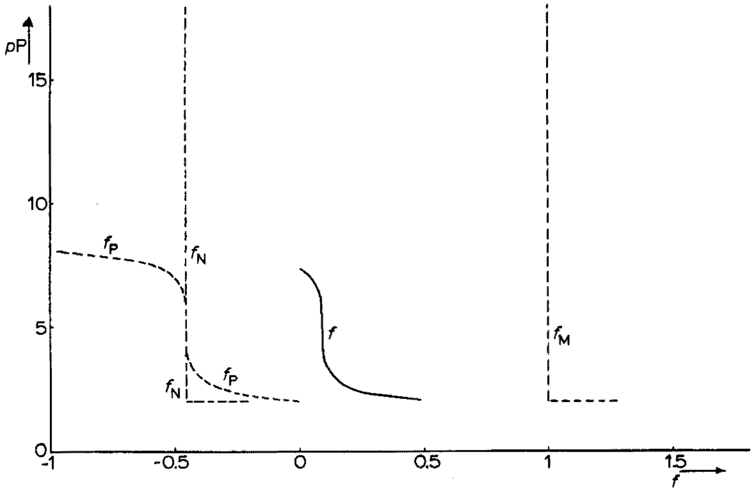

Fig. 1. Construction of the theoretical titration curve f–pP for the back-titration with the metal M of a solution in which the molarity of the metals N and P is 0.01 and that of the ligand Y 0.022. $f = f_M(1 + f_N + f_P)$. $\log K_{MY} = 20$; $\log K_{NY} = 14$; $\log K_{PY} = 8$.

The condition for a sharp break at the equivalence point is calculated in the usual way[2].

The upper part of the potential break is the value of pP at

$$f_- = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} - 10^{-2}\,\frac{c_N + c_P}{c_Y}$$

Under the conditions mentioned above, it is obvious, as can also be seen in Fig. 1, that at f_- the value of $f_N = -c_N/c_Y$ and that $f_M = 1$.

We can therefore write

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

Furthermore, it can be assumed that $(c_P - [P]_-)/c_P = 1$. After rearrangement we then get

$$[P]_- = \frac{10^2 c_P}{(c_N + c_P)\,K_{PY}} \text{ and}$$

$$pP_- = \log\,(c_N + c_P) + \log K_{PY} - \log c_P - 2 \qquad (2)$$

The lower limit of the potential break is the value of pP at

$$f_+ = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} + 10^{-2}\,\frac{c_N + c_P}{c_Y}$$

It can again be assumed that $f_M = 1$ and $f_N = -c_N/c_Y$, hence:

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

If it is assumed that $[P]_+ K_{PY} \gg 1$, then

$$-\frac{c_P}{c_Y} + 10^{-2}\,\frac{c_N + c_P}{c_Y} = -\frac{c_P}{c_Y}\,\frac{c_P - [P]_+}{c_P}$$

and

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

$$pP_+ = -\log\,(c_N + c_P) + 2 \qquad (3)$$

The condition for a pP jump of 2pP units may be found by putting $pP_- - pP_+ = 2$, for eqns. (2) and (3). Thus:

$$\frac{(c_N + c_P)^2}{c_P}\,K_{PY} = 10^6 \qquad (4)$$

However, since c_N and c_P are of the same order of magnitude, and since the conditional stability constants are rarely known exactly, it is reasonable to simplify eqn. (4) to

$$K_{PY} c_N = 10^6 \qquad (4a)$$

$c_N \approx c_P;\ K_{NY} \gg K_{MY} \gg K_{PY}$

It can easily be seen from eqn. (1) and Fig. 1 that this combination will lead to exactly the same condition (4a) as in the previous case.

$c_N \approx c_P;\ K_{MY} \gg K_{PY} \gg K_{NY}$

A titration curve of this type is plotted in Fig. 2. Two equivalence points are found, the first one at

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

when the excess of Y has been titrated, and the second one at $f = 1 - c_P/c_Y$ when NY has been quantitatively converted into N.

The condition for a sharp end-point at

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

is, as can be seen from Fig. 2, determined by f_P and f_N. The value of $[P]_-$ at f_- is again given by eqn. (2). The lower limit of the pP jump, pP_+, is determined by f_N, because at this value of [P], we may take $f_M = 1$ and $f_P = -c_P/c_Y$.

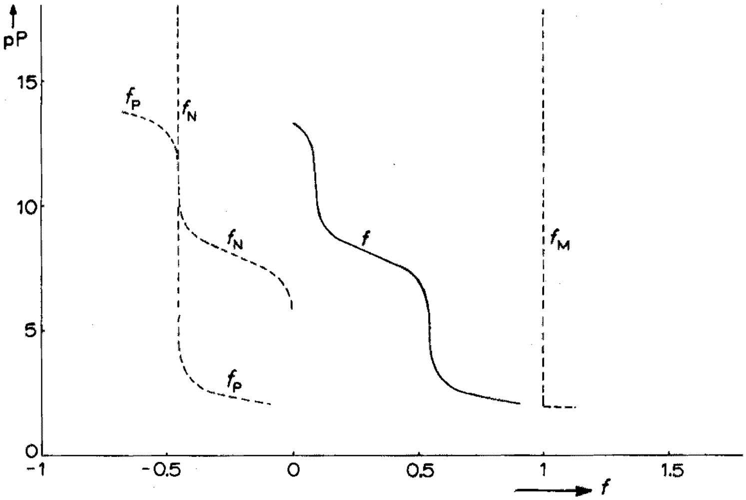

Fig. 2. Construction of the theoretical titration curve f–pP for the back-titration with the metal M of a solution in which the molarity of the metals N and P is 0.01 and that of the ligand Y 0.022. $f = f_M(1 + f_N + f_P)$. $\log K_{MY} = 20$; $\log K_{NY} = 8$; $\log K_{PY} = 14$.

Hence:

$$f_+ = 1 - \frac{c_N}{c_Y} - \frac{c_P}{c_Y} + 10^{-2}\frac{c_N + c_P}{c_Y} = 1 - \frac{c_N}{c_Y}\left(\frac{[P]_+}{c_P - [P]_+}\frac{K_{PY}}{K_{NY}} + 1\right)^{-1} - \frac{c_P}{c_Y}$$

which results in

$$[P]_+ = \frac{c_P}{1 + \dfrac{K_{PY}}{K_{NY}}\left(\dfrac{10^2 c_N}{c_N + c_P} - 1\right)} \tag{5}$$

As c_N and c_P are of the same order of magnitude, $10^2 c_N/(c_N + c_P) \gg 1$. Furthermore, $K_{PY}/K_{NY} \gg 1$.

This leads to

$$[P]_+ = \frac{c_P(c_N + c_P)}{10^2 c_N} \cdot \frac{K_{NY}}{K_{PY}}$$

or

$$pP_+ = \log c_N - \log(c_N + c_P) - \log c_P - \log K_{NY} + \log K_{PY} + 2 \tag{6}$$

Combination of eqns. (2) and (6) leads to a condition for a pP jump of two pP units at

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

$$\frac{(c_N + c_P)^2}{c_N} K_{NY} = 10^6 \tag{7}$$

which may be simplified for practical use to

$$K_{NY} c_N = 10^6 \tag{7a}$$

The second jump at $f = 1 - c_P/c_Y$ is again determined by f_N and f_P. For the value $[P]_-$, determining the upper limit of the second jump, we may assume, as is obvious from Fig. 2, that $f_M = 1$ and $f_P = -c_P/c_Y$.
Hence

$$f_- = 1 - \frac{c_P}{c_Y} - 10^{-2}\frac{c_P}{c_Y} = 1 - \frac{c_N}{c_Y}\left(\frac{[P]_-}{c_P - [P]_-}\,\frac{K_{PY}}{K_{NY}} + 1\right)^{-1} - \frac{c_P}{c_Y}$$

which leads to

$$[P]_- = \frac{c_P}{10^{-2}\,\dfrac{c_P}{c_N}\,\dfrac{K_{PY}}{K_{NY}} + 1}$$

Since $10^{-2}\,\dfrac{c_P}{c_N}\,\dfrac{K_{PY}}{K_{NY}} \gg 1$, this results in

$$[P]_- = 10^2\, c_N \frac{K_{NY}}{K_{PY}} \text{ or}$$

$$pP_- = -\log c_N - \log K_{NY} + \log K_{PY} - 2 \tag{8}$$

At the lower limit of this jump it can be assumed that $f_M = 1$ and $f_N = 0$. Hence:

$$f_+ = 1 - \frac{c_P}{c_Y} + 10^{-2}\frac{c_P}{c_Y} = 1 - \frac{c_P}{c_Y}\,\frac{1 + [P]_+ K_{PY}}{[P]_+ K_{PY}}\,\frac{c_P - [P]_+}{c_P}$$

As $[P]_+ K_{PY} \gg 1$, then

$$[P]_+ = 10^{-2} c_P \text{ or}$$

$$pP_+ = -\log c_P + 2 \tag{9}$$

The condition for a sharp end-point at $f = 1 - c_P/c_Y$ is found from eqns. (8) and (9):

$$\frac{c_P}{c_N}\,\frac{K_{PY}}{K_{NY}} = 10^6 \tag{10}$$

which can be simplified to

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

$c_P < 10^{-3} c_N$; $K_{MY} \gg K_{NY} \gg K_{PY}$ *and* $c_P < 10^{-3} c_N$; $K_{NY} \gg K_{MY} \gg K_{PY}$

Titration conditions are now derived for two cases in which the indicator metal P is added to the sample in trace amounts.

Whenever $K_{PY} \ll K_{NY}$ and $K_{PY} \ll K_{MY}$, it is irrelevant whether $K_{MY} \ll K_{NY}$ or $K_{NY} \ll K_{MY}$, since both cases lead to exactly the same titration curve, which is obvious from Fig. 3.

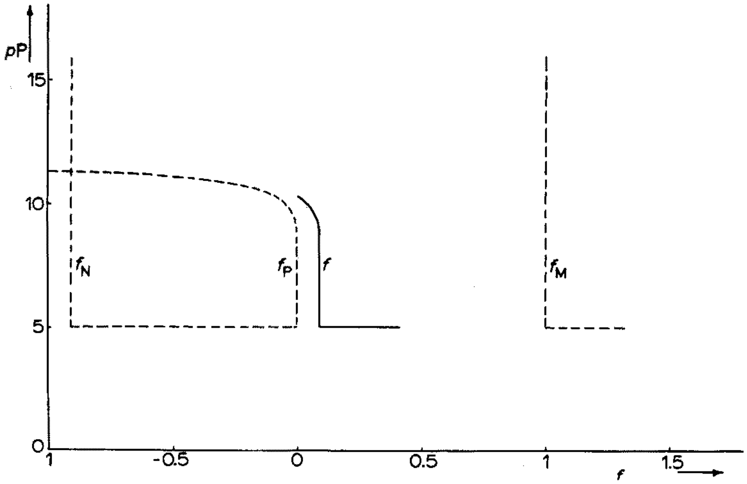

Fig. 3. Construction of the theoretical titration curve f–pP for the back-titration with the metal M of a solution in which the molarity of the metal N is 0.02, of P 10^{-5} and that of the ligand Y 0.022. $f = f_M(1 + f_N + f_P)$. $\log K_{MY} = 20$; $\log K_{NY} = 14$; $\log K_{PY} = 8$.

It may be noted that a right angle occurs in the titration curve. Up to $f = 1 - c_N/c_Y$, where the pP-break occurs (c_P/c_Y may be neglected because $c_P \ll c_N$), the titrant reacts with the excess of ligand Y. Then all of the indicator ion P is "at once" released from its complex PY, which leads to a sharp bend in the titration curve.

At the upper limit of the pP jump, $f_M = 1$ and $f_N = -c_N/c_Y$. Hence eqn. (2) can be modified by substituting c_N for $c_N + c_P$. Thus:

$$pP_- = \log c_N - \log c_P + \log K_{PY} - 2 \tag{2a}$$

It can be seen from Fig. 3, though it can also easily be derived, that $[P]_+ = c_P$. Hence:

$$pP_+ = -\log c_P \tag{11}$$

Combination of eqns. (2a) and (11) leads to the condition for a sharp end-point in this case

$$K_{PY}c_N = 10^4 \tag{12}$$

All other calculations follow the same lines.

The results of these calculations are summarized in Tables I and II. Table I shows the results for those cases in which c_N and c_P are of the same order of magnitude, whereas Table II contains those cases where c_P has been added in trace amounts. It can be seen from Table I that the conditions for a sharp end-point when the excess of ligand has been consumed is always $Kc_N = 10^6$ in which K is the smallest of the three K-values.

A second jump only occurs in two cases.

When $c_N \gg c_P$, then as in the previous case, the condition for a sharp end-point

TABLE I

CONDITIONS FOR SHARP END-POINTS; $c_N \approx c_P$

Stability constants	*pP jump*[a]	
	f-value	*Condition*
$K_{MY} \gg K_{NY} \gg K_{PY}$	$1 - \frac{c_P}{c_Y} - \frac{c_N}{c_Y}$	$K_{PY}c_N = 10^6$
$K_{NY} \gg K_{MY} \gg K_{PY}$	See previous case	
$K_{MY} \gg K_{PY} \gg K_{NY}$	$1 - \frac{c_P}{c_Y} - \frac{c_N}{c_Y}$	$K_{NY}c_N = 10^6$
	$1 - \frac{c_P}{c_Y}$	$\frac{K_{PY}}{K_{NY}} = 10^6$
$K_{NY} \gg K_{PY} \gg K_{MY}$	$1 - \frac{c_P}{c_Y} - \frac{c_N}{c_Y}$	$K_{MY}c_N = 10^6$
$K_{PY} \gg K_{MY} \gg K_{NY}$	$1 - \frac{c_P}{c_Y} - \frac{c_N}{c_Y}$	$K_{NY}c_N = 10^6$
	$1 - \frac{c_P}{c_Y}$	$\frac{K_{MY}}{K_{NY}} = 10^6$
$K_{PY} \gg K_{NY} \gg K_{MY}$	$1 - \frac{c_P}{c_Y} - \frac{c_N}{c_Y}$	$K_{MY}c_N = 10^6$

[a] All jumps are normal S-shaped curves.

TABLE II

CONDITIONS FOR SHARP END-POINTS; $c_N \gg c_P$

Stability constants	*Condition for sharp break at* $f = 1 - c_N/c_Y$
$K_{MY} \gg K_{NY} \gg K_{PY}$	$K_{PY}c_N = 10^4$; curve with sharp bend
$K_{NY} \gg K_{MY} \gg K_{PY}$	See previous case
$K_{MY} \gg K_{PY} \gg K_{NY}$	$K_{NY}c_N = 10^6$; S-shaped curve; a second jump occurs at $f = 1$ when $K_{PY}/K_{NY} = 10^4$; sharp bend
$K_{NY} \gg K_{PY} \gg K_{MY}$	$K_{MY}c_N = 10^6$; S-shaped curve
$K_{PY} \gg K_{MY} \gg K_{NY}$	$K_{NY}c_N = 10^6$; S-shaped curve; a second S-shaped pM jump at $f = 1$ when $K_{MY}/K_{NY} = 10^6$
$K_{PY} \gg K_{NY} \gg K_{MY}$	$K_{MY}c_N = 10^6$; S-shaped curve

when the excess of ligand has been consumed is $Kc_N = 10^6$, except in the case when the curve possesses a rectangular bend (Table II). The Kc_N value is then 10^4 instead of 10^6, but in experimental work such rectangular bends are seldom found. The curves in these cases generally show a considerable rounding off, so that in all cases a value of 10^6 is to be preferred.

The second jump which is also mentioned in Table II has of course only little analytical significance in this case.

Discussion

It is obvious from the calculations in the previous section that potentiometric back-titrations offer great possibilities in compleximetry. As to the stability constants of the metal complexes involved, the only requirement that has to be fulfilled for the determination of the excess of ligand is that the product Kc_N should exceed 10^6 for all the stability constants involved.

The determinations of mixtures of metals is possible only in a few special cases. Certain strict requirements concerning the stability constants have then to be fulfilled.

In practice, the use of mercury(II) as the indicator ion is of importance. The use of trace amounts of mercury(II) is of particular interest since precipitation of mercury(II) compounds rarely occurs in this case.

PRACTICAL APPLICATIONS

A successful attempt has been made to demonstrate the feasibility of potentiometric back-titrations of metal ions with another metal which forms a stronger complex with the ligand, an indicator metal ion with comparatively lower stability constant ($K_{MY} \gg K_{PY}$) being applied. Mercury(II) was used as the indicator ion and thorium(IV) as the back-titrant to determine copper, zinc, bismuth and nickel, EDTA being the ligand. As the interaction of thorium(IV) with acetate, which was present in the buffer, is unknown, the conditional stability constant of the thorium–EDTA complex under the conditions of the titration was unknown. Therefore, a comparison of the theoretical and the experimental titration curves was not possible. It can, however, be assumed that $K_{ThY} > K_{NY} > K_{HgY}$ in these cases.

It proved possible to determine the amounts of copper, zinc, bismuth and nickel in concentrations down to 10^{-5} *M*, a range in which little work has been done with this method of end-point indication. Thorium first reacts with the excess of

TABLE III

DETERMINATION OF COPPER, BISMUTH, ZINC AND NICKEL BY POTENTIOMETRIC BACK-TITRATION WITH THORIUM(IV)

(Acetate buffer pH = 5, volume 10 ml)

Metal ion concentration (M)			*Error (%)*
Metal	*Present*	*Found*	
Zn	$2.070 \cdot 10^{-4}$	$2.064 \cdot 10^{-4}$	0.3
	$5.175 \cdot 10^{-5}$	$5.073 \cdot 10^{-5}$	2.0
	$2.59 \cdot 10^{-5}$	$2.67 \cdot 10^{-5}$	3.0
	$2.59 \cdot 10^{-5}$	$2.66 \cdot 10^{-5}$	2.7
Ni	$1.843 \cdot 10^{-4}$	$1.867 \cdot 10^{-4}$	1.3
	$1.990 \cdot 10^{-4}$	$2.008 \cdot 10^{-4}$	0.9
	$7.16 \cdot 10^{-5}$	$7.30 \cdot 10^{-5}$	2.0
	$4.78 \cdot 10^{-5}$	$4.91 \cdot 10^{-5}$	2.7
Cu	$1.009 \cdot 10^{-4}$	$1.001 \cdot 10^{-4}$	0.8
	$1.009 \cdot 10^{-4}$	$1.018 \cdot 10^{-4}$	0.9
	$2.02 \cdot 10^{-5}$	$2.04 \cdot 10^{-5}$	1.0
	$2.02 \cdot 10^{-5}$	$2.05 \cdot 10^{-5}$	1.5
Bi	$1.250 \cdot 10^{-4}$	$1.260 \cdot 10^{-4}$	0.8
	$8.33 \cdot 10^{-5}$	$8.37 \cdot 10^{-5}$	0.5
	$4.99 \cdot 10^{-5}$	$5.13 \cdot 10^{-5}$	2.8
	$1.33 \cdot 10^{-5}$	$1.40 \cdot 10^{-5}$	5.3

EDTA and then breaks up the mercury(II)–EDTA complex, resulting in a jump in the titration curve. The results of some representative determinations are given in Table III.

Reagents

Reagent-grade chemicals were used to prepare stock solutions in twice-distilled water; the solutions were diluted to the required concentrations with the same type of water. Pure copper was dissolved in nitric acid to obtain a standard solution and this was used to standardise the EDTA solution, with murexide as indicator. Zinc, bismuth and nickel solutions were titrated against this EDTA solution, in the presence of erio T, murexide and xylenol orange, respectively, as indicators. The solution of thorium was standardised by EDTA solution potentiometrically and, when necessary, was diluted with dilute nitric acid.

Acetate buffer was used in all titrations, its concentration being kept low when dilute solutions were studied. Mercury(II) was added in the form of its complex with EDTA, which was prepared by the addition of mercury(II) solution to EDTA solution, the equivalence point being noted potentiometrically. The concentration of the mercury(II)–EDTA complex was 10^{-5}–10^{-6} M. The pH of the solutions was measured with a Radiometer pH meter type PHM 22 and adjusted to the desired values by adding nitric acid or potassium hydroxide. The titrations were performed with a Radiometer automatic titrator (TTT1, ABU 1 syringe burette and SBR2 recorder). An amalgamated gold rod was used as indicator electrode with a calomel electrode as reference electrode. The design and preparation of the electrode has been described elsewhere[3].

The authors wish to thank the Netherlands' Organization for the Advancement of Pure Research (Z.W.O.) for a fellowship awarded to one of them (S.P.) and Mrs. H. DE GROOT for her assistance in the experimental part of the work.

SUMMARY

Conditions are derived for sharp end-points in compleximetric back-titrations of mixtures of metals, by means of potentiometric indication of one of the metals of the mixture. Some applications are given for the determination of Cu, Zn, Bi and Ni with EDTA as the ligand and thorium(IV) as the titrant.

RÉSUMÉ

On a établi les conditions de titrage complexométrique en retour de deux métaux, l'un des deux étant utilisé pour l'indication potentiométrique du point final. Quelques applications sont présentées pour le dosage de Cu, Zn, Bi et Ni en utilisant EDTA comme ligand et Th(IV) comme titrant.

ZUSAMMENFASSUNG

Es werden die Bedingungen abgeleitet, unter denen sich bei komplexometrischen Rücktitrationen von Metallgemischen scharfe Endpunkte ergeben, wenn eines dieser Metalle für die potentiometrische Endpunktsanzeige benutzt wird. Es werden einige Beispiele für die Bestimmung von Cu, Zn, Bi und Ni angegeben, wobei ÄDTA als Ligand und Thorium(IV) als Titrant verwendet wird.

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

SHORT COMMUNICATIONS

Indirect atomic absorption spectrometric methods for the determination of cyanide

There are two general indirect methods for the determination of anions by atomic absorption spectrometry. One method involves the formation of an insoluble precipitate and the determination of either the metal incorporated in the precipitate or the determination of the excess metal ion in the supernatant solution. Chloride has been determined by precipitation of silver chloride, dissolution of the precipitate in an ammonia solution, and the atomic absorption spectrometric determination of the equivalent silver[1]. Sulfite has been determined by conversion to sulfate, precipitation of lead sulfate in an ethanolic solution, removal of the precipitate by centrifugation, and determination of the lead in the supernate by atomic absorption spectrometry[2].

The second general indirect method is based on the formation of a stoichiometric complex, isolation of the complex by extraction, and the determination of the metal in the complex by atomic absorption measurement. Perchlorate has been determined by the formation of perchlorato-bis(2,9-dimethyl-1,10-phenanthroline)-copper(I), extraction of this complex with ethyl acetate, aspiration of the extract into an acetylene–air flame, and the determination of the copper at the resonance line of 3247 Å[3]. Thiocyanate has also been determined by an indirect method based on the formation of a dithiocyanato-dipyridine copper(II) complex[4]. Other indirect atomic absorption methods are based on the formation and extraction of molybdoheteropoly complexes; thus, phosphate[5–8], silicate[6,8] and arsenate[9] have been determined. This paper proposes two indirect atomic absorption methods based on these two general methods.

A spectrophotometric method for the determination of cyanide based on the formation and extraction of the dicyano-bis(1,10-phenanthroline)–iron(II) complex was developed by Schilt[10]. The neutral dicyano-bis(1,10-phenanthroline)-iron(II) complex was extracted with chloroform and the absorbance of the extract measured at 597 nm. In the atomic absorption spectrometric method, the chloroform extract is evaporated and the residue dissolved in ethanol. The ethanol solution is aspirated directly into the air–acetylene flame and the iron, equivalent to the definite amount of cyanide ion, is determined. This indirect atomic absorption spectrometric method is slightly less sensitive than the spectrophotometric method, but is convenient, accurate, and highly selective for the determination of cyanide.

The formation of the highly insoluble precipitate of silver cyanide is the basis of a second indirect method for the determination of cyanide. The silver cyanide is quantitatively precipitated and the excess of silver ion in the supernate is determined by atomic absorption spectrometry. This indirect method for cyanide has a higher sensitivity than either the spectrophotometric method or the indirect method based on the ferroin reagent.

Reagents

Standard cyanide solution. Dissolve 2.5 g of reagent-grade potassium cyanide, and dilute to 1 l with distilled water. Standardize this solution potentiometrically with a standard silver nitrate solution[11]. This solution should contain approximately 1 mg of cyanide per ml and is used to prepare dilute standard solutions.

Ferroin reagent. Dissolve 1.96 g of iron(II) ammonium sulfate hexahydrate and 3.17 g of 1,10-phenanthroline monohydrate (G. Frederick Smith Chemical Company) in distilled water and dilute to 1 l. The resulting solution is 0.005 M in ferroin sulfate and 0.001 M with respect to 1, 10-phenanthroline.

Standard 0.001 M silver nitrate solution. Dissolve 0.1699 g of silver nitrate (99.9%) in distilled water and dilute to 1 l. Store in amber glass bottle.

Apparatus

The atomic absorption measurements involved in developing method I were made with a Techtron Model AA-4 Atomic Absorption Spectrophotometer, a Techtron burner assembly, and a Model DI-20 digital readout system. The iron hollow-cathode tube (Aztec) was neon-filled.

The atomic absorption measurements for method II were made with a Beckman Model 1301 Atomic Absorption Accessory, a Beckman Model DB prism spectrophotometer equipped with a Beckman potentiometric recorder, and a Techtron burner assembly. The silver hollow-cathode tube (Aztec) was neon-filled.

General procedure for Method I

Transfer the sample solution containing no more than 200 μg of cyanide in a total volume of 25 ml to a 50-ml volumetric flask, and add 5 ml of 1 M disodium hydrogen phosphate solution, 1 ml of 10% hydroxylamine hydrochloride solution and 4 drops of 0.1% thymol blue indicator. If the indicator color is not yellow, add 1 M acetic acid dropwise until the yellow color develops. Add 0.5 M sodium hydroxide dropwise until the indicator changes to blue; an intermediate light green color will be observed just before this point is reached. Add 5 ml of ferroin reagent and heat in a boiling water bath for 15 min with glass stopper in place. Cool in an ice bath for 10 min. Transfer the solution to a 60-ml separatory funnel, and extract with five 5-ml portions of chloroform. Combine the chloroform extracts in a 50-ml beaker, evaporate to dryness, then add 10 ml of ethanol and swirl to dissolve the extract. Transfer the solution to a 25-ml volumetric flask, rinse the beaker with 10 ml of ethanol, and dilute to volume with ethanol.

Adjust the current applied to the iron hollow-cathode tube at 10 mA. Adjust the air at 18.0 p.s.i. and acetylene at 4.5 p.s.i. Use a slit width of 50 μ and adjust the monochromator setting until a maximum transmittance reading is obtained at 248.3 nm. Aspirate a standard solution corresponding to 83 μg of cyanide in the ethanol extract and adjust the burner alignments to obtain maximum absorbance. Aspirate standard and unknown solutions. Prepare a calibration graph.

General procedure for Method II

To a sample containing no more than 110 μg of cyanide in a 50-ml volumetric flask, add 5 ml of standard 0.001 N silver nitrate solution, and adjust the pH to *ca.* 5.3 by adding dropwise 0.01 N sodium hydroxide. Dilute to 50 ml with distilled water, heat in a boiling water bath for 5 min, and cool in an ice bath for 15 min. Then transfer the solution to a 40-ml centrifuge tube and centrifuge for 25 min. Use the supernate for the atomic absorption spectrometric determination.

Use a silver hollow-cathode tube current of 15 mA, a luminous acetylene–air flame, and a slit width of 0.20 mm. Adjust the monochromator for the 328.1-nm wavelength and optimize settings while aspirating a solution containing 10.7 p.p.m. of silver. Aspirate standard and unknown (supernate) solutions, using the absorbance read-out of the recorder. Prepare a calibration graph.

Results

Method I. The indirect atomic absorption spectrometric method is slightly less sensitive than the spectrophotometric method. However, the sensitivity is satisfactory with a sensitivity limit of 0.06 p.p.m. of cyanide. A typical calibration graph is linear up to 5.0 p.p.m. of cyanide with ethanol as the solvent; the reagent blank gave a reading of zero absorbance. The most sensitive resonance line for iron is 248.3 nm[12].

An estimate of the precision of this method was ascertained from the results of six samples each containing 2.85 p.p.m. of cyanide. These samples gave a mean absorbance value of 0.239, with a standard deviation of 0.005 absorbance unit, or a relative standard deviation of 2.2%.

Method II. For this method, a typical calibration graph is linear from 0.3 to 2.5 p.p.m. of cyanide. The optimum concentration range is 0.3–2.1 p.p.m. of cyanide, and the sensitivity is 0.03 p.p.m. of cyanide. The most sensitive resonance line for silver is at 328.1 nm[12].

The precision of this method was established from the results of seven samples each containing 1.42 p.p.m. of cyanide. These samples gave a mean absorbance value of 0.262, with a standard deviation of 0.004 absorbance unit, or a relative standard deviation of 1.5%.

A study of the time required for centrifugation showed that 25 min was optimal.

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(Received November 16th, 1968)

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Titrimetric determination of iodide after twentyfour-fold amplification

The WINKLER method[1] for the titrimetric determination of iodide is the best-known and most useful amplification method. A six-fold amplification is achieved by oxidation of iodide to iodate with chlorine (or bromine) followed by reduction of the iodate with added iodide, to give six atoms of iodine for each original iodide ion. The iodine is titrated with a standard thiosulphate solution.

Under suitable conditions, iodide can be oxidized to iodate by periodate, to give four times the yield of iodate relative to the WINKLER procedure. WILLARD AND GREATHOUSE[2] used this reaction to determine 40–100 mg of iodide, but, as it was only possible to determine periodate in the presence of iodate and not *vice versa*, they completed the determination by titrating the excess of periodate. It would be more satisfactory, and more sensitive, to determine the iodate formed in the reaction, as in this instance, each original iodide gives rise to 24 iodine atoms. Recently, it was reported[3] that periodate can be masked by molybdate at pH 3, whereas iodate is unaffected. This observation has been applied to the titrimetric determination of iodate in the presence of periodate[3,4] and the detection and determination of *vic*-diols[5]. This paper describes, therefore, the development of a titrimetric method for the twentyfour-fold amplification of iodide based on the above reactions.

Investigation of reaction conditions

Oxidation of iodide by periodate to give iodate is slow[2] at pH 7; to achieve quantitative oxidation of 0.1 g of iodide by a small excess of periodate, WILLARD AND GREATHOUSE had to heat the reaction mixture on a boiling water bath for 20 min. In the present investigation, preliminary experiments were made at pH 3; periodate can be masked by molybdate at this pH, so that the final titration could be made without adjustment of pH. However, at this pH, quantitative oxidation of 127 μg of iodide was achieved only after heating in boiling water for 2 h in the presence of a 300-fold molar excess of periodate. Moreover, under these conditions, high blank titrations (several ml of 0.002 *M* thiosulphate solution) and poor precision, as well as the excessive reaction time, were serious disadvantages. The poor precision posed a particular problem in that a systematic investigation of the variables affecting the system was made extremely difficult.

The blank value was reduced if the stock sodium metaperiodate solution was acidified to pH 2; perchloric acid was better than other mineral acids in this respect but, at best, a typical blank value was 1.45 ml ($\equiv$15.4 μg of iodide). Further increases in acidity, both of the sodium metaperiodate solution and of the reaction mixture, gave only slightly reduced blank values, no increase in reaction rate and no improvement in precision. The use of potassium metaperiodate, especially if it had been recrystallized, markedly reduced the blank value, but did not improve the reaction rate or precision.

Bromide[2] and strontium(II)[6] have been reported to accelerate the iodide–periodate reaction, but they had no effect on the present reaction at pH 2 except that bromide caused an increase in the blank value. Microgram quantities of nitrite, bromine, iron(III), osmium(VIII), bromide plus manganese(II), or thiocyanate similarly affected only the blank value.

Spectrophotometric studies showed that the first step in the oxidation reaction, the formation of iodine:

$$2I^- + IO_4^- + 2H^+ \rightarrow I_2 + IO_3^- + H_2O \quad (1)$$

was extremely rapid at pH 1, but the subsequent oxidation of iodine:

$$I_2 + 5IO_4^- + H_2O \rightarrow 7IO_3^- + 2H^+ \quad (2)$$

was slow at this pH, as was found by PESCHANSKI[7]. The rate of reaction (1) decreases with decreasing acidity[6], whereas that of reaction (2) increases. It was decided, therefore, to raise the pH of the reaction medium to see if the overall reaction rate increased. The effect of pH is summarised in Table I. It shows that at pH 7 (borate buffer), the conditions used by WILLARD AND GREATHOUSE, the rate was sufficient to allow a ten-fold reduction in the amount of periodate used (and hence reduce the blank to an acceptable level) and to reduce the reaction time to 30 min. Moreover, under these conditions, the results were more precise. Such results are summarised in Table II.

TABLE I

EFFECT OF pH ON OXIDATION OF 102 μg OF IODIDE BY PERIODATE

(The results were obtained by the recommended procedure with solutions adjusted to the pH given below)

pH	1	2	3	4	5	6	7
% Recovery	53	56	65	87	92	92	100
Blank (ml)	0.20	0.20	0.20	0.20	0.20	0.25	0.20

TABLE II

DETERMINATION OF IODIDE BY TWENTYFOUR-FOLD AMPLIFICATION

Iodide taken (μg)	*No. of detns.*	*Average % recovery*	*Standard deviation*
10.2[a]	8	102	2.0
25.5	12	99.8	1.0
64	8	99.1	0.5
102	5	99.8	0.3
153	6	99.5	0.6
204	5	99.6	0.6
255	10	98.2	0.5
509	8	98.4	0.2

[a] 0.96 ml of 0.002 *M* thiosulphate solution.

The procedure can be used to determine 10–200 μg of iodide with reasonable accuracy. Larger amounts of iodide are incompletely oxidized under the recommended conditions, but an increase in periodate concentration would solve this problem. The method is three orders of magnitude more sensitive than the WILLARD AND GREATHOUSE procedure, is almost as rapid and is experimentally simpler. The latter method requires the approximate iodide concentration to be known beforehand, and the reactant solutions have to be kept separate until they are at 97°. The present procedure requires only a very rough knowledge of the iodide concentration and merely involves heating a mixture of reactants.

The blank value, for a freshly prepared periodate solution, was 0.2 ml of 0.002 M thiosulphate solution; this increased to 0.5 ml when a week-old periodate solution was used. As in the acidic solutions, bromide gave increased blank values without affecting the rate or yield of iodide oxidation; 160 μg of bromide doubled the blank, so that no more than 20 μg of bromide could be tolerated, unless its concentration were known, in which case the same amount of bromide could be added to the blank solution. Phosphate had no effect on the reaction, but the yellow phosphomolybdate formed in the masking procedure appeared to decrease the sharpness of the end-point of the titration.

Experimental

Potassium metaperiodate solution. Dissolve 1.750 g of potassium metaperiodate, previously recrystallized from water, in small portions of hot water (100 ml in total), and make up to 500 ml with water. Add 3 ml of saturated borax solution, to give a pH of less than 7.3. Store in a dark glass bottle. All other reagents were analytical-reagent grade.

Amplification procedure (for 10–200 μg of iodide). To the iodide solution in a 5- or 10-ml graduated flask add 2.5 ml of the periodate solution, and make up to the mark with water. Hold down the stopper with wire and allow the flask to stand at room temperature for 5–10 min. Lower the flask carefully into boiling water, and leave for 30 min. Cool the reaction mixture, transfer to a conical flask and add 5 ml of a freshly prepared, 25% ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) solution and 5 ml of a pH 2.2 acetate buffer solution (made from 8 ml of 0.2 M sodium acetate and 20 ml of glacial acetic acid) to give a pH of 3.0–3.6. Add 2.5 ml of 10% potassium iodide solution, allow to stand for 2 min, and titrate with 0.002 M sodium thiosulphate solution, using Thyodene as indicator. Take a blank of distilled water through the whole procedure.

J.W.H. thanks the Association of Commonwealth Universities for a Commonwealth Scholarship, and the Uganda Government for study leave.

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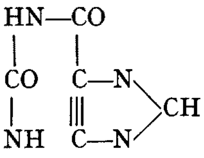
(Received November 5th, 1969)

Detection of theophylline and theobromine by reactions with mercury(II) cyanide*

An interesting field for the application of spot tests concerns the differentiation of isomeric organic compounds and the verification of structures through a positive or negative response for functional groups[1]. With this objective in mind, studies were made on the behaviour of xanthine and its most important methyl derivatives towards a test for acidic organic compounds[1], which is based on dry heating (150–180°) of the solid sample with excess of mercury(II) cyanide; volatile hydrogen cyanide is released which can be sensitively detected by the blueing of filter paper moistened with a solution of copper(II) ethylacetoacetate and tetrabase in chloroform[2]. This behaviour permits the detection of all kinds of acidic compounds including those which show no or only faintly acidic characteristics by conventional methods. In this category belong the amphoteric compounds xanthine (I), theophylline (1,3-dimethylxanthine) (II) and the theobromine (3,7-dimethylxanthine) (III).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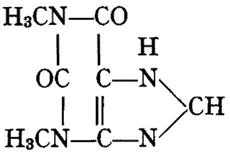
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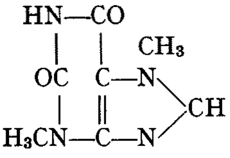
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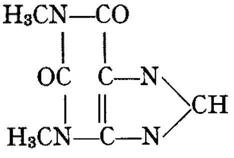
IV

As shown by the structures I–IV, and assuming that the acidic character may be due to enolisation of carbonyl groups or to intact imine groups, it was to be expected that compounds I–III would react pyrolytically with mercury(II) cyanide, whereas caffeine (1,3,7-trimethylxanthine) (IV) would remain unaltered because of the lack of the two above-mentioned groups. This expectation was confirmed experimentally with mg-amounts of the pertinent samples. The different behaviour can be applied to prove the presence or absence of theophylline or theobromine in caffeine preparations.

An interesting fact came to light when compounds I, II, III and IV, dissolved or suspended in water, were heated with an aqueous 5% (w/v) solution of mercury(II) cyanide. By this treatment which can be carried out in the spot test technique, only I and II split off cyanide. Clearly, the acidic imino group in the 7-position (imidazole nucleus) is involved in the reaction with neutral mercury(II) cyanide in the wet way. The different behaviour of theophylline and its isomer theobromine towards the neutral solution is a fine example of the differentiation of two isomers by means of a spot test.

It is noteworthy that this differentiation is not maintained if a diluted sulfuric acid solution of mercury(II) cyanide is used as a reagent. In this case, theophylline as well as theobromine releases hydrogen cyanide.

The reaction of theophylline with mercury(II) cyanide in the wet way likewise takes place with salts and addition compounds of this alkaloid. The following proce-

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* Dedicated to Prof. R. BELCHER on the occasion of his 60th birthday.

dure makes use of the fact[3] that a sulfuric acid solution of mercury(II) cyanide is stable even when warmed (80–90°) but releases hydrogen cyanide if compounds are added which react with mercury(II) cyanide to form cyanide ions.

Recommended procedure

Place the test solution or a small amount of the solid sample in a micro test tube, and add 1 drop of a 1% solution of mercury(II) cyanide and 1 drop of 0.1 *N* sulfuric acid. Heat the tube in a water bath and cover its mouth with a piece of filter paper moistened with a solution containing 5% of tetrabase and 5% of copper(II) ethylacetoacetate in chloroform. The rapid appearance of a blue fleck on the reagent paper indicates a positive response.

The above procedure also allows the detection of theobromine.

The following table illustrates the reaction possibilities in the system alkaloid–mercury(II) cyanide. The limits of identification obtained are included.

TABLE I

REACTIONS AND LIMITS OF IDENTIFICATION

Alkaloid examined	*Release of HCN when treated with*		
	$Hg(CN)_2$ *150–180°*	*5%* $Hg(CN)_2$	$Hg(CN)_2+H_2SO_4$
Xanthine	+ (2 μg)	+ (5 μg)	+ (1 μg)
Theophylline	+ (2.5 μg)	+ (10 μg)	+ (5 μg)
Theobromine	+ (25 μg)	—	+ (50 μg)
Caffeine	—	—	—

It should be noted that many organic compounds release hydrogen cyanide if heated with mercury(II) cyanide in the wet or dry way[1]. The value of the tests described here lies in the following applications: they permit a microchemical differentiation of theophylline and its isomer theobromine and the detection of these two alkaloids in caffeine.

The Conselho Nacional de Pesquisas is thanked for financial support.

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(Received November 25th, 1969)

Redox reactions on the ring-oven
Part I. Microdetermination of mercury

The toxicity of mercury and its use in many industrial processes, warrant the development of a fast and simple method for its determination in the atmosphere. The principle of reduction has been applied by JANJIC *et al.*[1] for the microdetermination of easily reducible elements by the ring-oven technique without prior separation from other elements. The ring-oven, which has proved to be a simple and efficient tool in air pollution work, was chosen for this work.

In the method which is proposed mercury is brought to the ring where it is reduced to the metallic condition with hydroxylamine hydrochloride while rings formed by colored ions are washed out. Excellent selectivity is obtained. The limit of detection of mercury is 0.5 μg. The range 1.0–9 μg is recommended for quantitative work.

Experimental

Standard stock mercury solution. Prepare a standard solution (0.1 μg mercury per μl) by dissolving 100 mg of pure mercury in a few drops of concentrated nitric acid and diluting with distilled water as necessary.

Apparatus. A Weisz ring-oven with accessories (National Appliance Co., Portland, Oreg.), a powerstat (Superior Electric Co., Bristol, Conn., Type 2PF10), and calibrated microliter pipets were used.

Qualitative procedure. Place the filter paper (Whatman No. 2) on the heated ring-oven with the powerstat maintained at reading 28. Add the appropriate volume of the mercury standard or of the unknown solution, followed by two 10-μl portions of 0.05 *M* hydrochloric acid and two 10-μl portions of aqueous 1% (w/v) hydroxylamine hydrochloride solution, followed by two further 10-μl portions of the hydrochloric acid. After the transfer to the ring zone has been completed and the paper is about dry, remove it and expose it to the fumes of hot concentrated ammonia solution. A black ring is formed when mercury is present.

Elimination of interferences

A number of ions, mostly colored, interfere under these conditions of operation. Various masking agents were investigated, but proved unsatisfactory because they either reduced the sensitivity of the mercury reaction or prevented it completely.

Washing the colored rings in various acids of different strength did not give satisfactory results, the mercury being often removed. It was found, however, that dipping the filter paper in a 1% (w/v) solution of tin(II) chloride in 0.1 *M* hydrochloric acid removed the effect of most interfering ions while the mercury rings actually deepened in color.

Procedure. Dip the filter paper, after being exposed to ammonia fumes, in the tin(II) chloride solution for 1 min, then press it between two filter papers and allow to dry. Black rings, the intensities of which depend on the concentration of mercury, will appear against the white background of the paper. Running a blank leaves no ring whatsoever on the filter paper.

Results and discussion

Choice of filter paper. An investigation of the characteristics of a number of filter papers showed that the best results were obtained with Whatman No. 1 or No. 2 filter papers. These are qualitative analysis filter papers that have not been washed with hydrochloric and hydrofluoric acids. In fact double acid-washed filter papers failed to show a reaction or gave very poor rings. Whatman No. 2 was finally chosen.

Analysis of an unknown. The preparation of rings for the standard scale and for an unknown followed the above procedure. A standard scale was prepared by making rings with 1, 3, 5, 7, 9 and 10-μl aliquots of a solution containing 0.1 μg of mercury per μl. Three rings made from different numbers of μl-aliquots of the sample solution sufficed for each unknown. The color of each of the 3 rings was matched with the standard scale and it was decided whether it matched one of the rings or fell between 2 rings. The quotient obtained from dividing the total number of microliters of the 3 unknown rings, by the total number of microliters of the matching standard ring, when multiplied by the concentration of the standard solution gave the concentration of the unknown[2].

Interferences and foreign ions. The effect of foreign ions was investigated by developing two rings for each species using the above procedure. The first ring contained 100 μg of the foreign ion while in the second ring 100 μg of the foreign ion and 1 μg of mercury were present. No interference was recorded for all cases when the first ring gave a blank or gave a ring less intense than 0.5 μg mercury, and the second matched a ring containing 1 μg mercury when judged visually.

The following ions did not interfere:

Group I. Li(I), Na(I), K(I), Rb(I), and Cs(I).
Group II. Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II) and Cu(II).
Group III. Al(III), Ce(IV), Tl(I) and BO_2^-.
Group IV. Carbonate, acetate, oxalate, tartrate, citrate, Zr(IV), Sn(IV), Pb(II) and Th(IV).
Group V. NH_4(I), NO_3^-, HPO_4^{2-}, VO_3^-, $HAsO_3^{2-}$, $HAsO_4^{2-}$, Sb(III) and Bi(III).
Group VI. S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, TeO_3^{2-}, Cr(III), CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, WO_4^{2-} and UO_2^{2+}.
Group VII. F^-, Cl^-, ClO_3^-, ClO_4^-, Mn(II), MnO_4^-, Br^-, BrO_3^-, I^-, IO_3^-, CN^- and SCN^-.
Group VIII. Co(II) and Ni(II).

The following ions were found to interfere: Ag(I), Au(III), Sn(II), Fe(III), Pt(IV), Pd(II), Rh(III), $(Fe(CN)_6)^{4-}$ and $(Fe(CN)_6)^{3-}$.

Although tin alone gives no reaction, 100 μg of tin(II) interfere by reduction of mercury(II); when the concentration of tin is reduced to 10 μg no interference is observed. When iron(III) is present in concentrations of 100 μg, the filter paper must be dipped in 2% tin(II) chloride solution. Concentrations of iron up to 50 μg do not interfere; 10 μg of silver(I) does not interfere but 50 μg of silver interfere. The interference of Au(III), Pt(IV), Pd(II), Rh(III), $(Fe(CN)_6)^{4-}$ and $(Fe(CN)_6)^{3-}$ are of no practical significance in air pollution work.

Accuracy and reproducibility of quantitative method. The accuracy and reproducibility of this method for the microdetermination of mercury was ascertained by the method of WEISZ[2]. Standard scales covering the range 0.5–7 μg mercury were prepared by the described procedure. Rings obtained from 10, 30, 50, and 70 μl of an unknown solution were also developed and matched with standard rings, and results were calculated by the above method. The concentrations found for two unknown solutions

TABLE I

DETERMINATION OF MERCURY

Taken (μg)	*Found (μg)*[a]
1.00	0.99 ± 0.02[b]
3.00	3.04 ± 0.04[b]

[a] Based on averaging 5 values calculated from 3 rings each.
[b] Calculated at 90% confidence limit.

are shown in Table I.

This investigation was supported by Public Health Service Research Grant AP 00117 from the Division of Air Pollution, Bureau of State Services and by the Research Committee of the School of Arts and Sciences, of the American University of Beirut.

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(Received September 11th, 1969)

Redox reactions on the ring-oven
Part II. Microdetermination of silver

There is an increasing interest in determining trace quantities of silver in drinking waters, particularly since the U.S. Public Health Service set standards limiting its maximum permissible concentration. Methods for determining small quantities of silver include: atomic absorption, spectrophotometry, paper chromatography, potentiometry, polarography, neutron activation, and radioactivation. However, there is a need for a fast and reliable method using simple equipment within the financial possibilities of small institutions.

Velculescu[1] showed that the principle of photography, namely the formation of silver nuclei when silver halides are exposed could provide a very sensitive test of silver; it is possible to detect 0.05 μg of silver by this means. The combination of the physical development method for the detection of silver and the ring-oven technique seemed promising.

In the method which is proposed, silver is brought to the ring zone and converted to silver bromide. The latter is reduced with a modified photographic developer and then fixed. The method is fast and simple and very few ions interfere. It is suitable for the determination of silver in the range 0.1–1 μg with a limit of identification of 0.05 μg.

Reagents and stock solutions

Developer. Dissolve 2.5 g of potassium hydroxide, 20 g of anhydrous sodium sulfite, 0.3 g of potassium bromide, and 5.5 g of hydroquinone in distilled water and dilute to 100 ml.

Fixer. Dissolve 20 g of sodium hyposulfite and 2.5 g of sodium hydrogen sulfite in water and dilute to 100 ml.

Standard stock silver solution. Prepare a standard solution (0.01 μg of silver per μl) dissolving 100 mg of pure silver in a few drops of concentrated nitric acid and diluting with distilled water as necessary.

Apparatus

The ring-oven and accessories were the same as described in Part I[2].

Procedure

Place the filter paper (Munktells No. OK) on the ring-oven with the powerstat maintained at reading 28. Add the appropriate volume of the standard silver solution or of the unknown silver solution followed by four 10-μl portions of concentrated ammonia solution. Add one 10-μl portion of aqueous 0.05% (w/v) potassium bromide solution followed by four 10-μl portions of distilled water. After the transfer to the ring zone has been completed and the paper is almost dry, remove it and dip it in the developer for 2 min. Remove the filter paper from the developer, wash it twice with distilled water and dip it in 0.05 *M* acetic acid solution for 10 min. Dip the filter paper in a beaker of distilled water and in the fixer solution and dry it in a stream of hot air. A black ring indicates silver. The above procedure gives a limit of determination of silver of 0.05 μg; the recommended range covers 0.1–0.7 μg of silver.

Results and discussion

Choice of filter paper. An investigation of the characteristics of a number of filter papers showed that the best results were obtained with Munktells No. OK, OO, OOH and O. These papers, which are available already washed with hydrochloric and hydrofluoric acids, produced no blank and had uniform concentric diffusion; their strength while wet was good and the speed of diffusion was satisfactory. Munktells No. OK was finally chosen.

Analysis of an unknown. The preparation of rings for the standard scale and for an unknown followed the above procedure. A standard scale was conveniently prepared by making rings with 1, 3, 5, 7 and 9 10-μl portions of a solution of silver containing 0.01 μg per μl. Three rings made from different numbers of microliters of solution were sufficient for each unknown. The method of calculation was the same as described previously[2,3].

Interferences and foreign ions. The effect of interfering ions was investigated by preparing two rings for each ion. The first ring contained 10 μg of the potential interfering ion and the second, 0.1 μg of silver in presence of 10 μg of interfering ion. No interference was recorded for all cases when the first ring gave a blank or gave a ring less intense than 0.05 μg of silver, and the second matched a ring containing 1 μg of silver when judged visually. The following ions did not interfere:

Group I. Li(I), Na(I), K(I), Rb(I) and Cs(I).
Group II. Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II) and Cu(II).
Group III. Al(III), Ce(IV), Tl(I) and BO_2^-.
Group IV. Carbonate, acetate, oxalate, tartrate, citrate, Zr(IV), Sn(IV), Pb(II) and Th(IV).
Group V. NH_4(I), NO_3^-, HPO_4^{2-}, VO_3^-, $HAsO_3^-$, $HAsO_4^{2-}$, Sb(III) and Bi(III).
Group VI. S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, TeO_3^{2-}, Cr(III), CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, WO_4^{2-} and UO_2^{2+}.
Group VII. F^-, Cl^-, ClO_3^-, ClO_4^-, Mn(II), MnO_4^-, Br^-, BrO_3^-, I^-, IO_3^-, CN^-, SCN^-, $(Fe(CN)_6)^{4-}$ and $(Fe(CN)_6)^{3-}$.
Group VIII. Fe(III), Co(II), Ni(II), Rh(III), Pd(II) and Pt(IV).

Mercury(I and II), tin(II) and gold(III) were found to interfere. Mercury(I and II) interfered in 10-μg amounts, but if the filter paper was dipped in a 10% sodium fluoride solution for 1 h before it was dipped in acetic acid, no interference was observed. Tin(II) at the 10-μg level interfered by preventing the formation of the silver ring, but 1 μg did not interfere.

Accuracy and reproducibility of quantitative method. The accuracy and reproducibility for the microdetermination of silver was ascertained by the method of WEISZ[3]. Standard scales covering the range 0.05 μg–0.7 μg of silver were prepared by the described procedure. Rings obtained from 10, 30, 50 and 70 μl of an unknown were also developed and matched with standard rings. The results are shown in Table I.

TABLE I

DETERMINATION OF SILVER

Taken (μg)	*Found (μg)*[a]
0.100	0.102 ± 0.004[b]
0.300	0.298 ± 0.004[b]

[a] Based on averaging 5 values calculated from 3 rings each.
[b] Calculated at 90% confidence limit.

This investigation was supported by the Research Committee of the School of Arts and Sciences, of the American University of Beirut.

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(Received September 11th, 1969)

Separation of high-boiling cyclic diolefins by an improved silver nitrate g.l.c. column

In the isomerization of *cis, trans*-1,5-cyclodecadiene by rhodium chloride trihydrate in ethanol[1], the following isomer distribution is obtained: *cis, cis*-1,6-cyclodecadiene (94%), *cis, cis*-1,5-cyclodecadiene (5%), *cis, trans*-1,6-cyclodecadiene ($<$ 0.3%), and *cis*-cyclodecene ($<$ 0.3%); *cis, trans*-1,6-cyclodecadiene is possibly present as a trace.

The olefin distribution is a function of its symmetry and strain. Since the strain due to hydrogen–hydrogen interaction across the ring[2], as found in *cis, trans*-1,5 cyclodecadiene, is absent, the *cis–cis* isomers are more symmetrical. This leads to stable dimeric complexes with rhodium(I) chloride. The *cis–trans* isomers seem to form large polymeric complexes with silver(I), copper(II) and gold(I) with different stability considerations[3,4]. G.l.c. retention times with columns containing silver(I) ions allow comparisons of relative stabilities[5]; they seem to indicate that the complexes having large polymeric structures form the most stable complexes.

Considerations of these relative stabilities form the basis for the g.l.c. separation of olefins with silver nitrate with various liquid substrates such as tetraethylene glycol, glycerol, and benzyl cyanide[6]. The features of this type of column have been described by ZLATKIS *et al.*[7].

TABLE I

G.L.C. COLUMNS SCREENED

Column	*Support*	*Liquid phase*		*% Wt. of liquid phase*	*Column dimensions*
		% $AgNO_3$	*% Stationary phase*		
1	Firebrick 40–60 mesh	0	100% Polyethylene glycol 400 distearate	25	10′ × 1/8″
2	Firebrick 40–60 mesh	0	100% Polyethylene glycol 400 distearate	20	10′ × 1/8″
3	Firebrick 40–60 mesh	0	100% Polyethylene glycol 400 distearate	10	10′ × 1/8″
4	Firebrick 40–60 mesh	0	100% Silicone oil DC-200	40	10′ × 1/8″
5	Firebrick 40–60 mesh	0	100% Carbowax 1540	40	10′ × 1/8″
6	Chrom W 80–100 mesh	0	100% SE-30	10	6′ × 1/8″
7	Chrom W 60–80 mesh	0	100% DC-710	10	6′ × 1/8″
8	Firebrick 40–60 mesh	40% of 50% aq. $AgNO_3$	60% Polyethylene glycol 400 distearate	20	10′ × 1/8″
9	Firebrick 40–60 mesh	40	60% Polyethylene glycol 400 distearate	20	10′ × 1/8″
10	Firebrick 40–60 mesh	60	40% Carbowax 20M	20	10′ × 1/8″
11	Firebrick 40–60 mesh	47% of 50% aq. $AgNO_3$	53% Carbowax 20M	11	10′ × 1/8″
12	Firebrick 40–60 mesh	40% of 50% aq. $AgNO_3$	60% Tetraethylene glycol	20	10′ × 1/8″
13	Firebrick 40–60 mesh	35	65% Carbowax 20M	20	10′ × 1/8″
14	Firebrick 40–60 mesh	40	60% Carbowax 1540	20	10′ × 1/8″

G.l.c. analysis of the isomerized C_{10} diolefins by the silver nitrate–tetraethylene glycol column is slow with peak broadening for most of the diolefins. A series of columns, Table I, were therefore prepared and screened, with a C_{10} diolefin mixture to investigate their properties for rapid analysis, symmetrical peaks, and extended column lifetime. A 20% (w/w) loading of (35% silver nitrate + 65% Carbowax 20M) or (40% silver nitrate + 60% Carbowax 1540) on 40–60 mesh firebrick accomplish the best separation of the isomeric diolefins yet reported.

Two recent reports[8,9] on the separation of C_9 and C_{10} diolefins describe the use of a silver nitrate–Carbowax 20M column but the composition and conditions for these columns were not reported.

Experimental

The column packing was prepared in subdued light or in vessels protected from the light because of the photosensitivity of silver nitrate in solution. Silver nitrate was dissolved in warm absolute ethanol; Carbowax 20M was dissolved in CH_2Cl_2–$CHCl_3$. These two solutions were thoroughly mixed before the addition of the firebrick. The solvent was withdrawn with a rotary evaporator at 30 mm Hg pressure at room temperature.

A Perkin-Elmer 810 Flame Ionization Gas Chromatograph was used with a

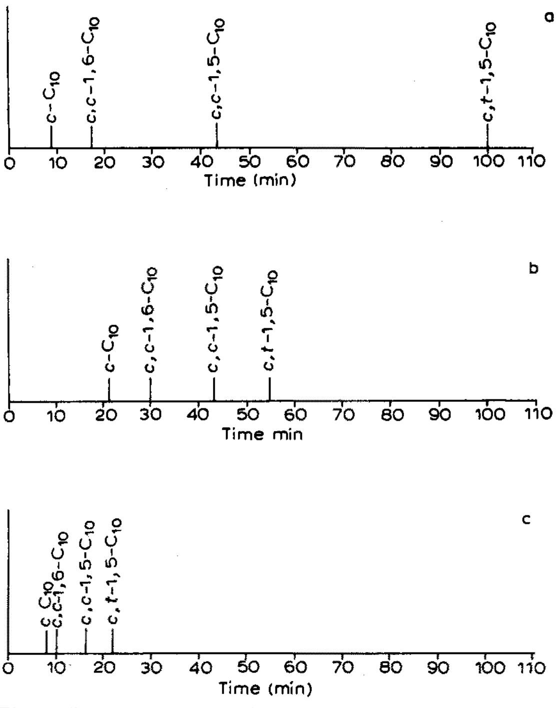

Fig. 1. Retention times of cyclodecadienes on various columns. c-C_{10} = *cis*-cyclodecene; *c,c*-1,6-C_{10} = *cis,cis*-1,6-cyclodecadiene; *c,c*-1,5-C_{10} = *cis,cis*-1,5-cyclodecadiene; *c,t*-1,5-C_{10} = *cis, trans*-1,5-cyclodecadiene. (a) Column 12 (Table I) in aluminum tubing. N_2 flow, 40 cm^3 min^{-1}. Temperature, 82°. (b) Column 13 in copper tubing. He flow, 30 cm^3 min^{-1}. Temperature, 82°. (c) Column and flow as for b. Temperature 108°.

Speedomax G 0–1 mV scale recorder. Injector temperature was 150° with the detector temperature at 120°. Sample size was 1–2 μl of 10–20% (w/w) solutions. Helium or nitrogen was used as a carrier gas.

The cyclodecadienes were supplied by Columbian Carbon Company. Cyclooctadienes of commercial grade were used without further purification.

Discussion

Figure 1 compares the retention times of some cyclodecadiene isomers in the new silver nitrate–Carbowax 20M column with the silver nitrate–tetraethylene glycol column at 82° and shows that the retention time is decreased by 50%. The new column can also be used at higher temperatures whereas for the old column above 85° substrate bleeding and decomposition of silver nitrate seems to occur. At a temperature of 112° the retention time of the cyclodecadienes on the silver nitrate–Carbowax 20M column is further decreased appreciably. Below 90° peak broadening is observed for this column.

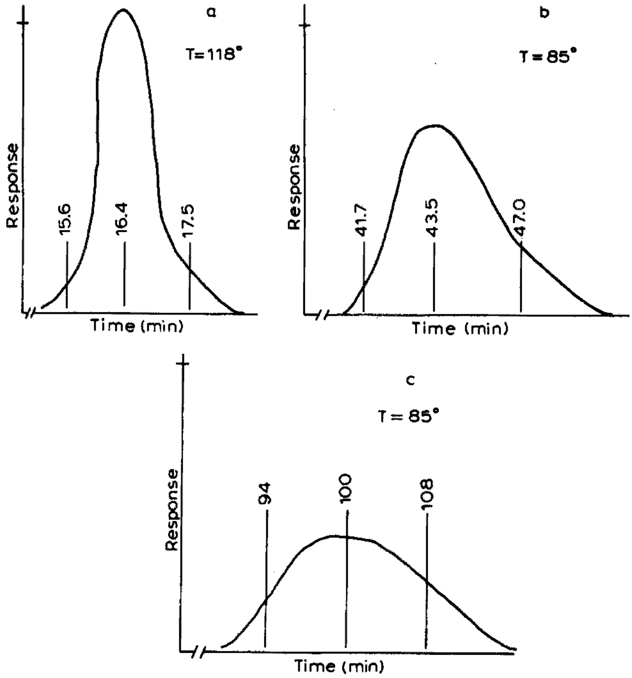

Fig. 2. Peaks obtained for *cis, trans*-1,5-cyclodecadiene under different conditions. (a,b) Column 13 in copper tubing. He flow 30 cm^3 min^{-1}. (c) Column 12 in aluminum tubing. N_2 flow 40 cm^3 min^{-1}.

Figure 2 illustrates the peak shapes for *cis, trans*-1,5-cyclodecadiene at various temperatures. Proper choice of column temperatures makes it possible to obtain symmetrical peak shapes for all the isomers of the cyclic C_8 and C_{10} diolefins and to separate those components which do not differ much in adsorption.

Figure 3 shows the influence of heat on a 20% (w/w) (40% AgNO$_3$+60%

Carbowax 1540) column in the retention of the isomers of cyclic C_{10} system. Chromatogram a shows the separation of *cis*-cyclodecene and *cis, cis*-1,6-cyclodecadiene at 119° on a freshly prepared column. The column was then heated to 175° for 10 h with a helium flow rate of 15 cm^3 min^{-1}. Chromatogram b (T =92°) illustrates that the column has deteriorated very markedly since at 119° no separation occurs; at 92°, however, cyclodecene appears as a shoulder on the *cis, cis*-1,6-cyclodecadiene peak. This indicates that even after such extreme treatment, the silver ions still retain some of their complexing action.

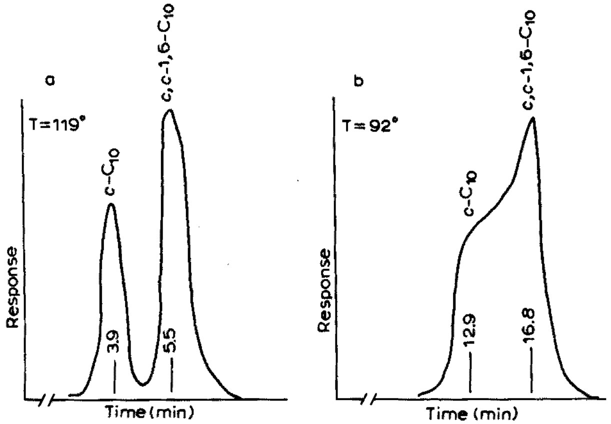

Fig. 3. Effect of temperature. Column 14 in copper tubing. He flow 32 cm^3 min^{-1}.

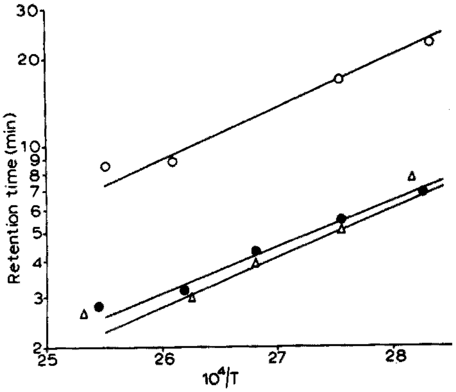

Fig. 4. Retention time *vs.* temperature for the cyclic C_8 system. (○) 1,5-cyclooctadiene, (●) 1,3-cyclooctadiene, (△) *cis*-cyclooctadiene.

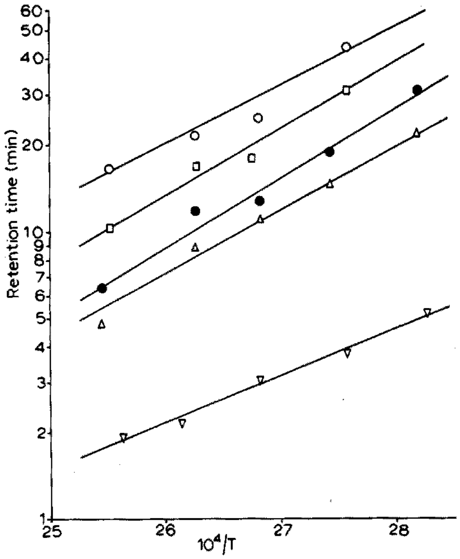

Fig. 5. Retention time *vs.* temperature for the cyclodecadienes: (○) becomes *cis,trans*-1,5-cyclodecadiene, (□) becomes *cis,cis*-1,5-cyclodecadiene, (●) becomes *cis,cis*-1,6-cyclodecadiene, (△) becomes *cis,cis*-cyclodecene, (▽) becomes 1-decene.

In Fig. 4 the log retention time is plotted against reciprocal temperature for the cyclic C_8 system over the temperature range 80°–120°. Temperature programming improves the separation of *cis*-cyclooctene and the 1,3-cyclooctadiene. The order of elution is in agreement with that reported by MUHS AND WEISS[5] for silver nitrate–glycol columns at 40° and the retention times follow the increase in the stability of the silver(I) complexes.

Figure 5 indicates that even the linear C_{10} terminal olefin shows excellent separation from the cyclic C_{10} diolefins. The order of elution again follows the order of the stability of the silver(I) complexes. A study of Dreiding Models of the four cyclic C_{10} diolefins species indicates that the stability of the silver(I) complexes and the retention times are a function of the steric strain of the four unsaturates. This is most pronounced in a comparison of the *cis, cis*-1,5- and *cis,cis*-1,6-cyclodecadienes. The *cis, cis*-1,5-cyclodecadiene is more strained and seems to form the more stable silver complex. From the elution order the following order for the stability of the complexes can be determined: *cis*-cyclodecene < *cis,cis*-1,6-cyclodecadiene < *cis, cis*-1,5-cyclodecadiene < *cis, trans*-1,5-cyclodecadiene.

We wish to thank Columbian Carbon Company for the cyclodecadienes and Dr. JAN HAMER for the use of his gas chromatograph.

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(Received October 4th, 1969)

Anal. Chim. Acta, 49 (1970) 580–584

Vacuum-fusion determination of oxygen in Al–Mg–Al_2O_3–MgO composites

The direct determination of the Al_2O_3 and MgO contents of Al–Mg–Al_2O_3–MgO composites, which are currently being studied for potential usage as canning and structural materials in nuclear reactors, is presently a difficult task: thus only the magnesium oxide is directly determined by a chemical method[1], and the aluminium oxide is calculated by difference from the total oxygen content of the sample as determined by activation analysis. The activation analysis equipment is very expensive and therefore not in general use in metallurgical laboratories. Thus, a study was made of the determination of the total oxygen by a cheaper and more widely available method, *viz.* the vacuum-fusion method. A flux technique was used which, in order to reduce the evaporation of volatile metals, provides for sealing the sample with the flux (in this case, copper) in a small graphite capsule firmly closed with a screwed cover, which is dropped into the hot crucible of the instrument for the analysis.

Such a technique has been previously used for the determination of oxygen in Al–Al_2O_3 composites[2], and only minor modifications were made. Owing to the presence of magnesium, which has a high vapour pressure, and the very refractory magnesium oxide, difficulties were expected from a possibly enhanced volatility of the sample with consequent getter effects, and from a higher stability to the carbon reduction. After the reduction reaction, total oxygen was determined as carbon monoxide; full details of this determination and the instrument used (Heraeus VH6) have been described previously[2].

Procedure

Place samples of the composite (30–60 mg) together with the copper flux (in small pieces) in a weight ratio of about 1/4, into the capsules, screw up the covers and place the filled capsules (4–6) in the sample container of the instrument. Before weighing, file the surfaces of the composite (if in pieces) and wash the copper with dilute nitric acid followed by ethanol and toluene. If the composite is in powder form, simply pour it into the capsule and cover with the appropriate amount of copper, treated as before.

Evacuate the furnace, with the capsules at the same vacuum, degas the crucible at high temperature, and, when the blank of the instrument is low and constant, begin the analyses. Drop the first capsule into the crucible at 1100°, hold at this temperature for 15 min and discard the extracted gases (see *Discussion*). Then raise the temperature to 1650–1700°, which is maintained for 15 min, during which time some surges to 1750–1800° lasting a total of 5–7 min are made. The ionization gauge mounted near the furnace, facilitates the following of the degassing; when this is finished, the surges in temperature do not change appreciably the prevailing pressure, which is usually in the range of $1\text{–}3 \cdot 10^{-5}$ mm Hg. Then analyse the extracted gases and from the total carbon monoxide evolved, calculate the oxygen content of the sample, making allowance for the carbon monoxide coming from the capsule, flux and blank of the instrument. Analyse all the capsules of the set in succession.

Measure the instrumental blanks at the beginning and after each two capsules, following the crucible temperature cycle of the second 15-min period of gas extraction from the sample.

Results

Table I shows the composition and the results obtained from some specimens analyzed by both vacuum-fusion and activation methods. Except for the presence of traces of carbon, iron and silicon in the range 50–1500 p.p.m., the difference from 100% for the pieces is aluminium. The powders, which are the starting material for the preparation of pieces, also contain small amounts of silicone grease (max. 0.4%) as lubricant, the oxygen of which did not appear to be lost during the period at 1100°.

TABLE I

COMPOSITION OF THE SPECIMENS AND RESULTS

Sample	*Free Mg*[a] (%)	*MgO*[b] (%)	*Al_2O_3*[c] (%)	*Vacuum fusion*			*Activation* % O
				No. of detns.	% O	*Std. dev.*[d]	
1[e]	0.48	2.25	1.29	4	1.41	0.07	1.30
2[e]	2.55	3.10	0.72	4	1.48	0.06	1.57
3[e]	0.77	1.63	4.58	4	2.73	0.05	2.80
4[e]	0.61	6.24	1.95	12	3.41	0.24	3.40
5[e]	0.13	2.70	8.49	3	5.04	0.04	5.06
6[e]	0.51	6.20	8.16	3	6.29	0.16	6.30
7[f]	4.55	0.33	3.02	3	1.37	0.02	1.55
8[f]	1.73	0.28	6.05	4	2.86	0.09	2.95
9[f]	3.75	1.25	11.9	2	6.10	0.05	6.10

[a] From the total Mg determined by a chemical method and the Mg bound as MgO; the incorrectly named "free Mg" is in reality bound with Al to give an intermetallic compound.

[b] Directly determined by a chemical method[1].

[c] From the total oxygen determined by activation analysis and the oxygen bound as MgO.

[d] Std. deviation = $\left(\frac{\Sigma(X-\bar{X})^2}{n-1}\right)^{\frac{1}{2}}$; despite its slight statistical significance, the standard deviation is given even for 2–3 determinations, in order to show roughly the maximum fluctuation of the single results from the average.

[e] Sample as pieces.

[f] Sample as powder.

Discussion

Samples which contain large amounts of oxygen may be difficult to degas by the above method. In such cases, the procedure is modified as follows: the capsule is loaded with a sample weighing only 10–20 mg (a smaller sample is taken because the instrument cannot handle large amounts of gases), with the flux, and with 40–60 mg of aluminium (the amount is not critical) of low oxygen content*. The ratio of flux to sample + aluminium is maintained equal to 4. Difficult samples can be smoothly degassed by this modified procedure.

The success of the aluminium addition can be attributed to the fact that carbon dissolves very slightly in liquid copper and only when sufficient aluminium is present in the melt does sufficient carbon become available for the reduction reaction, because of the great tendency of aluminium to form a carbide. The higher the oxygen content of the samples, the higher the carbon, *i.e.* the aluminium, concentration needed to complete the reaction. Samples 5, 6 and 9 of Table I were analyzed under these conditions.

Details of the capsules and copper flux have been given previously[2]. After the capsules have been produced on the lathe, they are strongly predegassed at 1750–1800° in the instrument itself in order to reduce their initially large gas content. However, contrary to the previous statement[2] that predegassed capsules should be stored until required in a desiccator under rotary pump vacuum, storage in an open beaker is now preferred; capsules stored thus and analysed empty by the above procedure still showed an oxygen content in the range 0.3–0.8 p.p.m. (for a maximum tested storage of two months) but the amount of gases evolved at 1100° and discarded (see *Procedure*) was decreased. In fact, the degassing at 1100° which does not affect the oxygen content of the sample, evolves the gases adsorbed during storage from

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* Aluminium 99.5% or of greater purity contains usually only some ten p.p.m. of oxygen and serves well for the purpose.

the capsules, which then become practically independent of their previous history. Clearly, such adsorbed gases were mainly vapours from the rotary pump.

The copper used as flux, placed in the capsules and analysed by the above procedure, showed an average oxygen content of about 15 p.p.m. Although the capsules were firmly closed, evaporation in the furnace occurred during the analyses at high temperature; nevertheless, Table I shows that getter effects, if any, were negligible. After each working day the furnace was dismantled, cleaned and reinstalled for the next analyses.

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(Received October 20th, 1969)

A rapid method for the determination of cobalt in seawater*

Cobalt is one of the more difficult trace ions to determine in seawater. Although several reagents are known which form highly colored complexes with cobalt, most require that the cobalt be concentrated before their use. The usual procedure requires a time-consuming preconcentration by co-precipitation[1–4] or co-crystallization[5–7]. After preconcentration, the cobalt may be separated from interfering ions by some particular technique before the final determination. Although solvent extraction has shown great promise in the concentration of trace elements in seawater, its application to cobalt apparently is rare. The employment of 1-nitroso-2-naphthol for the solvent extraction of cobalt from small volumes of aqueous solutions by several workers[8–10] suggested its use for seawater. A procedure is described which makes possible the determination of cobalt in seawater by solvent extraction with 1-nitroso-2-naphthol followed by spectrophotometric determination of the 1-nitroso-2-naphthol chelate. The advantages of the method are: elimination of preconcentration, quantitative extraction at the pH of seawater, simplicity, satisfactory sensitivity, reproducibility and precision at the concentration of cobalt normally found in seawater, absence of a salt effect and rapidity. A complete analysis can be achieved in less than 1 h.

Reagents

All solutions, except the hydrochloric acid, were prepared from analytical-grade reagents. It was found necessary to purify the reagent-grade hydrochloric acid by distillation before use. Aqueous solutions were prepared from doubly distilled deionized (mixed bed) water. All are stable with time unless otherwise noted.

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* Hawaii Institute of Geophysics Contribution No. 306.

Stock cobalt solution. Dissolve 4.7696 g of $CoSO_4 \cdot 7H_2O$ in a little water and dilute to 1000 ml (1 mg/ml cobalt).

Standard cobalt solution. Dilute 1 ml of stock cobalt solution to 1000 ml (1 μg/ml); dilute 10 ml of this solution to 100 ml (0.10 μg/ml) for use in the preparation of working curves in the 0.0–1.0 μg/l concentration range. Prepare fresh solution daily.

1-Nitroso-2-naphthol. Dissolve 1.0 g of 1-nitroso-2-naphthol in 100 ml of ethanol. Add 0.5 g of activated charcoal (powdered) to the reagent flask; swirl and filter just before each use. The reagent is stable for several weeks.

Basic wash solution. To 50 ml of 1.0 *M* sodium hydroxide solution, add 10 ml of aqueous 20% (w/v) sodium citrate solution and 1 ml of 30% hydrogen peroxide solution and dilute to 100 ml. Saturate the wash solution with chloroform just before use. Use Matheson Coleman and Bell low-carbonate sodium hydroxide, or its equivalent, for preparing the 1 *M* sodium hydroxide solution. The transition element assay of this A.C.S. grade reagent is an order of magnitude less than many analytical-grade reagents on the market.

Instrumentation

Spectrophotometer, Cary 14 recording. Matched standard volume (30-ml) and low volume (20-ml) cells of 10 cm path length.

Calibration curve

Prepare a calibration curve by adding appropriate amounts, 2.0–10.0 ml (0.2 μg–1.0 μg) for seawater determinations, of the diluted standard cobalt solution to 750-ml aliquots of seawater, or distilled water, and carrying out the analytical procedure. Subtraction of the appropriate blank from each of the absorbance values should result in a straight line passing through the origin with a slope of about 0.19 absorbance units per μg of cobalt, or about 0.1 absorbance unit per μg of cobalt if standard volume (30-ml) 10-cm path length cells are used.

Procedure

To a 750-ml sample of seawater filtered by gravity through a 1.2 μ Selas Flotronic silver filter, add 25 ml of aqueous 20% (w/v) sodium citrate reagent, 1 ml of 30% hydrogen peroxide solution and 1 ml of 1-nitroso-2-naphthol solution. Mix thoroughly and allow to stand for 10 min. In a separatory funnel fitted with a Teflon stopcock, extract the cobalt 1-nitroso-2-naphtholate once into 8 ml of chloroform followed by three extractions into 4-ml portions of chloroform. Collect all the extracts (*ca.* 15 ml) into a small separatory funnel. Take care to transfer all of the organic layer each time, even to the extent of transferring one or two drops of aqueous layer if necessary. Back-extract the excess of reagent into three 5-ml portions of the basic wash solution, again taking care to transfer all of the organic layer, but none of the flocculent precipitate which may form in the aqueous layer. Shake for 60 sec for each extraction. Strip the interfering metal ions into the aqueous phase by shaking the organic layer vigorously with 5 ml of 2 *M* hydrochloric acid. Back-extract any reagent released in the acid stripping step with 5 ml of the basic wash solution. Develop the cobalt 1-nitroso-2-naphtholate color with a final wash in 5 ml of 2 *M* hydrochloric acid. Draw off the chloroform layer into a 25-ml volumetric flask (use a 50-ml flask if standard 10-cm path length cells are being used) and make up to volume with ethanol. Small amounts of water are soluble in this mixed matrix, and no special precautions need be taken to keep the equipment dry. Read the absorbance at 410 nm against a blank carried through the same procedure. The complex is stable for several hours.

Discussion and results

Reagent blank. The absence of a salt effect was demonstrated by identical calibration curves obtained from both seawater and distilled water over the range 0–2.5 μg of cobalt. This suggested that the reagent blank could be obtained by adding the reagents to distilled water, carrying out the analytical procedure, and measuring the absorbance. The blank thus determined varied slightly and averaged about 0.016 absorbance unit.

Extrapolation. In order to confirm the reagent blank determined in distilled water, a large volume (*ca.* 4 l) of seawater was enriched with cobalt (*ca.* 2.00 μg/l); 100-ml, 200-ml and 500-ml volumes of this water were analyzed for cobalt by the procedure above. The absorbances of the samples were then plotted against their volumes, and an extrapolation made to zero volume. The absorbance at this point, caused by the reagents, was 0.014 absorbance unit, and was in good agreement with the blank determined in distilled water.

Interfering ions. Copper(II), iron(II), iron(III), tin(II), nickel(II) and palladium(II) form extractable (in chloroform) complexes with 1-nitroso-2-naphthol. Copper and nickel can be stripped from the organic extract with 2 *M* hydrochloric acid; palladium, in the concentration normally found in seawater, will not interfere. Iron(III), which is present in large concentration in analytical-grade sodium hydroxide, must be complexed in both the seawater sample and in the basic wash solution with sodium citrate. Tin(II) is oxidized to tin(IV) by the hydrogen peroxide and thus is prevented from interfering. Iron(II) is oxidized in the same manner.

Effect of pH and time. Studies carried out on the effect of pH on extraction and time on the formation of the complex indicate that complex formation is complete in 5 min at pH 8–9. The minimum time of 5 min is doubled and 10 min is specified in the procedure.

Absorbance of complex and reagent. 1-Nitroso-2-naphthol is a highly colored reagent which has an absorbance peak at about 365 nm in an ethanol–chloroform (1 + 1) solution. Its cobalt complex absorbs at 410 nm in the same matrix. STARÝ[11] has reported the absorbance at 530 nm; this is near the absorbance of the cobalt complex formed with the 2-nitroso-1-naphthol isomer, and can be considered an error. Incomplete back-extraction of the excess of reagent will result in erratic absorbance readings. Furthermore, freshly prepared reagent, as well as reagent which has been purified and allowed to stand, may contain impurities which will seriously interfere with the determination of trace quantities of cobalt. Several schemes were tried to reduce this last effect. Activated charcoal, recommended by SANDELL[12], seems the simplest, and results in a solution stable for many weeks.

Recovery. The fact that identical calibration curves are obtained from seawater and distilled water indicates that the extraction of cobalt in seawater is essentially complete, although this has not been established conclusively. A similar analysis for cobalt following perchloric and nitric acid treatment can be carried out in order to determine total and, by difference, "naturally complexed" cobalt.

Reproducibility. In order to establish the reproducibility of the method, replicate analyses were carried out at the 1 μg/l level in standard 10-cm cells, and at the 0.3 μg/l level in low-volume 10-cm cells. The results of 7 determinations at the 1.0 μg/l level and 5 determinations at the 0.3 μg/l level are summarized in Table I.

TABLE I

ABSORBANCE REPRODUCIBILITY OF COBALT 1-NITROSO-2-NAPHTHOLATE

	1.0 μg/l (standard cell)	*0.3 μg/l (low-volume cell)*
Mean	0.103	0.058
Fractional std. dev.[a]	4%	8%
Std. dev. $(\Sigma d^2/n-1)^{\frac{1}{2}} =$	0.004	0.005

[a] The fractional standard deviation is the ratio of the standard deviation to the mean, expressed as a percentage.

Accuracy. The uncertainty in the method is the sum of two contributions; random, or indeterminate errors, and systematic errors. The first is most conveniently estimated by means of replicate analysis, as in Table I. Systematic error is fixed by the method and the instrumentation, and is, therefore, constant over the range of concentrations being measured. It is evaluated by summing the uncertainties in all the spectrophotometer readings necessary to establish a net absorbance (sample minus blank) for the sample, together with the machine uncertainty (reproducibility of readings from day to day). The total uncertainty thus analyzed is 17% at the 0.3 μg/l level, and 52% at the 0.1 μg/l level when the Cary 14 spectrophotometer was used. In dealing with water of low cobalt concentration, the systematic error becomes relatively large and it is recommended that the sample volume be increased to 1500 ml in order to reduce this uncertainty.

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(Received November 1st, 1969)

Potentiometric determination of the stability constants of zinc thiocyanate and zinc azide complexes

In a continuation of previous work[1] on thiocyanate and azide complexes, the zinc–thiocyanate and zinc–azide systems have been examined. FRANK AND HUME[2] have studied the zinc–thiocyanate system by polarography, with potassium nitrate as supporting electrolyte.

However, since nitrate competes seriously with the complexing agent in the cadmium–thiocyanate reaction[1], it was of interest to redetermine the formation constants of the zinc–thiocyanate complexes in a non-complexing medium; literature data[3] on zinc–thiocyanate and –azide complexes are incomplete and mostly experimentally unsatisfactory.

Another point of interest was to test the use of a dropping amalgam electrode in potentiometric measurements of complex equilibria, and to compare this technique with conventional polarographic methods. Amalgam electrodes are more reproducible than metal electrodes, and have been used in potentiometric studies of metal complex formation[4]. The high reproducibility of dropping sodium amalgam electrodes in potentiometric measurements has been shown[5] and the convenience of dropping amalgam electrodes has been demonstrated[6–8].

The dropping zinc amalgam electrode was used in the potentiometric determination of the stepwise stability constants. These constants were used to calculate the electrode potential in the complexing solution in order to compare them with the experimental data and thus evaluate the reproducibility of the measurements.

Equipment

A Leeds & Northrup student potentiometer, calibrated with a Weston standard cell of the "unsaturated" type, and checked against a more precise Leeds & Northrup K-3 potentiometer, was used; the scale reading was reliable to 0.1 mV. Polarograms were obtained with a Sargent Model III polarograph and half-wave potentials were estimated as described previously[1].

The potentiometric cell was the same as that used in previous polarographic work[1], the intermediate compartment being filled with 2.0 *M* sodium perchlorate. The reference electrode was a sodium-chloride saturated calomel electrode with an agar plug. The junctions present in the cell were:

$|(2.0-x)M\ \mathrm{NaClO_4}\cdot x\ M\ \mathrm{NaX(a)}|2.0\ M\ \mathrm{NaClO_4(b)}|\mathrm{satd.\ NaCl(c)}|$, x varying from 0 to 2.0 *M* and X being the thiocyanate or azide ion.

Reagents and solutions

All the reagents were C.P. grade. Sodium thiocyanate solutions were standardised by VOLHARD's procedure, and sodium azide solutions by treating with an excess of standard sulfuric acid, boiling out the hydrazoic acid, and titrating the excess of the strong acid. Zinc perchlorate and sodium perchlorate solutions were standardised by means of Amberlite IR-120 exchange resin. The 0.2 *M* zinc stock solution was $2.35\cdot10^{-3}$ *M* in perchloric acid to avoid hydrolysis.

Metallic zinc (30 mesh, Fisher Certified Reagent) was treated with dilute hydrochloric acid, washed with ethanol and dried. A 0.100 *M* amalgam was prepared by heating the weighed zinc with 50.00 ml of distilled mercury under a layer of 1% acetic acid solution, in a flow of pure nitrogen, at 50° until complete dissolution was achieved. After removal of the supernatant, the amalgam was dried with filter paper and transferred to a conventional polarographic dropping electrode assembly, previously filled with nitrogen and protected with a layer of mineral oil.

Working solutions were prepared by suitable dilution of the standard solutions. The thiocyanate or azide concentrations were 0–2.00 M, the zinc concentration was $4.0 \cdot 10^{-3}$ M in all solutions, and the ionic strength was held at 2 by addition of sodium perchlorate. The acidity of all working solutions was $5.4 \cdot 10^{-4}$ M. The hydrazoic acid displaced in the azide medium was considered in the estimation of free ligand concentration.

Procedure

The cell containing about 8 ml of the working solution was kept at 25 ± 0.02°. The dropping electrode was attached to compartment "a" only after bubbling the solution for at least 5 min with pure nitrogen, and bubbling was maintained during the measurements. Under these conditions the potential readings were very steady and independent of the drop time. The potential measurements were not affected by 0.01% of gelatin in the working solutions. All measurements were done in duplicate; if the results varied by more than 0.3 mV, a third measurement was made. Only average values are tabulated.

Methods of calculation

The method described by YATSIMIRSKII AND VASIL'EV[9] was used. The LEDEN "complexity" function $F_0(\mathrm{X})$ can be calculated from the potentiometric measurements at 25° by the equation:

$$F_0(\mathrm{X}) = \text{antilog} - \frac{n\Delta E_{\mathrm{x,s}}}{0.05915} \tag{1}$$

where $\Delta E_{\mathrm{x,s}}$ is the electrode potential change after the addition of the complexing agent. For stepwise complex equilibria LEDEN's function is considered in the following form[9]:

$$F_0(\mathrm{X}) = 1 + \beta_1[\mathrm{X}] + \beta_2[\mathrm{X}]^2 + \ldots\ldots + \beta_j[\mathrm{X}]^j \tag{2}$$

where β_1 is the overall formation constant and [X] the effective equilibrium concentration of the complexing agent. Treatment of experimental $F_0(\mathrm{X})$ data by LEDEN's procedure[9,10] to obtain the constants β_1 involves the calculation of subsidiary functions $\mathrm{F}_n(\mathrm{X})$ and extrapolation to zero complexing agent concentration. The average ligand number $\bar{n}$, conceived by BJERRUM[9], is calculated for 25° from

$$\frac{\mathrm{d}E_{\mathrm{x}}}{\mathrm{dlog\,X}} = -\frac{0.05915}{n} \cdot \bar{n} \tag{3}$$

The $\bar{n}$ values are important in LEDEN's treatment of the $F_0(\mathrm{X})$ function, in weak successive complex formation, to obtain the equilibrium ligand concentration from the total ligand concentration C_{x} according to

$$[\mathrm{X}^-] = C_{\mathrm{x}} - C_{\mathrm{M}^{n+}} \cdot \bar{n} \tag{4}$$

The junction potential between compartment "b" and "c" is obviously constant and that between "a" and "b", after total replacement of the perchlorate by the complexing agent was approximately calculated by LEWIS–SARGENT's equation[11]. Variation in the junction potential should be negligible because of the close equivalent conductances of sodium perchlorate (110 ohm^{-1}cm^2)[12], sodium thiocyanate (110.5 ohm^{-1} cm^2)[12] and sodium azide (109 ohm^{-1} cm^2)[13].

Results and discussion

In preliminary experiments, the performance of the dropping amalgam electrode was evaluated and the optimum conditions established. The Nernst equation was closely obeyed in the range $2\cdot10^{-2}$–$2\cdot10^{-4}$ *M* zinc(II). Variable responses were observed for zinc concentrations less than 10^{-5} *M*, or when the acid content (hydrogen ion or hydrazoic acid) exceeded 0.01 *M*. The zinc content of the amalgam decreased slowly on storage owing to oxidation; after 50 days, a change of *ca.* 3 mV was observed in the potential measurements. However, the $\Delta E_{x,s}$ measurements, required in this study, were independent of storage time.

The satisfactory behaviour of the zinc amalgam electrode in complexing media was proved by the close agreement between polarographic and potentiometric measurements: a potential displacement of −0.122 V observed on replacing the 2.0 *M*

TABLE I

ANALYSIS OF POTENTIAL DATA OF ZINC–THIOCYANATE SYSTEM[a]

C_{SCN^-}	$-E(V)$	$\bar{n}'$	$\bar{n}$	$[SCN^-]$	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	1.0237		0.00						
		0.000							
0.0500	1.0273		0.22	0.0491	1.32	6.5			
		0.29							
0.0750	1.0288		0.36	0.0737	1.49	6.6	14.9		
		0.49							
0.100	1.0306		0.50	0.0980	1.71	7.2	17.3		
		0.56							
0.150	1.0335		0.75	0.147	2.15	7.8	15.6		
		1.03							
0.200	1.0373		0.99	0.196	2.88	9.6	20.9		
		1.15							
0.250	1.0406		1.20	0.245	3.73	11.1	22.9		
		1.41							
0.300	1.0436		1.74	0.293	4.71	12.7	24.6		
		1.70							
0.400	1.0499		1.82	0.393	7.69	17.0	29.3	38.9	48.1
		2.13							
0.500	1.0560		2.16	0.491	12.4	23.2	36.0	44.8	50.5
		2.59							
0.750	1.0695		2.76	0.739	35.5	46.7	55.8	56.6	49.5
		3.00							
1.000	1.0806		3.18	0.987	84.0	84.1	79.6	66.5	47.4
		3.35							
1.250	1.0902		3.46	1.236	177	142	110	77.7	46.7
		3.55							
1.500	1.0985		3.58	1.486	339	227	149	90.8	47.6
		3.59							
1.750	1.1056		3.67	1.735	589	335	192	103	47.8
		3.67							
2.000	1.1119		3.70	1.985	962	484	246	114	47.4

[a] $\beta_1 = 5.5$; $\beta_2 = 14$; $\beta_3 = 20$; $\beta_4 = 48$.

sodium perchlorate solution by 2.0 *M* sodium azide, corresponded to a variation of -0.118 V in $E_{\frac{1}{2}}$. This small difference may be attributed to some irreversibility in the polarographic reduction of zinc in azide medium.

Tables I and II list the values of the potentials referring to the zinc complex systems and of the auxiliary functions derived from these potential values. First, the medium ligand numbers, $\bar{n}'$, were calculated by means of eqn.(3) from the data for $\Delta E_{x,x'}$ and $\Delta \log C_x$; graphical interpolation on $\bar{n}'$ *vs.* intermediate log[X] plots gave better $\bar{n}$ values, which were then used to obtain [X] values from eqn.(4). The calculated $F_0(X)$ and $F_i(X)$ functions were treated by conventional graphical procedures[2,10], to obtain the equilibrium constants. Plots of $F_3(X)$ and $F_4(X)$ *vs.* concentration were linear for the azide and thiocyanate systems, the measurements showing only very slight deviations. The Tables also include the constants determined.

Figures 1 and 2 show the distribution curves for the various thiocyanate and azide complexes, calculated from the constants.

The reliability of these determined constants was checked by comparing the experimental E_x values with those calculated from the constants that were established for the azide and thiocyanate complexes. First, $F_0(X)$ was calculated from eqn.(2), and then the $\Delta E_{x,s}$ value from eqn.(1); addition of the E_s value (-1.0237 V) gave the

TABLE II

ANALYSIS OF POTENTIAL DATA OF ZINC–AZIDE SYSTEM[a]

$C_{N_3^-}$	$-E(V)$	$\bar{n}'$	$\bar{n}$	$[N_3^-]$	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	1.0237		0.00						
		0.00							
0.0500	1.0278		0.32	0.0482	1.38	7.80	37.2		
		0.46							
0.0750	1.0302		0.52	0.0724	1.66	9.10	42.8		
		0.76							
0.100	1.0330		0.84	0.0961	2.06	11.0	52.8		
		1.15							
0.150	1.0390		1.40	0.1439	3.29	15.9	69.0		
		1.79							
0.200	1.0456		2.00	0.1915	5.15	23.6	91.8		
		2.30							
0.250	1.0522		2.50	0.2395	9.20	34.3	118		
		2.77							
0.300	1.0587		2.90	0.2879	15.2	49.5	151	448	792
		3.08							
0.400	1.0701		3.22	0.3866	37.1	93.3	226	528	797
		3.35							
0.500	1.0797		3.44	0.4857	78.3	159	315	603	789
		3.57							
0.750	1.0983		3.65	0.7349	333	452	607	796	784
		3.68							
1.000	1.1119		3.94	0.9845	964	978	987	980	772
		3.83							
1.250	1.1229		3.98	1.234	2270	1839	1485	1186	783
		4.01							
1.500	1.1323		4.00	1.484	4710	3173	2134	1423	811
		3.74							
1.750	1.1397		4.02	1.734	8394	4840	2788	1595	793
		3.79							
2.000	1.1462		4.04	1.983	13890	7004	3529	1769	781

[a] $\beta_1 = 6.0$; $\beta_2 = 22$; $\beta_3 = 220$; $\beta_4 = 780$.

E_x value. The average deviation between the calculated and experimental values was only 0.1–0.14 mV.

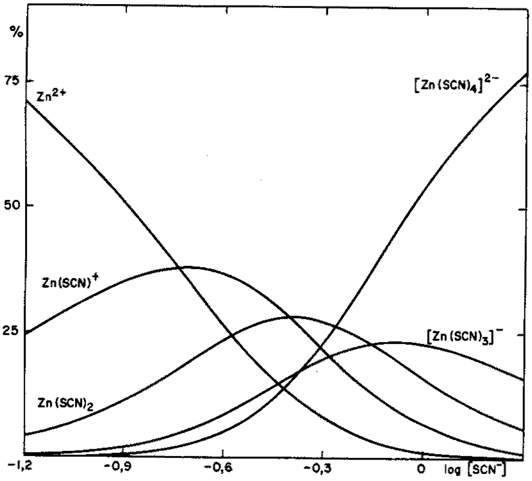

Fig. 1. Percentage of zinc in its various forms as a function of free thiocyanate ion concentration.

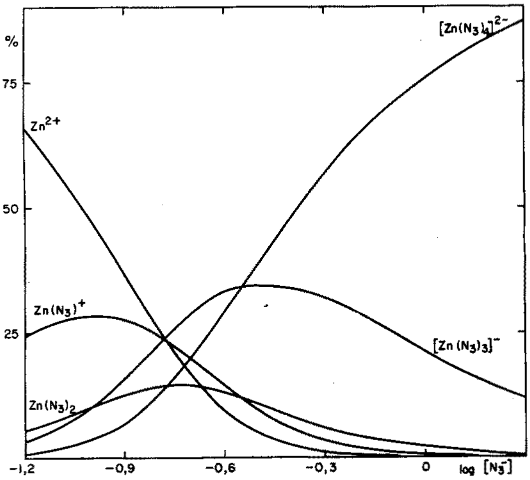

Fig. 2. Percentage of zinc in its various forms as a function of free azide ion concentration.

Polarographic data[2] on the zinc–thiocyanate reaction yielded the following values for the constants at 30° in potassium nitrate medium: $\beta_1=3$, $\beta_2=7$, $\beta_3=1$ and $\beta_4=20$. The present values at 25° in sodium perchlorate medium are: $\beta_1=5.5$, $\beta_2=14$, $\beta_3=20$ and $\beta_4=48$. Probably the main cause of the observed discrepancies is a competitive effect of nitrate ions for zinc, as observed for cadmium[1], resulting in lower $\Delta E_{\frac{1}{2}}$ values and lower constants. Furthermore, the comparison of calculated $(E_{\frac{1}{2}})_x$ values from the experimental polarographic data[2] showed a larger average deviation, *viz.* 0.8 mV, which affected the graphical extrapolation. In the cadmium–azide reaction[1] the agreement between experimental and calculated $E_{\frac{1}{2}}$ was ±0.5 mV. The smaller deviation is, however, explained by the greater shift of $E_{\frac{1}{2}}$ which increased the accuracy of the constants.

The use of a dropping amalgam electrode in the potentiometric study of complexes seems to offer several advantages over the conventional polarographic method. First, greater precision is attained; complicated and critical experimental conditions are minimized. It is not necessary to use a dropping electrode with definite characteristics, as in the measurement of diffusion currents; furthermore the potential measurements are not affected by cell resistance. The technique can be successfully applied in some cases where irreversibility is observed; for instance, the zinc–azide system could not be conveniently studied by polarographic methods, owing to some irreversibility in the reduction of the zinc complexes.

Analytical applications have been developed by taking advantage of the characteristics of the dropping amalgam electrode both in direct potentiometry for the determination of small amounts of some metal cations and as indicator electrode in potentiometric titrations. These studies will be published later.

We are indebted to Prof. Dr. P. Senise, for valuable suggestions and close cooperation; to Prof. Dr. P. Krumholz for helpful discussions; and to the "Ford Foundation", "Conselho Nacional de Pesquisas", Brazil and "Fundação de Amparo à Pesquisa do Estado de São Paulo", Brazil, for financial support.

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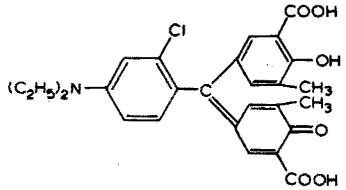
(Received August 19th, 1969)

The spectrophotometric determination of scandium with eriochrome brilliant violet B

Several organic compounds which have the hydroxydimethylfuchsone dicarboxylic acid structure have been used as spectrophotometric reagents for trace metals, *e.g.* eriochrome cyanine R (C. I. 43830)[1-3], chromazurol S (C. I. 43825)[4-6], pontachrome azure blue B (C. I. 43830)[7-9], chromal blue G (C. I. 43835)[10], and eriochrome azurol G (C. I. 43855)[11]. Spectrophotometric determinations of scandium with pontachrome azure blue B[9], chromal blue G[10], and eriochrome azurol G[11] have been described. Eriochrome brilliant violet B (2″-chloro-4″-diethylamino-4′-hydroxy-3,3′-dimethylfuchsone-5,5′-dicarboxylic acid; C. I. 43570; I) also gives a very sensitive color reaction with scandium in a slightly acidic medium similar to these reagents. In this paper, a new spectrophotometric determination of scandium with eriochrome brilliant violet B, which is similar in structure to pontachrome azure blue B, is described.



(I)

Experimental

Apparatus. Absorbances were measured with a Hitachi spectrophotometer, model 139, in 1-cm quartz cells. pH was measured with a Hitachi-Horiba (glass electrode) pH meter, model M-4.

Ion-exchange columns[12], 9 mm in diameter and 30 cm long, with glass wool and buret tap at the bottom were used. A strongly basic anion-exchange resin, Dowex 1-X 8 (100–200 mesh), was used, in a bed 21 cm high; before use, the resin was treated with the eluent, 0.1 *M* ammonium sulfate–0.025 *M* sulfuric acid solution.

Reagents. All chemicals were of reagent-grade quality.

Standard stock scandium solution (100 µg Sc cm^{-3}). Dissolve 0.153 g of scandium oxide in a small amount of hydrochloric acid and dilute to 1 dm^3 with water. Prepare working solutions by suitable dilution.

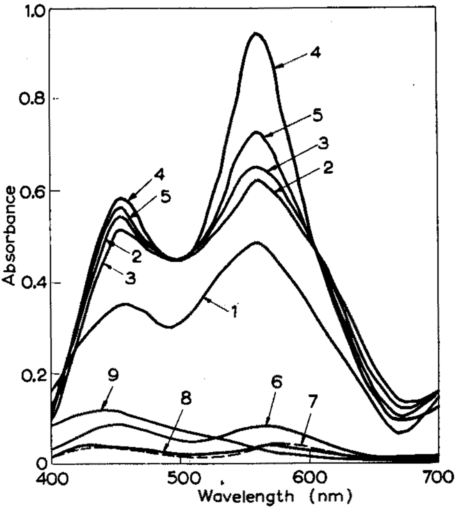
Eriochrome brilliant violet B solution. Purify the dye (Geigy Company Inc., New York, U.S.A.) by recrystallization from methanol. Use a 0.1% (w/v) solution in 95% ethanol. This is stable for at least a month.

Buffer solution (pH 6.0). Prepare by mixing 0.2 *M* acetic acid and 0.2 *M* sodium acetate solution.

Standard procedure. Transfer the sample solution containing 1–15 µg of scandium to a 25-cm^3 volumetric flask, and add 2 cm^3 of the dye solution; add 10 cm^3 of buffer pH 6.0, shake well, and dilute with water to the mark. After 20 min, measure the absorbance at 562 nm with a reagent blank solution as reference.

Results and discussion

Absorbance curves. The absorbance curves of eriochrome brilliant violet B at various pH values are shown in Fig. 1; below pH 6.5, two maxima occur, one at 465 nm and one at 570 nm. The color intensities of the solution decrease above pH 6. The absorbance curves of the scandium–eriochrome brilliant violet B complex at different pH values are shown in Fig. 2. Maxima occur at 562 nm above pH 4.5, and at 620 nm below pH 4.0; the curves obtained between pH 4.5 and 7.5 have a shoulder at about 485 nm.



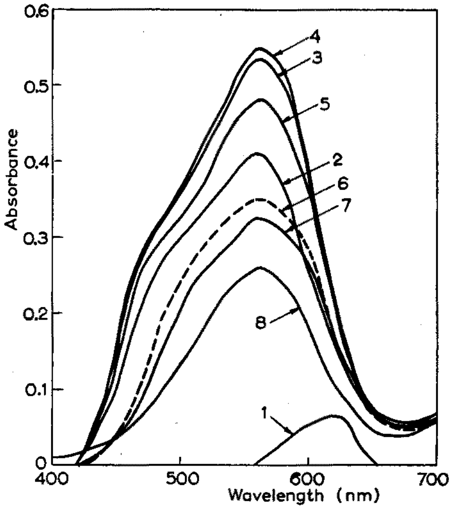


Fig. 1. Absorbance spectra of reagent at various pH values. Reagent 20 p.p.m.; pH: (1) 1.0, (2) 2.6, (3) 3.1, (4) 4.4–4.6, (5) 5.0, (6) 6.4, (7) 8.2, (8) 9.2, (9) 10.1.

Fig. 2. Absorbance spectra of scandium complex at various pH values measured against reagent blank. Sc 0.4 p.p.m.; reagent 80 p.p.m.; pH: (1) 4.0, (2) 5.0, (3) 5.5, (4) 5.8–6.0, (5) 6.5, (6) 7.0, (7) 8.0, (8) 8.5.

Effect of pH. The effect of pH on the color development of the scandium–eriochrome brilliant violet B complex was examined by measuring the absorbance at 562 nm of a solution containing 0.4 p.p.m. of scandium and 80 p.p.m. of the reagent, the pH being adjusted by adding an acetate–acetic acid buffer solution, dilute sodium hydroxide solution, or hydrochloric acid. Maximum intensity was obtained in the pH range 5.4–6.2, but for accurate measurements, the pH had to be kept constant (±0.1 pH unit). Acetate–acetic acid buffer solution, pH 6.0, was found to be satisfactory, and the volume added (5–10 cm^3) was not critical.

Rate of color development. The color of the scandium complex developed gradually at room temperature, but was fully developed within 20 min after preparation, and then remained almost constant for 2 h.

Effect of the amount of the reagent. The effect of the reagent concentration was examined for scandium concentrations of 0.2 p.p.m. and 0.4 p.p.m.; the general procedure was followed. The absorbance increased gradually as the reagent concentration increased above a certain ratio. A large excess of the reagent had therefore to be avoided, and the amount of the reagent kept constant; 2 cm^3 of a 0.1% reagent solution was found to suffice for less than 0.6 p.p.m. of scandium.

Effect of temperature. The absorbance of the complex remained constant over the range 10–30°; above 35°, the absorbance decreased.

Beer's law and sensitivity. Beer's law was obeyed up to 0.6 p.p.m. of scandium when the standard procedure was used. The optimum range for the absorbance measurement was 0.08–0.6 p.p.m. of scandium. The molar absorptivity was $6.4 \cdot 10^4$ at 562 nm. According to SANDELL's notation[13], the spectrophotometric sensitivity is $7 \cdot 10^{-4}$ μg of scandium per cm^2 at 562 nm, for $\log I_0/I = 0.001$.

Reproducibility. The precision of the method was tested by measuring 12 samples, each containing a final scandium concentration of 0.3 p.p.m. The mean absorbance was 0.428, with a standard deviation of 0.002.

Effect of diverse ions

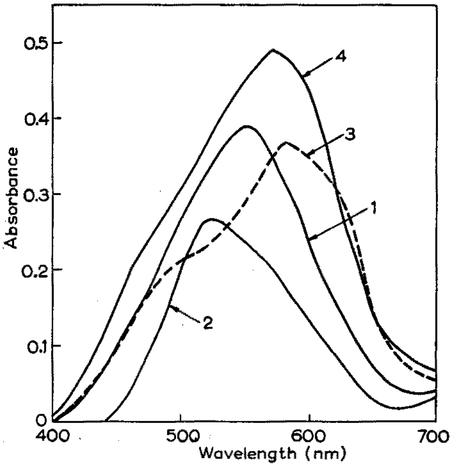
The effect of diverse ions on the determination of scandium was examined under the conditions of the standard procedure. The diverse ions were added, individually, to solutions containing 0.4 p.p.m. of scandium (in the final solution). The tolerance limit was taken as the amounts which caused absorbance errors not exceeding 3%. The results (Table I) indicate that Al, Be, Cd, Cr(III), Cu(II), Th, Fe(III), Pb, Y and the rare earth elements interfere seriously. These ions cause positive errors because they also form colored complexes with the reagent in a slightly acidic medium. Absorbance curves for the complexes of Be, Al, Fe(III), Cu(II), Y and some of the rare earth elements at pH 6.0 are shown in Figs. 3 and 4. The beryllium complex has an absorbance maximum at about 560 nm similarly to the scandium complex, but the absorbance maxima of the iron(III) and copper(II) complexes appear at slightly longer wavelengths, whereas that of the aluminum complex appears at a shorter wavelength. The absorbance spectra for the complexes of yttrium and the rare earths show two absorbance maxima (Fig. 4). Chloride, nitrate, sulfate, and acetate do not

TABLE I

TOLERANCE TO DIVERSE IONS

Ion	*Added as*	*Tolerance limit (p.p.m.)*	*Ion*	*Added as*	*Tolerance limit (p.p.m.)*
Al(III)	$Al(NO_3)_3$	0	Sr(II)	$SrCl_2$	10
B(III)	H_3BO_3	100	Th(IV)	$Th(NO_3)_4$	0.3
Ba(II)	$BaCl_2$	3	Ti(IV)	$Ti(SO_4)_2$	10
Be(II)	$BeCl_2$	0	U(VI)	$UO_2(NO_3)_2$	5
Ca(II)	$CaCl_2$	12	V(IV)	$VOCl_2$	20
Cd(II)	$CdCl_2$	1	Zn(II)	$ZnCl_2$	30
Co(II)	$CoSO_4$	8			
Cr(III)	Chromium alum	0.5	Y(III)	YCl_3	0.1
Cu(II)	$CuSO_4$	0.3	La(III)	$LaCl_3$	0.3
Fe(III)	$FeCl_3$	0	Ce(III)	$CeCl_3$	0.3
Fe(II)	$FeSO_4 \cdot (NH_4)_2SO_4$	2	Nd(III)	$NdCl_3$	0.2
Hg(II)	$HgCl_2$	3	Gd(III)	$GdCl_3$	0.3
			Dy(III)	$DyCl_3$	0.2
Mg(II)	$MgCl_2$	3	Er(III)	$ErCl_3$	0.2
Mn(II)	$MnSO_4$	3			
Mo(VI)	Na_2MoO_4	7	Acetate	$NaC_2H_3O_2$	> 4000
Ni(II)	$NiSO_4$	3	Chloride	NaCl	> 4000
Pb(II)	$Pb(NO_3)_2$	1	Nitrate	KNO_3	> 4000
Sn(IV)	$SnCl_4$	6	Sulfate	Na_2SO_4	> 4000

interfere, but oxalate, fluoride, citrate, and EDTA bleach the complex. These interfering ions must be removed or masked before the determination.



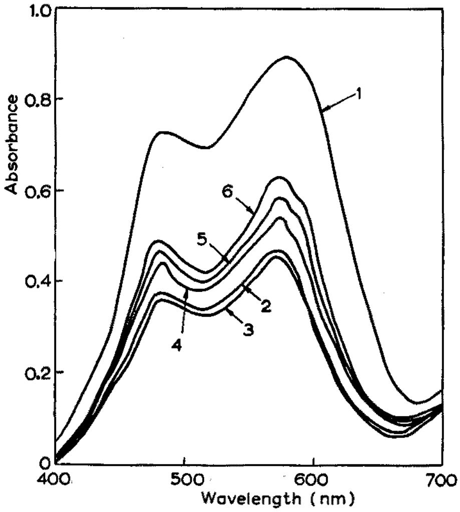


Fig. 3. Absorbance spectra of beryllium, aluminium, iron(III), and copper(II) complexes at pH 6.0, measured against a reagent blank. Reagent 80 p.p.m. (1) Be 0.06 p.p.m., (2) Al 0.1 p.p.m., (3) Fe(III) 0.2 p.p.m., (4) Cu(II) 2.0 p.p.m.

Fig. 4. Absorbance spectra of yttrium, lanthanum, neodymium, gadolinium, dysprosium, and erbium complexes at pH 6.0, measured against a reagent blank. Reagent 80 p.p.m. (1) Y 3.0 p.p.m., (2) La 3.0 p.p.m., (3) Nd 3.0 p.p.m., (4) Gd 3.0 p.p.m., (5) Dy 3.0 p.p.m., (6) Er 3.0 p.p.m.

Separation of scandium from interfering metals

Several methods were tested to eliminate the interfering ions, and the anion-exchange method[12] proved most satisfactory.

Procedure. Prepare the sample solution 0.1 M in ammonium sulfate and 0.025 M in sulfuric acid. Add 10 cm^3 of the solution to the column, and wash through with 60 cm^3 of 0.1 M ammonium sulfate–0.025 M sulfuric acid solution. This fraction contains yttrium, rare earths, Al, Be, Cu(II), Cd, Co(II) and many other ions[12]. Then elute scandium with 50 cm^3 of 1 M hydrochloric acid. Use a flow rate of 0.5–1.5 cm^3 min^{-1} throughout. Determine scandium in the final eluate.

The results obtained for scandium in the presence of other ions are shown in Table II. It can be seen that the interference of iron(III) was not completely eliminated; masking iron with tartaric acid or fluoride was not successful, but reduction of iron(III) with L-ascorbic acid was satisfactory. The addition of 3 cm^3 of 1% (w/v) L-ascorbic acid solution before the addition of the dye solution did not affect the color intensity of the required scandium complex and effectively eliminated the interference of iron(III) up to 1.2 p.p.m.; large amounts of L-ascorbic acid caused low results, hence if more than 30 μg of iron(III) is present, the 3-cm^3 addition of ascorbic acid solution must be made after the ion-exchange separation.

Comparison with other methods

Several sensitive organic reagents have been used for the spectrophotometric

TABLE II

DETERMINATION OF SCANDIUM

Solution analyzed		*Found Sc (p.p.m.)*	*Error (p.p.m.)*	*Solution analyzed*		*Found Sc (p.p.m.)*	*Error (p.p.m.)*
Ion	*Added (p.p.m.)*			*Ion*	*Added (p.p.m.)*		
(1) Al(III)	30.0			(4) Y(III)	10.0		
Be(II)	30.0			La(III)	10.0		
Sc(III)	3.0	3.08	+ 0.08	Nd(III)	10.0		
				Gd(III)	10.0		
(2) Fe(III)	3.0			Er(III)	10.0		
Sc(III)	3.0	3.86	+ 0.86	Sc(III)	3.0	2.95	− 0.05
		3.00[a]	± 0				
				(5) Al(III)	10.0		
(3) Al(III)	10.0			Y(III)	10.0		
Be(II)	10.0			Gd(III)	10.0		
Cu(II)	10.0			Th(III)	10.0		
Cd(II)	10.0			Sc(III)	3.0	3.02	+ 0.02
Fe(III)	10.0						
Sc(III)	5.0	5.98	+ 0.98				
		5.10[a]	+ 0.10				

[a] Addition of 3 ml of 1% L-ascorbic acid solution after ion exchange.

TABLE III

MOLAR ABSORPTIVITIES FOR VARIOUS SCANDIUM COMPLEXES

Method	*Molar absorptivity*	*Method*	*Molar absorptivity*
Oxine[14]	$6.9 \cdot 10^3$	α-(2,4-Dihydroxyphenylazo)-pyridine[20]	$2.21 \cdot 10^4$
Tiron[15]	$8.0 \cdot 10^3$	Xylenol orange[21]	$2.4 \cdot 10^4$
Naphthyl azoxine S[16]	$8.0 \cdot 10^3$	Chromazurol S[6]	$2.7 \cdot 10^4$
Pontacyl violet 4BSN[17]	$1.37 \cdot 10^4$	Eriochrome azurol G[11]	$2.96 \cdot 10^4$
Arsenazo[18]	$1.7 \cdot 10^4$	Chromal blue G[10]	$3.14 \cdot 10^4$
Pyrocatechol violet[19]	$1.73 \cdot 10^4$	Pontachrome azure blue B[9]	$3.15 \cdot 10^4$
Eriochrome cyanine R[3]	$1.9 \cdot 10^4$	Eriochrome brilliant violet B	$6.4 \cdot 10^4$

determination of scandium. The proposed method with eriochrome brilliant violet B has some advantages: no extraction of the scandium complex is required, since it is water-soluble; the procedure is simple and rapid; and the method is more sensitive than the other available methods. However, like other methods, the method is not selective. The sensitivities of some spectrophotometric methods are compared in Table III.

Composition of the complex

The method of continuous variation[22] was employed in order to establish the molar ratio of the scandium complex at pH 6.0. The results indicated that a 1:2 complex is formed between scandium and eriochrome brilliant violet B. These results were confirmed by the mole ratio method[23]. The apparent formation constant of the complex was determined spectrophotometrically as described previously[10]; the value found at 25° was $6.4 \cdot 10^9$.

The author wishes to express his thanks to Professor TSUNENOBU SHIGEMATSU of the Institute for Chemical Research, Kyoto University for his kind guidance, and to Dr. MASAYUKI TABUSHI and Dr. MASAKAZU MATSUI for their valuable advice.

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(Received August 4th, 1969)

ANNOUNCEMENT

8th INTERNATIONAL SYMPOSIUM ON GAS CHROMATOGRAPHY

Dublin, September 28–October 2, 1970

The 8th International Symposium on Gas Chromatography is being organised by the Gas Chromatography Discussion Group of the Institute of Petroleum in co-operation with the Institute of Chemistry of Ireland and will be held on the premises of the Royal Dublin Society from 28th September to 2nd October, 1970. There will also be held an exhibition of chromatographs and associated equipment in which many wellknown firms from Britain and overseas will be participating.

The technical programme will comprise invited papers, submitted papers and discussions on all aspects of Gas Chromatography. On at least one of the afternoons there will be informal discussion panels, and the final afternoon will be given over to a question session in which submitted questions (written) will be considered by a panel of experts. It is hoped to publish the full technical programme early in 1970.

A full social programme is being arranged for the guests not attending the technical sessions.

Attendance at the Symposium will be limited to 600 and the registration fee for delegates is expected to be £12. Fuller details of the Symposium and Exhibition may be obtained from the *Executive Secretary of the Organising Committee, Institute of Petroleum, 61 New Cavendish Street, London W1M 8AR, England.*

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

BOOK REVIEWS

J. B. PATTISON, *A Programmed Introduction to Gas-Liquid Chromatography*, Heyden and Son, Ltd., London, 1969 (in cooperation with Sadtler Research Laboratories, Philadelphia, Pa. 19104), pp. xv+303, price £2.5, $4.95.

The novel philosophy and presentation of this book, which is undoubtedly the forerunner of others of similar type, presents problems for the reviewer who must assess specific aims and attempt to ascertain if these have been achieved. The claims made are indeed comprehensive, *i.e.* that the book provides the answer to the problem of training the complete novice or the experienced analyst in the practise and necessary theory of gas chromatography.

Since the basic premise is that a programmed teaching style provides the optimal method, and a "Criterion test" and validation report are included, an individual critic who has not used the book for class work must necessarily be somewhat subjective. The programme style is straightforward, being mainly of a "branched" type, but with two sections treated by a "linear" method. The beginning level is absolutely basic, and this is perhaps consistent with the disconcerting tendency to talk down to the reader and reiterate trivia. Repetition is necessary to the concept but frequently seems laboured. The student is conducted with a minimum of mental exertion through basic chromatographic concepts and practise, and a complex subject is undoubtedly simplified. However, one is left with the feeling that the student could grasp the whole content if it were succinctly presented in 20–30 pages. The second objective, as a useful reference text, is largely lost within the general programme framework.

To return to the prospective user of this book, reluctantly one feels that it can scarcely be recommended as of anything but marginal interest to the serious student of analytical or instrumental chemistry, as large fields of technique go unmentioned. As for the training of technicians, avowedly a major aim of the book, this must clearly be judged by results, but it is doubtful if many laboratories will favour this method of approach.

PETER C. UDEN

Anal. Chim. Acta, 49 (1970) 604

L. S. BARK AND S. M. BARK, *Thermometric Titrimetry*, International Series of Monographs in Analytical Chemistry, Vol. 33, Pergamon Press, Oxford, 1969, ix+126 pp., price 45 s.

Thermometric titrations have acquired special importance recently owing to their sensitivity and relative cheapness of instrumentation, and this makes the present volume warmly welcome. After a brief introduction, the basic principles of the technique are discussed (Chapter 1), followed by a chapter on instrumentation (2). Then neutralisation (3), oxidation–reduction (4), precipitation (5) and complexation (6) titrations are critically reviewed, together with an account of titrations in non-aqueous media (7). The rest of the text is arranged into three further chapters containing rather diverse material. Chapter 8 entitled "The use of solvent as an indicator" deals mainly with catalimetric–thermometric titrations, which are remarkable for their extremely high sensitivity. Industrial applications (9) and additional data obtainable from enthalpograms (10) are then briefly discussed. Author and subject indexes conclude the book.

The presentation is clear and logical. One likes especially the original presentation of the theory, though the chapter on instrumentation is also highly commendable. One might have liked a more detailed treatment in the last three chapters, but on the whole the book is a well balanced, up-to-date monograph and can be recommended as a useful text to analytical chemists.

G. SVEHLA

Anal. Chim. Acta, 49 (1970) 604–605

GALEN W. EWING, *Instrumental Methods of Chemical Analysis*, 3rd Edn., McGraw-Hill, New York, x+627 pp., price 117 s.

Since 1960, the second paperback edition of this text has been almost the only book on instrumental analysis sufficiently comprehensive yet suitably priced for students. The new edition, therefore, has been awaited with great interest by teachers of analytical chemistry. In the last decade, instrumental analysis has progressed extensively, both in the development of new techniques and the refinement of existing ones. These advances are reflected in the well-balanced selection of additions to, and deletions from, the old edition. Chromatographic techniques (especially GLC), mass spectrometry, atomic absorption spectrophotometry, and thermal methods of analysis, all receive detailed attention, and new branches of spectroscopy (far infrared, laser Raman, atomic fluorescence, attenuated total reflectance, phosphorimetry, circular dichroism, electron spin resonance, etc.), as well as ion-selective electrodes, a.c., pulse and square-wave polarography and stripping analysis are briefly introduced.

Much of the remainder of the text of the second edition has been extensively revised, with separate chapters for fluorimetry and flame spectroscopy. Developments in electronics are also included, and the section on transistorized devices has been expanded. Finally, almost half the practical exercises have been revised or replaced. In contrast, the sections of emission spectrography and ion-exchange have been attenuated, and refractometry has been eliminated.

Naturally, the selection of topics is a personal matter, but the reviewer was a little disappointed by the brief treatment accorded to neutron activation, X-ray emission spectrography and organic polarography. The curious referencing of figures and tables also deserves comment, and would be difficult to follow for readers unfamiliar with the second edition. Finally, the sensitivity comparisons for the use of various instrumental methods for a number of metals have been abandoned in favour of a far less meaningful comparison of number of elements detected *versus* absolute detection limits for the various methods.

However, these are minor criticisms of a worthwhile successor to earlier editions. If the new book is also to appear as a paperback, it will be of excellent value to students, their teachers, and all others interested in an introduction to instrumental analysis.

A. TOWNSHEND

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PRINTED IN THE NETHERLANDS