

# ANALYTICA CHIMICA ACTA

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

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

DR. A. M. G. MACDONALD, Department of Chemistry, The University, P.O. Box 363, Birmingham 15 (Great Britain)

*Manuscripts*

Authors should submit two copies in double-spaced type with adequate margins on pages of uniform size. Acknowledgements, summary and references should be placed at the end of the paper.

Tables should be typed on separate pages and numbered in Roman numerals in the order in which they are mentioned in the text. All Tables should have descriptive titles. The use of chemical formulae and conventional abbreviations is encouraged in Tables and Figures but chemical formulae should not be used in the text unless they are necessary for clarity. Units of weight, volume, etc., when used with numerals should be abbreviated and unpunctuated (e.g., 2%, 2 ml, 2 g, 2  $\mu$ l, 2  $\mu$ g, 2 ng, 2 cm, 200 m $\mu$ ).

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1. J. J. LINGANE AND A. M. HARTLEY, *Anal. Chim. Acta*, 11 (1954) 475.

2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516. For multi-author references, **all** authors must be named, and initials given, in the reference list, although the use of, for example, SMITH *et al.*, is desirable in the text.

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## Some Forthcoming Papers in CCR

- K. W. Bagnall (Harwell), Coordination Chemistry of Actinide Halides
- L. Belford and R. G. Denning (Urbana, Ill.), Magneto-Circular Dichroism
- D. C. Bradley (London), Metal Oxide Alkoxide Polymers
- G. R. Choppin (Tallahassee, Fla.), Lanthanide Chemistry
- N. F. Curtis (Wellington, New Zealand), Tetradentate Heterocyclic Metal Complexes
- A. J. Edwards (Birmingham), Second and Third Row Transition Metal Halides
- J. E. Fergusson (Christchurch, New Zealand), Rhenium Chemistry
- W. P. Griffith (London), Metal Oxygen Bonding
- R. E. Hester (York), Raman Studies in Coordination Chemistry
- R. J. Irving (London), Thermochemistry of Coordination Complexes
- B. R. James (Vancouver, B.C.), Rhodium Chemistry
- L. H. Jones (Los Alamos, N. Mex.), The Significance of Force Constants of a General Quadratic valence force field. Applications to  $\text{Au}(\text{CN})_2^-$ ,  $\text{PtCl}_4^{2-}$ ,  $\text{AuCl}_4^-$ ,  $\text{AuBr}_4^-$  and  $\text{Au}(\text{CN})_2\text{Cl}_2^-$
- G. B. Kauffman (Fresno, Calif.), Separation of Isomers
- S. Kirschner (Detroit, Mich.), Optical Rotatory Dispersion and Circular Dichroism
- J. A. McCleverty (Sheffield), Transition Metal Dithiolate Chemistry
- P. C. H. Mitchell (Reading), Coordination Compounds of Molybdenum
- D. Nicholls (Liverpool), Coordination Chemistry of Vanadium
- R. V. Parish (Manchester), Eight-Coordinate Complexes
- J. Selbin (Baton Rouge, La.), Vanadyl Complexes
- L. M. Venanzi (Oxford), Group V Ligand Complexes
- J. Wood (Southampton), Recent X-Ray Studies
- S. Yamada (Osaka), Schiff Base Complexes

# SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 37, No. 1, January 1967

## THEORY OF TITRATION CURVES

### PART VI. THE SLOPES AND INFLECTION POINTS OF POTENTIOMETRIC CHELOMETRIC TITRATION CURVES

Exact general descriptions are given of the slopes, the relative precisions, and the locations of the inflection points obtained in potentiometric titrations of a metal ion  $M$  with a chelon  $Y$  to give the soluble 1:1 chelonate  $MY$ , using an ideally cation-responsive indicator electrode. The relative precision depends on the conditional formation constant  $k$  of the chelonate, the initial concentration  $C_M^0$  of the metal ion, and the dilution parameter  $r$ , which is the ratio of the concentration of the chelon solution to  $C_M^0$ . Criteria for the existence and number of inflection points are given. When there is a point of maximum slope, it always precedes the equivalence point. If  $r$  exceeds a certain value, which depends on the value of  $kC_M^0$ , a point of minimum slope also appears; if  $kC_M^0$  is large this appears at the very start of the titration curve when  $r = 1$  and approaches a point two-thirds of the way to the equivalence point as  $r$  increases. The exact locations of the inflection points are given under various conditions, and equations are also given that permit them to be closely approximated in titrations for which  $kC_M^0$  is large.

L. MEITES AND T. MEITES,  
*Anal. Chim. Acta*, 37 (1967) 1-11

### DETERMINATION OF VANADIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Methods for the determination of vanadium, in the range 0.5-100 mg/l, by atomic absorption spectroscopy in an oxy-acetylene as well as in a nitrous oxide-acetylene flame are presented. For use with oxy-acetylene flames, vanadium is extracted as vanadium cupferrate into a mixture of methyl isobutyl ketone and oleic acid (78:22, v/v) and the organic phase is aspirated to the flame. The sensitivity is 0.7 mg/l of vanadium in the organic phase. For nitrous oxide-acetylene flames, an aqueous solution of vanadium is aspirated directly. The sensitivity is further improved by the use of methyl isobutyl ketone, addition of  $Al^{3+}$  and diethylene glycol diethyl ether. Many potential interferences were examined and methods to overcome those found are given.

S. L. SACHDEV, J. W. ROBINSON AND P. W. WEST,  
*Anal. Chim. Acta*, 37 (1967) 12-19

### DETERMINATION OF COPPER, CADMIUM AND ZINC BY ATOMIC ABSORPTION SPECTROSCOPY

A procedure for the direct determination of zinc, cadmium and copper in air and water has been developed. The possible interference effects of numerous anions and cations have been investigated. Few interferences were found, and these were eliminated by the addition of EDTA. The sensitivities found were 2 p.p.b. for cadmium, 8 p.p.b. for copper and 2 p.p.b. for zinc.

T. V. RAMAKRISHNA, J. W. ROBINSON AND P. W. WEST,  
*Anal. Chim. Acta*, 37 (1967) 20-26

#### THE DETERMINATION OF SILVER IN SULPHIDE MINERALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Silver can be determined in sulphide minerals by atomic absorption spectrophotometry after decomposition with nitric and/or sulphuric acid with addition of tartaric acid to prevent precipitation of antimonious acid. The amount of silver retained in the residue is negligible if the acids used are completely chloride-free or if mercury(II) nitrate is added.

I. RUBEŠKA, Z. ŠULCEK AND B. MOLDAN,  
*Anal. Chim. Acta*, 37 (1967) 27-32

#### THE DETERMINATION OF COPPER IN ZINC MATERIALS BY NEUTRON ACTIVATION ANALYSIS USING THE $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$ REACTION

The nondestructive and destructive determinations of copper in zinc materials by neutron activation using  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  reaction are described. Observed cross-sections of  $^{64}\text{Zn}(n,p)^{64}\text{Cu}$  and  $^{66}\text{Zn}(n,p)^{66}\text{Cu}$  reactions for fission spectrum neutrons were 28 and 0.51 mb respectively. A double irradiation technique with one sample wrapped in cadmium foil and another bare, was employed for the correction of the concurrent formation of  $^{66}\text{Cu}$  by (n,p) reaction. 100 p.p.m. of copper in zinc sulfide was determined nondestructively by  $\gamma$ -ray spectrometry using a thermal flux of  $5 \cdot 10^{11}$  n/cm<sup>2</sup>/sec, while 0.5 p.p.m. of copper in zinc was determined by a thermal flux of  $2.5 \cdot 10^{10}$  n/cm<sup>2</sup>/sec, and by a rapid chemical separation involving copper(I) thiocyanate precipitation. The proposed activation procedures were compared with the spectrophotometric dibenzylthiocarbamate procedure.

K. TOMURA AND H. HIGUCHI,  
*Anal. Chim. Acta*, 37 (1967) 33-41

#### RAPID DETERMINATION OF MAGNESIUM IN THE PRESENCE OF CALCIUM AND PHOSPHATE BY TITRATION WITH CDTA

A method is presented for the accurate determination of magnesium in phosphate rock and phosphoric acid down to 0.03% magnesium oxide in the presence of 0-70% phosphorus pentoxide by titration with cyclohexanediaminetetraacetic acid (CDTA). Interference from heavy metals for which inaccurate empirical corrections have previously been made in the combined magnesium and calcium titration are linearly and unequivocally determined and subtracted from the combined titration. Magnesium oxide is determined in less than 20 min after sample digestion for Ca:Mg ratios from 1:9 to 850:1.

D. E. JORDAN AND D. E. MONN,  
*Anal. Chim. Acta*, 37 (1967) 42-48

## "PALLADIAZO" A NEW SELECTIVE METALLOCHROMIC REAGENT FOR PALLADIUM

### PART I. THE MAIN CHARACTERISTICS OF THE PURE REAGENT AND ITS REACTION WITH PALLADIUM(II)

The synthesis and purification of 2,7-bis(4-azophenylarsono)-1,8-dihydroxynaphthalene 3,6-disulphonic acid is reported. Because of its selectivity for palladium(II), the name palladiazole is suggested for the reagent. Aqueous solutions of palladiazole are very stable and exhibit 2 absorption maxima located at 540 and 625 nm, the molar absorptivities being  $3.3 \cdot 10^4$  and  $1.7 \cdot 10^4$ , respectively. Palladiazole changes color stepwise and reversibly with increase in hydrochloric acid concentration from 0 to 13 M. A negatively charged complex of type  $M_2L_3$  is formed with Pd(II) at pH 2.5-3.5, and shows an absorption maximum at 640 nm with a molar absorptivity of  $5.7(\pm 0.1) \cdot 10^4$ ; the complex can be readily extracted with diphenylguanidine chloride or quaternary ammonium salts dissolved in *n*-butanol or higher alcohols. The complex obeys Beer's law at 675 nm in the concentration range 10-250  $\mu\text{g}$  Pd(II)/50 ml. Pb(II), Bi(III), Ce(III) and the rare-earth elements are the only expected cationic interferences.

J. A. PÉREZ-BUSTAMANTE AND F. BURRIEL-MARTÍ,  
*Anal. Chim. Acta*, 37 (1967) 49-61

## ANALYTICAL APPLICATION OF ARSENAZO III TO THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

### PART I. PRELIMINARY INVESTIGATION OF THE COMPLEX FORMATION IN THE ARSENAZO III-Pd(II)-H<sub>2</sub>O SYSTEM

The reaction of arsenazo III with palladium(II) was investigated. Complex species of types  $M_2L$  and  $ML$  are formed at pH 2-4; the complex  $M_2L$  shows a very sharp maximum at 630 nm while the  $ML$  species shows maximum absorption at 620 nm. The molar absorptivities of the complexes are  $4.2(\pm 0.1) \cdot 10^4$  and  $1.6(\pm 0.2) \cdot 10^4$ , respectively. The complex  $ML$  conforms to Beer's law at 620 nm in the range 10-250  $\mu\text{g}$  Pd(II)/50 ml. The sensitivity of the reaction of Pd(II) with arsenazo III is about the same as that of a new reagent, palladiazole, but the latter is more selective for Pd(II). Serious interferences might be caused by  $\text{UO}_2^{2+}$ ,  $\text{U}^{4+}$ ,  $\text{Th}^{4+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Y}^{3+}$  and the rare-earth elements.

J. A. PÉREZ-BUSTAMANTE AND F. BURRIEL-MARTÍ,  
*Anal. Chim. Acta*, 37 (1967) 62-74

## DETERMINATION OF TRACE QUANTITIES OF SCANDIUM IN SILICATE ROCKS BY A COMBINED ION EXCHANGE - SPECTROPHOTOMETRIC METHOD

A spectrophotometric determination of scandium in silicate rocks has been developed with arsenazo as the color reagent. After the decomposition of samples with a hydrofluoric-perchloric acid mixture, traces of scandium are separated from interferences by cation- and anion-exchange in acid sulfate media and anion exchange in hydrochloric acid solution. The successive 3 steps, with an intermediate concentration step, yield scandium in a sufficiently pure state for spectrophotometric determination.

T. SHIMIZU,  
*Anal. Chim. Acta*, 37 (1967) 75-80

## THE EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM WITH TETRAPHENYLARSONIUM CHLORIDE

A rapid and accurate spectrophotometric method for niobium is described. Tetraphenylarsonium chloride is used to form an aqueous insoluble ion-pair, tetraphenylarsonium thiocyanato-niobate, which upon extraction into 9:2 chloroform-acetone solution has a molar absorptivity of 36,000/M/cm at 390 nm. Niobium is masked with fluoride before a separation step in which the interferences of molybdenum, tungsten, and iron are removed by reduction and extraction. Niobium is subsequently extracted after being demasked with boric acid. The method has been applied successfully to 3 NBS steels and 2 heat-resisting alloys.

H. E. AFFSPRUNG AND J. L. ROBINSON,  
*Anal. Chim. Acta*, 37 (1967) 81-90

## SPECTROPHOTOMETRIC DETERMINATION OF COBALT AND NICKEL WITH PYRIDINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE

Pyridine-2-aldehyde-2-quinolyldrazone (PAQH) is a selective and sensitive reagent for cobalt or nickel. The reagent reacts with only a few metals to give coloured complexes; with the exception of palladium, the cobalt chelate is the only complex relatively stable towards protons and PAQH is a very selective reagent for cobalt. In the presence of thioglycolic acid only nickel reacts with PAQH; the chelate is extracted with chloroform and its absorbance measured at 492 nm. The high molecular extinction coefficients ( $30 \cdot 10^3$  and  $51 \cdot 10^3$ ) permit the determination of 0.2-2 p.p.m. of cobalt and 0.1-1 p.p.m. of nickel.

S. P. SINGHAL AND D. E. RYAN,  
*Anal. Chim. Acta*, 37 (1967) 91-96

## SPECTROPHOTOMETRIC DETERMINATION OF TIN IN STEEL

A new spectrophotometric method for the determination of traces of tin in steel is presented. The tin is isolated by an acid sulfide separation and a double carbamate-chloroform extraction and then determined by a phenylfluorone method in which the selectivity is increased by the use of peroxide and oxalate as masking agents and the sensitivity is increased by extracting the colored tin compound into a small volume of MIBK for the spectrophotometric analysis.

C. L. LUKE,  
*Anal. Chim. Acta*, 37 (1967) 97-101

## SEPARATION OF AMINES BY LIGAND EXCHANGE

### PART IV. LIGAND EXCHANGE WITH CHELATING RESINS AND CELLULOSIC EXCHANGERS

Chelating, sulfonic and cellulosic exchangers were compared in ligand exchange chromatography. Chelating resins retain metal ions the best, but have a low ligand binding capacity. Cellulosic exchangers show excessive metal leakage. Sulfonated polystyrene resins loaded with nickel ions give best results in most cases. Data are presented on ligand exchange chromatography of simple aliphatic amines, hydrazine and substituted hydrazines, purine and pyrimidine bases.

K. SHIMOMURA, L. DICKSON AND H. F. WALTON,  
*Anal. Chim. Acta*, 37 (1967) 102-111

## ADSORPTION CHARACTERISTICS OF TRACES OF SILVER ON SELECTED SURFACES

A study of materials used for the storage of dilute aqueous solutions of silver established the adsorption characteristics of Teflon, Vycor, polypropylene, polystyrene and coatings of paraffin, acrylic spray, and Tygon paint. None of these materials or coatings was found satisfactory for prolonged storage of water samples containing trace quantities of silver. As in an earlier study, it was necessary to complex the silver in the sample with sufficient sodium thiosulfate to insure less than 1% adsorption to containers over a 30-day contact period.

F. K. WEST, P. W. WEST AND F. A. IDDINGS,  
*Anal. Chim. Acta*, 37 (1967) 112-121

## A SEMI-QUANTITATIVE METHOD FOR THE DETERMINATION OF MICROGRAM AMOUNTS OF MANGANESE ON MILLIPORE FILTERS

A method is described in which the intensity of coloration of brown manganese dioxide on white Millipore filters is taken as the measure of the manganese content. A solution of manganese(II) is made strongly basic, whereupon manganese dioxide precipitates via its auto-oxidation. Optimum conditions for the precipitation are studied. Less than 0.5  $\mu\text{g}$  of manganese can be determined.

F. J. FELDMAN AND R. E. BOSSHART,  
*Anal. Chim. Acta*, 37 (1967) 122-126

## ELECTRODE REACTIONS OF TUNGSTATE IONS IN THE PRESENCE OF CARBON MONOXIDE

Tungstate ions may be reversibly reduced at platinum, rhodium and mercury electrodes in phosphoric acid according to the reaction  $\text{WO}_4^{2-} + e^- \rightleftharpoons \text{WO}_4^{3-}$ . The specific rate constants ( $k_s$ ) on Pt, Rh and Hg are  $1.2 \cdot 10^{-2}$ ,  $7.0 \cdot 10^{-3}$ , and  $6.5 \cdot 10^{-4}$  cm/sec, respectively. In the presence of carbon monoxide, hydrogen evolution at Pt and Rh is blocked while the electron transfer for tungstate reduction is unhindered. This is used as a criterion for a surface dissociation or recombination step in an electrochemical reaction. Two methods may be used with platinum or rhodium electrodes for the determination of tungstate, either rotating the electrode at a constant speed and measuring the diffusion current, or measuring the reduction peak height at a constant potential scan rate.

P. STONEHART,  
*Anal. Chim. Acta*, 37 (1967) 127-134

## SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM USING o-DIHYDROXYCOUMARINS (Short Communication)

B. D. JAIN AND H. B. SINGH,  
*Anal. Chim. Acta*, 37 (1967) 135-138

# SUBMICRO METHODS OF ORGANIC ANALYSIS

by R. BELCHER

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

6 × 9", ix + 173 pages, 12 tables, 35 illus., 186 lit. refs., 1966, Dfl.27.50, 55s., \$10.00

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

# TECHNIQUES OF OSCILLOGRAPHIC POLAROGRAPHY

Second Edition, completely revised and enlarged

by R. KALVODA

Institute of Polarography, Czechoslovak Academy of  
Sciences, Prague, Czechoslovakia

with a preface by Professor J. Heyrovský

6 × 9", 213 pages, 3 tables, 90 illus., 263 lit. refs., 1965, Dfl. 30.00, 60s., \$12.50

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

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

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

9½ × 6½", xix + 392 pages, 1965, Dfl. 50.00, £5.10.0, \$18.00

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

# STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

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

by K. MACEK AND I.M.HAIS

7 × 10", 358 pages, 69 tables, 135 illus., 494 lit. refs., 3 coloured plates, 1965, Dfl. 47.50, £5.0.0, \$17.00

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



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# SPOT TESTS IN ORGANIC ANALYSIS

*Seventh English Edition, completely revised and enlarged*

by FRITZ FEIGL in collaboration with VINZENZ ANGER

6 x 9", xxiii + 772 pages, 18 tables, over 2000 lit.refs., 1966, Dfl. 85.00, £8.10.0, \$30.00

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

Comparison with the 6th edition reveals the following differences:

	Number in	
	6th Edn.	7th Edn.
Preliminary tests	32	45
Functional group tests	70	109
Individual compound tests	133	148
Detection of particular structures and types of compounds	0	74
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Applications in the testing of materials etc.	111	131

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## THEORY OF TITRATION CURVES

## PART VI. THE SLOPES AND INFLECTION POINTS OF POTENTIOMETRIC CHELOMETRIC TITRATION CURVES

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(Received June 23rd, 1966)

Earlier papers<sup>1-3</sup> in this series have described the slopes and the locations of the inflection points on the potentiometric titration curves obtained for single-step ion-combination titrations, including titrations of strong acids with strong bases and both isovalent and heterovalent precipitation titrations, as well as for titrations of weak acids with strong bases.

The form of the titration curve for an ion-combination titration depends on the initial concentration of the substance titrated, the magnitude of  $K_t$  for the titration reaction, and the extent to which the titration mixture is diluted as reagent is added. If both the initial concentration and  $K_t$  are large, and if the extent of dilution is sufficiently small, the curve shows only a single inflection point, which is a point of maximum slope. If no dilution occurred at all, this inflection point would coincide with the equivalence point, but the condition is one that is almost, if not completely, impossible to satisfy\*. Because dilution does occur on titration with a reagent solution, the point of maximum slope always precedes the equivalence point if the titration reaction is isovalent; only if it is heterovalent can this inflection point coincide with or follow the equivalence point.

The discrepancy between the point of maximum slope and the equivalence point in an isovalent ion-combination titration increases as the initial concentration decreases, as  $K_t$  decreases, and as the extent of dilution increases. As the concentration of the titrant decreases, the extent of dilution increases, and this gives rise to a second inflection point, which is a point of minimum slope. If the concentration of the reagent is large and just equal to that of the solution being titrated, this inflection point occurs at the very start of the titration; as the reagent becomes more dilute, the point of minimum slope moves toward the point halfway between the start of the titration and the equivalence point. At the same time, the point of maximum slope moves toward the start of the titration curve. The two inflection points eventually coalesce and vanish.

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\* It is generally accepted that there is no volume change in a coulometric titration with an internally generated reagent. However, this is true only to a first approximation; it is most unlikely that the partial molar volumes of the reactants and products would be so related as to make it exactly true. It is not at all impossible for the volume to decrease slightly as such a titration progresses, and this would correspond to a negative value of  $v$  in the equations that follow.

This paper describes the slopes and the location of the inflection points of the titration curves obtained in the potentiometric titration of a metal ion with a chelon, such as ethylenediaminetetraacetate, to form a soluble chelonate in a titration medium of invariant composition. The titration curve is considered to be a plot of  $\text{pcM}$  ( $= -\log_{10}[\text{M}]$ , where  $[\text{M}]$  is the concentration of free metal ion) *versus* the volume of reagent or some equivalent parameter. The indicator electrode might be an electrode of the first kind or a reversible cation-responsive glass or membrane electrode, but the following discussion will not be applicable to  $\text{pM}$  electrodes<sup>4</sup> because the potentials of these electrodes depend on the concentration of the metal chelonate as well as on that of the free metal ion. It is assumed that the activity coefficients and liquid-junction potential remain constant throughout the titration, and that the conditional formation constant of the metal chelonate is fixed. To justify these assumptions, the composition (*i.e.*, the  $\text{pH}$ , ionic strength, buffer concentration, etc.) of the medium must not only be constant but must be such that the free metal ion exists only in mononuclear forms.

The properties of these titration curves are qualitatively very similar to those for isovalent ion-combination titrations. Perhaps the most striking difference is that the point of maximum slope on the chelometric titration curve can never coincide with the equivalence point even in the absence of dilution.

#### THE EQUATION FOR THE TITRATION CURVE

We consider the titration of a metal ion  $\text{M}$  with a chelon  $\text{Y}$  to form the  $1-1$  chelonate  $\text{MY}$ , for which the conditional formation constant is  $k$ :



Charges are omitted for the sake of simplicity. The titration parameter  $f$  is defined by

$$f = V_{\text{Y}}C_{\text{Y}}/V_{\text{M}}^0C_{\text{M}}^0 \quad (2)$$

where  $V_{\text{M}}^0$  is the volume (ml) and  $C_{\text{M}}^0$  the concentration ( $F$ ) of the solution titrated, and  $V_{\text{Y}}$  and  $C_{\text{Y}}$  are the volume and concentration of the reagent solution in the same units. The dilution parameter  $r$  is defined by

$$r = C_{\text{M}}^0/C_{\text{Y}} \quad (3)$$

Assuming that volumes are additive, conservation equations may be written for both  $\text{M}$  and  $\text{Y}$ :

$$[\text{M}] + [\text{MY}] = V_{\text{M}}^0C_{\text{M}}^0/(V_{\text{M}}^0 + V_{\text{Y}}) = C_{\text{M}}^0/(1 + rf) \quad (4)$$

and

$$[\text{MY}] + [\text{Y}] = V_{\text{Y}}C_{\text{Y}}/(V_{\text{M}}^0 + V_{\text{Y}}) = fC_{\text{M}}^0/(1 + rf) \quad (5)$$

The fundamental equation for the titration curve is obtained by combining eqns. (1), (4) and (5):

$$k[\text{M}]^2 - \left( \frac{1-f}{1+rf} kC_{\text{M}}^0 - 1 \right) [\text{M}] - \frac{C_{\text{M}}^0}{1+rf} = 0 \quad (6)$$

It is instructive to compare this with the corresponding equation for the titration of a strong acid with a strong base:

$$k'[\text{H}^+]^2 - \left(\frac{1-f}{1+rf}\right) k' C_a^0 [\text{H}^+] - 1 = 0 \quad (7)$$

where  $k'$  is the formation constant of water and is equal to  $1/K_w$ , while  $C_a^0$  is the initial concentration of the acid. These equations have different forms even in the absence of dilution (which corresponds to  $r = 0$ ), for the concentration of the chelate increases as the titration proceeds whereas that of water remains constant. On taking dilution into account, as should always be done in describing titrimetric equilibria, the difference becomes even more marked because dilution decreases the concentration of the chelate but does not affect that of water.

On solving eqn. (6) for  $[\text{M}]$ , transforming the result into an expression for  $\text{pcM}$ , and differentiating with respect to  $f$ , one obtains an explicit equation for the slope of the titration curve. It is convenient to write this in terms of the subsidiary variable  $\phi$  defined by the equation

$$\phi = \frac{1-f}{1+rf} k C_M^0 - 1 \quad (8)$$

and the result is

$$\frac{d(\text{pcM})}{df} = \frac{0.434 k C_M^0 (1+r)}{(1+rf)^2 \sqrt{\phi^2 + \frac{4k C_M^0}{1+rf}}} + \frac{0.868 r k C_M^0}{(1+rf)^2 \sqrt{\phi^2 + \frac{4k C_M^0}{1+rf}} \left( \phi + \sqrt{\phi^2 + \frac{4k C_M^0}{1+rf}} \right)} \quad (9)$$

For the strong acid-strong base titration the analogous expression is

$$\frac{d(\text{pcH})}{df} = \frac{0.434 k' C_a^0 (1+r)}{(1+rf)^2 \sqrt{\phi'^2 + 4k'}} \quad (10)$$

where

$$\phi' = \frac{1-f}{1+rf} k' C_a^0 \quad (11)$$

THE SLOPE OF THE TITRATION CURVE AT THE EQUIVALENCE POINT. THE RELATIVE PRECISION OF THE TITRATION

At the equivalence point, where  $f = 1$  and  $\phi = -1$ , eqn. (9) becomes, if  $r = 0$ ,

$$\left( \frac{d(\text{pcM})}{df} \right)_{r=0, f=1} = \frac{0.434 k C_M^0}{\sqrt{1+4 k C_M^0}} \quad (12)$$

For the titration to be practical  $k C_M^0$  must be large, and when it is, one may write

$$\left( \frac{d(\text{pcM})}{df} \right)_{r=0, f=1} = \frac{0.434 k^{\frac{1}{2}} (C_M^0)^{\frac{1}{2}}}{2} \quad (13)$$

Under similar conditions eqn. (10) becomes, since  $\phi' = 0$  when  $f = 1$ ,

$$\left( \frac{d(\text{pcH})}{df} \right)_{r=0, f=1} = \frac{0.434 k'^{\frac{1}{2}} C_a^0}{2} \quad (14)$$

Comparison of eqns. (13) and (14) shows that the slope at the equivalence point decreases in each case as the concentration of the solution being titrated decreases,

but that it does so much less rapidly in the chelometric titration.

Consequently the relative precisions of ion-combination and chelometric titrations are very differently affected by changes in the concentration of the solution titrated. BENEDETTI-PICHLER<sup>5</sup> defined the relative precision of an acid-base titration as the fraction of the stoichiometric quantity of reagent consumed in traversing the region bounded by two pH values, one 0.1 pH unit below and the other 0.1 pH unit above the pH at the equivalence point. In the present notation this corresponds to the value of  $\Delta f$  described by the equation

$$\Delta f = \Delta(\text{pcH}) / \left( \frac{d(\text{pcH})}{df} \right)_{f=1} = 0.2 / \left( \frac{d(\text{pcH})}{df} \right)_{f=1} \quad (15)$$

Combining this with eqn. (14), taking  $k' = 10^{14}$  in the latter, shows that, if  $r = 0$ , a relative precision of 0.001 is just attainable in a strong acid-strong base titration when  $C_a^0 = 9.21 \cdot 10^{-5} F$ . In a chelometric titration for which  $r = 0$  and  $k = 10^{14}$ , on the other hand, the same relative precision would correspond to  $C_M^0 = 8.48 \cdot 10^{-9} F$  if  $\Delta(\text{pcM})$  were 0.2. Similarly, in a chelometric titration for which  $\Delta(\text{pcM}) = 0.2$ ,  $r = 0$ , and  $C_M^0 = 0.01 F$ , a relative precision of 0.001 should be attainable even if  $k$  is as small as  $8.48 \cdot 10^7$ .

The first term on the right-hand side of eqn. (9) reflects the variation of pcM that results from the consumption of M by the titration reaction  $M + Y = MY$  and from dilution of the untitrated M. Whenever  $r$  is finite, however, the addition of an aliquot of reagent also leads to a decrease of the concentration of the chelone already formed. This has the effect of increasing the rate of variation of pcM, and is described by the second term on the right-hand side of eqn. (9).

If  $r$  is finite but very much smaller than  $4kC_M^0$ , the first term on the right-hand side of eqn. (9) becomes practically equal to  $0.217 \sqrt{kC_M^0/(1+r)}$  while the second becomes practically equal to  $0.217r/(1+r)$ . If, for example,  $kC_M^0 = 10^{14}$  and  $r = 1$ , the numerical values of these two terms are  $1.54 \cdot 10^6$  and 0.108, respectively. Thus it is justifiable to neglect the second term on the right-hand side of eqn. (9) in any practicable titration even when a finite value is assigned to  $r$ .

When this is done, the relative precision of a chelometric titration in which  $\Delta(\text{pcM}) = 0.2$  may be described by the equation

$$\Delta f = 0.921 \left( \frac{1+r}{kC_M^0} \right)^{\frac{1}{2}} \quad (16)$$

whereas that of a strong acid-strong base titration in which  $\Delta(\text{pcH}) = 0.2$  may be written

$$\Delta f = 0.921 \left( \frac{1+r}{k'C_a^0} \right)^{\frac{1}{2}} \left( \frac{1+r}{C_a^0} \right)^{\frac{1}{2}} \quad (17)$$

Thus the minimum value of  $C_M^0$  at which any given relative precision can be obtained in a chelometric titration is directly proportional to  $(1+r)$  and inversely proportional to  $k$ .

#### THE EQUATION FOR THE INFLECTION POINT

An expression for  $d^2(\text{pcM})/df^2$  can of course be obtained by straightforward



differentiation of eqn. (9), but its form renders it ill-suited for inquiry into the existence and location of an inflection point. A far more tractable result is obtained by solving eqn. (6) for  $f$ :

$$f = \frac{(kC_M^0 - 1 - k[M])[M] + C_M^0}{(kC_M^0 + r + rk[M])[M]} \quad (18)$$

Two differentiations, of which the second employs the relation

$$\frac{d^2f}{d(\text{pcM})^2} = \frac{d\left(\frac{df}{d(\text{pcM})}\right)}{d[M]} \frac{d[M]}{d(\text{pcM})} \quad (19)$$

proceed uneventfully to yield

$$\begin{aligned} \frac{d^2f}{d(\text{pcM})^2} &= \frac{2(2.303)^2 rk^2 C_M^0 [M] (k[M] + r + rk[M])}{(kC_M^0 + r + rk[M])^3} \\ &+ \frac{(2.303)^2 C_M^0 \{ (kC_M^0 + r + 2rk[M]) - k^2 [M]^2 (1+r) \}}{[M] (kC_M^0 + r + rk[M])^2} \end{aligned} \quad (20)$$

An inflection point on the titration curve is a point where  $d^2(\text{pcM})/df^2 = 0$ , and is also a point where  $d^2f/d(\text{pcM})^2 = 0$ . This is true because  $df/d(\text{pcM})$  must have a minimum value at any point where  $d(\text{pcM})/df$  has a maximum value, and *vice versa*. Equating the left-hand side of eqn. (20) to zero and simplifying yields

$$\frac{2rk^2 [M] (k[M] + r + rk[M])}{kC_M^0 + r + rk[M]} + \frac{kC_M^0 + r + 2rk[M]}{[M]} = k^2 [M] (1+r) \quad (21)$$

as the fundamental description of any point of inflection on the titration curve.

#### THE CONSEQUENCES OF NEGLECTING DILUTION

It is of interest to investigate the location of the inflection point when  $r = 0$ . Equation (21) then becomes

$$[M] = (C_M^0/k)^{\frac{1}{2}} \quad (22)$$

while eqn. (6) becomes

$$k[M]^2 - \{(1-f)kC_M^0 - 1\}[M] - C_M^0 = 0 \quad (23)$$

Combining eqns. (22) and (23) yields

$$f = 1 - \frac{1}{kC_M^0} \quad (24)$$

This result has three important consequences. The first is that, since eqn. (24) is single-valued, there is only one inflection point if  $r = 0$ ; this is a point of maximum slope. The same thing is true in ion-combination titrations. The second is that the inflection point on a chelometric titration curve cannot coincide with, but must always precede, the equivalence point even if  $r = 0$ . The third is that the location of the inflection point when  $r = 0$  depends on the value of  $kC_M^0$ . In an isoivalent ion-combination titration, on the contrary, the inflection point obtained when  $r = 0$  is not

only coincides with the equivalence point but does so regardless of the value of  $K_t$  and the concentration of the solution titrated.

The difference between the inflection point and the equivalence point in a chelometric titration increases as  $r$  increases, as will be shown below and as is also true in an ion-combination titration, and may not be negligible even if  $r = 0$ . If the end-point is reproducible to  $\pm 0.01$  pCM unit, which is not very far beyond the capabilities of several currently available autotitrators, and if  $kC_M^0 = 100$ , the above equations show that the values of  $f$  at the end-points of replicate titrations could not differ more than 0.009 unit (that is, the relative precision would be 0.009), whereas the inflection point would occur at  $f = 0.990$ , so that the bias of the mean would exceed its standard deviation.

#### CONDITIONS FOR THE EXISTENCE AND NUMBER OF INFLECTION POINTS IN REAL CHELOMETRIC TITRATIONS

To investigate the existence, number, and locations of the inflection points obtained when  $r$  is finite, it is most convenient to rewrite eqn. (21) in the form

$$k^2(C_M^0)^2 + \{2r + 3rk[M] - k^2[M]^2(1+r)\}kC_M^0 + \{r^2(1+k[M])^3 + rk^2[M]^2(rk[M] - 1)\} = 0 \quad (25)$$

This may be regarded as a quadratic in  $kC_M^0$ , and accordingly it has, in general, two roots. These correspond to two inflection points: one, which can be shown to be a point of minimum slope, occurring at the smaller value of  $f$ ; and the other, which can be shown to be a point of maximum slope, occurring at the larger value of  $f$ .

The following criteria govern the number of inflection points actually obtained.

(a) There can be no inflection point unless the discriminant of eqn. (25) is positive:

$$b^2 - 4ac > 0 \quad (26a)$$

where  $a$ ,  $b$ , and  $c$  are the coefficients of the successive terms in eqn. (25). Introducing their values into eqn. (26a) and simplifying yields

$$k[M] > \frac{(5+4\sqrt{2})r}{1+r} = 10.657 \frac{r}{1+r} \quad (26b)$$

as one criterion for the existence of a physically significant point of inflection. As this cannot be satisfied anywhere if it is not satisfied at  $f = 0$ , where  $[M] = C_M^0$ , it may be written

$$kC_M^0 > 10.657 \frac{r}{1+r} \quad (26c)$$

This would indicate that, if  $r = 0$ , an inflection point could exist regardless of the value of  $kC_M^0$ , but eqn. (24) shows that this is not so: because the value of  $f$  at the inflection point must be positive as well as real, one must actually have  $kC_M^0 \geq 1$  if  $r = 0$ . Equation (26c) is therefore a necessary but insufficient criterion for the existence of an inflection point. For each of a number of values of  $kC_M^0$ , the second column of Table I gives the maximum value of  $r$  at which an inflection point is permitted by this criterion. If  $kC_M^0 \geq 10.657$ , an inflection point is permitted at any value of  $r$ .

TABLE I

CRITERIA FOR THE EXISTENCE OF POINTS OF MAXIMUM AND MINIMUM SLOPE ON POTENTIOMETRIC CHELOMETRIC TITRATION CURVES

(The values of  $r$  in the second, third, and fourth columns are calculated from eqns. (26c), (27), and (28), respectively)

$kC_M^0$	No inflection point if $r$ exceeds	No point of maximum slope if $r$ exceeds	Two inflection points if $r$ exceeds
1	0.1036	0	0
2	0.231	0.222	0.264
5	0.884	$\infty$	0.574
10	15.22	$\infty$	0.751
20	$\infty$	$\infty$	0.864
50	$\infty$	$\infty$	0.942
100	$\infty$	$\infty$	0.971
200	$\infty$	$\infty$	0.985
500	$\infty$	$\infty$	0.994
1000	$\infty$	$\infty$	0.997

(b) There will be a point of maximum slope if the preceding criterion is satisfied and if the larger root of eqn. (25) corresponds to a value of  $C_M^0$  that equals or exceeds the value of  $[M]$  at the inflection point it describes. This is equivalent to demanding that  $f \geq 0$  at the point of maximum slope. Increasing the value of  $r$  causes the point of maximum slope to move toward a smaller value of  $f$ , and therefore the value of  $r$  that produces a point of maximum slope at  $f = 0$ , where  $[M] = C_M^0$ , is the largest value of  $r$  at which there can be a physically significant point of maximum slope. This value of  $r$  is obtained by setting  $[M] = C_M^0$  in eqn. (25) and solving for  $C_M^0$ ; the result is

$$2kC_M^0 + 3kC_M^0 r + 2r - k^2(C_M^0)^2(1+r) - kC_M^0 \sqrt{[kC_M^0(1+r) - 5r]^2 - 32r^2} = 0 \quad (27)$$

If  $kC_M^0 = 1$ , this equation is satisfied by  $r = 0$ , so that, in agreement with eqn. (24) and the discussion in the preceding paragraph, no physically significant inflection point can be obtained at any finite value of  $r$ . In this situation eqn. (27) is more restrictive than eqns. (26): although the latter permit an inflection point as long as  $r$  does not exceed 0.1036, the inflection point has no actual existence because it corresponds to a negative value of  $f$ . As  $kC_M^0$  increases, however, the maximum value of  $r$  obtained from eqn. (27) increases very rapidly. Even if  $kC_M^0$  is equal to 2.5 eqn. (27) has no real positive root, which means that a point of maximum slope can exist (although it may be experimentally invisible) no matter how large  $r$  may be.

(c) There will also be a point of minimum slope if the two preceding criteria are satisfied and if the smaller root of eqn. (25) corresponds to a value of  $C_M^0$  that equals or exceeds the value of  $[M]$  at the inflection point it describes. In this case, the value of  $r$  that causes the point of minimum slope to occur at  $f = 0$  is the smallest value that permits it to appear at all. Setting  $[M] = C_M^0$  in eqn. (25), squaring to remove the radical, and solving the resulting quadratic in  $r$  yields the following description of this minimum value of  $r$ :

$$r = \frac{-(kC_M^0)^2 + kC_M^0 \sqrt{(kC_M^0)^4 + 2(kC_M^0)^3 + (kC_M^0)^2 - 2(kC_M^0) - 1}}{(1 + kC_M^0)^3} \quad (28)$$

TABLE II  
LOCATIONS OF INFLECTION POINTS ON POTENTIOMETRIC CHELOMETRIC TITRATION CURVES

$r = 1$				$r = 3$					
$k[M]$ at inflection point	For point of minimum slope $kC_M^0$	$f$	For point of maximum slope $kC_M^0$	$f$	$k[M]$ at inflection point	For point of minimum slope $kC_M^0$	$f$	For point of maximum slope $kC_M^0$	$f$
6			38.37	0.832	10			210.24	0.898
7	13.00	0.327	62.00	0.898	11			283.00	0.930
8	13.26	0.266	88.74	0.929	12			366.90	0.947
10	14.54	0.195	153.46	0.960	13	95.10	0.671	456.75	0.958
11	15.33	0.173	191.67	0.968	14	96.25	0.648	553.58	0.966
12	16.17	0.155	233.83	0.974	16	104.35	0.604	769.65	0.976
15	18.86	0.118	384.14	0.984	18	111.40	0.585	1016.6	0.982
20	23.60	0.085	714.40	0.9916	20	119.04	0.571	1295.0	0.986
30	33.38	0.054	1674.6	0.9964	30	160.73	0.532	3163.3	0.994
50	53.21	0.031	4794.8	0.9987	50	248.66	0.505	9295.3	0.9981
100	102.6	0.0127	19595	0.9997	100	472.34	0.485		
1000	1002.5	0.00125	1.996 · 10 <sup>6</sup>	0.999997	200	921.5	0.476		
10000	10002.5	0.000125	1.9996 · 10 <sup>8</sup>	0.99999997					

As  $kC_M^0$  increases, the value of  $r$  described by eqn. (28) obviously approaches 1. The manner in which it does so is shown in the last column of Table I. This behavior is almost perfectly analogous to that observed in isovalent ion-combination titrations.

#### LOCATIONS OF THE INFLECTION POINTS

Because eqn. (25) is a cubic in the concentration of M, the exact calculation of the value of  $f$  at an inflection point from assumed values of  $kC_M^0$  and  $r$  is tedious. It is much simpler to adopt the following procedure. Substituting assumed values of  $k[M]$  and  $r$  into eqn. (25) gives a quadratic in  $kC_M^0$ . The physically significant roots (for which  $kC_M^0 \geq k[M]$ ) are extracted and combined with eqn. (6), which is linear in  $f$  and is most conveniently rearranged into the form

$$f = \frac{(kC_M^0 - k[M])(k[M] + 1)}{k[M] \{kC_M^0 + 3(k[M] + 1)\}} \quad (29)$$

to obtain the corresponding values of  $f$ . Table II shows the results of such calculations for  $r = 1$  and  $r = 3$ .

Because a small value of  $k[M]$  at the point of maximum slope corresponds to a small value of  $kC_M^0$ , as is illustrated by Table II, and because a small value of  $kC_M^0$  corresponds in turn to a large (*i.e.*, poor) relative precision in accordance with eqn. (17), the value of  $k[M]$  at the point of maximum slope must be fairly large if the titration is to be feasible. Expressions describing the locations of the inflection points in feasible titrations are easily obtained by writing the roots of eqn. (25) in general form, neglecting terms of the order of  $(k[M])^{-1}$  or less, and combining these with eqn. (29). The results are

$$f_{\text{min. slope}} = \frac{2r^2 - r - 1}{r(3r + 1)} + \frac{13r^3 + 9r^2 - r - 1}{r(3r + 1)^2 k[M]} \quad (30)$$

and

$$f_{\text{max. slope}} = 1 - \frac{6r^3 + 11r^2 + 6r + 1}{(r + 1)^3 (k[M])^2} \quad (31)$$

These may be written in the forms

$$f_{\text{min. slope}} = a + b/k[M] \quad (32)$$

and

$$f_{\text{max. slope}} = 1 - c/(k[M])^2 \quad (33)$$

respectively; values of  $a$ ,  $b$ , and  $c$  are given for various values of  $r$  in Table III.

When  $k[M]$  is large at the point of maximum slope, the discrepancy between this point and the equivalence point is small, and one can therefore easily transform eqn. (33) into an expression that will yield a nearly exact prediction of the location of this point from known values of  $kC_M^0$  and  $r$ . This is advantageous because values of  $kC_M^0$  are available *a priori* while those of  $k[M]$  at the point of maximum slope are not. At  $f = 1$  eqn. (6) may be written

$$kC_M^0 = (1 + r)(k[M])^2 \quad (34)$$

because  $k[M] \ll (k[M])^2$  under these conditions. Combining this with eqn. (33),

$$f_{\text{max. slope}} = 1 - \frac{(1 + r)c}{kC_M^0} \quad (35)$$

For example, the point of maximum slope in a titration for which  $r = 1$  (so that  $c = 3$  according to Table III) and  $kC_M^0 = 2 \cdot 10^4$  would lie at  $f = 1 - 3 \cdot 10^{-4} = 0.9997$  according to eqn. (35). This is in essentially exact agreement with the value given (for  $k[M] = 100$  or  $kC_M^0 = 1.9595 \cdot 10^4$ ) in Table II.

TABLE III

PARAMETERS FOR THE ESTIMATION OF  $f$  AT THE INFLECTION POINTS WHEN  $k[M]$  IS LARGE

$r$	Parameters for eqn. (32)		Parameter for eqn. (33)
	$a$	$b$	$c$
0			1
0.1			1.289
0.3			1.799
0.5			2.222
1	0	1.25	3.000
1.5	0.2424	1.358	3.520
2	0.3571	1.398	3.889
3	0.4667	1.427	4.375
4	0.5192	1.436	4.680
5	0.5500	1.440	4.889
6	0.5702	1.443	5.041
8	0.5950	1.444	5.247
10	0.6097		5.380
20	0.6385		5.671
30			5.776
100			5.931
$\infty$	0.66667	1.44444	6.00000

Estimates of  $f$  at points of minimum slope in titrations in which  $kC_M^0$  is large may be obtained by a similar, though slightly more lengthy, procedure. We shall illustrate this procedure by making such an estimate for a titration in which  $kC_M^0 = 160$  and  $r = 3$ ; according to Table II, the value of  $f$  at the point of minimum slope is 0.532. Before employing eqn. (32) and the parameters in Table III to evaluate  $f$ , it is necessary to make an estimate of  $k[M]$  at the point of minimum slope. This is most easily done by combining eqns. (6) and (32) to obtain the quadratic

$$(1 + ar)(k[M])^2 + [(a - 1)kC_M^0 + (1 + ar + br)]k[M] + [(b - 1)kC_M^0 + br] = 0 \quad (36a)$$

which, if  $kC_M^0$  is large, has the approximate solution

$$k[M] = \frac{1 - a}{1 + ar} kC_M^0 \quad (36b)$$

From Table III, the value of  $a$  is 0.4667 when  $r = 3$ , and eqn. (36b) yields the estimate  $k[M] = 35.5$  at the point of minimum slope. Combining this result with eqn. (32) and the appropriate values of  $a$  and  $b$  from Table III yields  $f = 0.507$  at the point of minimum slope. Though this is not in exact agreement with the true value, 0.532, the discrepancy arises from the fact that the value of  $kC_M^0$  in this example is not very large, so that the approximations embodied in eqns. (32) and (36b) are not very closely satisfied. However, even under these rather unfavorable conditions the estimated value of  $f$  at the point of minimum slope is in error by only 0.025, which is probably too little to be detected experimentally.

## SUMMARY

Exact general descriptions are given of the slopes, the relative precisions, and the locations of the inflection points obtained in potentiometric titrations of a metal ion  $M$  with a chelon  $Y$  to give the soluble 1:1 chelate  $MY$ , using an ideally cation-responsive indicator electrode. The relative precision depends on the conditional formation constant  $k$  of the chelate, the initial concentration  $C_M^0$  of the metal ion, and the dilution parameter  $r$ , which is the ratio of the concentration of the chelon solution to  $C_M^0$ . Criteria for the existence and number of inflection points are given. When there is a point of maximum slope, it always precedes the equivalence point. If  $r$  exceeds a certain value, which depends on the value of  $kC_M^0$ , a point of minimum slope also appears; if  $kC_M^0$  is large this appears at the very start of the titration curve when  $r = 1$  and approaches a point two-thirds of the way to the equivalence point as  $r$  increases. The exact locations of the inflection points are given under various conditions, and equations are also given that permit them to be closely approximated in titrations for which  $kC_M^0$  is large.

## RÉSUMÉ

Les auteurs ont effectué une étude théorique des courbes de titrage: pentes et points d'inflexion obtenus lors de titrage potentiométrique d'un ion métallique  $M$  avec un chélon  $Y$  donnant un chélonate  $MY$  soluble (1:1). La précision relative dépend de la constante de formation  $k$  du chélonate, de la concentration initiale  $C_M^0$  de l'ion métallique, et du paramètre de dilution  $r$  (concentration du chélon en solution  $C_M^0$ ). La localisation exacte des points d'inflexion est donnée dans diverses conditions.

## ZUSAMMENFASSUNG

Es werden exakte, allgemeine Beschreibungen der Neigungen, der relativen Genauigkeiten und der Umschlagspunkte angegeben, wie man sie bei der potentiometrischen Titration eines Metallions  $M$  mit einem Chelat  $Y$  unter Bildung des löslichen 1:1-Chelats  $MY$  erhält, wenn eine ideale Indikatorelektrode verwendet wird. Die relative Genauigkeit hängt ab von der Bildungskonstanten  $k$  des Chelats, der Anfangskonzentration  $C_M^0$  des Metallions und dem Verdünnungsparameter  $r$  (Verhältnis der Konzentration der Chelonlösung zu  $C_M^0$ ). Es werden Kriterien für die Existenz und die Zahl der Umschlagspunkte angegeben. Wenn es einen Punkt maximaler Neigung gibt, geht er immer dem Äquivalenzpunkt voraus. Falls  $r$  einen bestimmten Wert überschreitet, der von  $kC_M^0$  abhängt, tritt auch ein Punkt minimaler Neigung auf; falls  $kC_M^0$  gross ist, erscheint dieser beim wahren Start der Titrationskurve, wenn  $r = 1$ , und nähert sich mit wachsendem  $r$  einem Punkt, der etwa zu  $\frac{2}{3}$  auf dem Wege zum Äquivalenzpunkt liegt. Die genaue Lokalisation des Umschlagspunktes wird für verschiedene Bedingungen angegeben und durch Gleichungen ausgedrückt.

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## DETERMINATION OF VANADIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY\*

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The technique of atomic absorption spectroscopy has provided an elegant means for the determination of a large number of metals at levels of a few parts per million or even less. Very little work has been published concerning the determination of vanadium by atomic absorption spectroscopy. The first atomic absorption measurement for vanadium was made by ROBINSON<sup>1</sup>, who observed a very weak absorption signal (limit of detection 300 mg/l) by using an oxy-cyanogen flame. Later, FASSEL AND MOSSOTTI<sup>2</sup>, and SLAVIN AND MANNING<sup>3</sup> reported sensitivities of 10 mg/l and 7 mg/l, respectively, by using a fuel-rich oxy-acetylene flame. Recently WILLIS<sup>4</sup> demonstrated the advantages of the nitrous oxide-acetylene flame from a premix-type burner, for the determination of refractory metals and reported a sensitivity of 1.5 mg/l of vanadium in aqueous solution for 1% absorption of the signal. The effect of various water-soluble and water-insoluble organic solvents on the oxy-acetylene flames of various compositions was studied by the authors<sup>5</sup>. The present paper describes the use of mixed organic solvents to improve the sensitivity for the determination of vanadium in fuel-rich oxy-acetylene flame and the effect of various interfering ions and compounds on the absorption signal for vanadium in oxy-acetylene as well as nitrous oxide-acetylene flame. As a result of the investigation, selective and sensitive methods for the determination of vanadium by the use of fuel-rich oxy-acetylene and nitrous oxide-acetylene flames have been developed.

## EXPERIMENTAL

*Apparatus*

Atomic absorption spectrophotometer (Perkin-Elmer Model 303), Perkin-Elmer premix-type burner with nitrous oxide head, 3 large bore oxy-acetylene atomizer burners (Beckman Instruments, Inc. No. 4090), and a vanadium hollow-cathode lamp (Ransley Glass Instruments, Melbourne, Australia).

*Reagents*

*Standard solution of vanadium.* A stock solution containing 10 g/l of vanadium was prepared by dissolving 22.80 g of pure ammonium metavanadate in 100 ml of 9 M sulfuric acid, and the volume of the solution was made up to a liter with doubly-distilled water. Various other concentrations were made by diluting the stock solution.

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*Cupferron solution.* Cupferron solution should be freshly prepared by dissolving 6 g of ammonium salt of N-nitrosophenylhydroxylamine in 100 ml of distilled water.

Other solutions such as those used for interference studies were prepared from analytical-grade chemicals.

#### *Procedure for extraction*

An aqueous solution of vanadium was mixed with  $1/10$  of its volume of concentrated sulfuric acid, and the resultant solution cooled in an ice bath. The solution was transferred to a separatory funnel and an appropriate volume of cupferron solution was added (1 ml per mg of the extractable ion). The precipitate that formed was extracted into a desired volume of methyl isobutyl ketone (MIBK) or a mixture of MIBK and oleic acid (78:22).

#### *Setting of the instrument*

*Absorption wavelength.* Various lines for vanadium were examined. The absorption of the 3183.9 Å line has been found to be the most sensitive and useful for atomic absorption studies of vanadium. The instrument used, however, was not capable of resolving this line from the 3183.41 Å and 3185.4 Å lines. Sensitivities for some intense vanadium lines in a nitrous oxide-acetylene flame are given in Table I.

TABLE I

SENSITIVITY OF THE STRONGEST ABSORPTION LINES OF VANADIUM

(Flame conditions: highly reducing  $N_2O$ -acetylene flame)

<i>Wavelength (Å)</i>	<i>Sensitivity (mg/l of vanadium for 1% absorption)</i>	<i>Wavelength (Å)</i>	<i>Sensitivity (mg/l of vanadium for 1% absorption)</i>
3183.9	2	4379.2	11
3902.2	30	4384.7	9
4111.8	13	4389.9	11

*Lamp current.* The lamp was operated at a current of 30 mA and has been found to be giving good service even after 80 working hours of service.

*Slit-opening.* The slit should be kept at a minimum to reduce electronic noise due to flame back-ground radiation which is quite high in reducing oxy-acetylene and nitrous oxide-acetylene flames. In the experiments described, a slit width of 0.3 mm (or 2 Å) was found to be satisfactory.

#### *Burner assembly*

*Beckmann total consumption oxy-acetylene burner.* A special rack was fitted for the use of one or more Beckman oxy-acetylene burners in the place of the Perkin-Elmer premix-type burner. The position of burners could be adjusted by means of a 3-axis positioning device, so that the beam from the hollow-cathode lamp passed through the upper portion of the inner luminous cone of oxy-acetylene flame. Two stage regulators were used on the gas tanks and a flow meter in the gas lines.

*Nitrous oxide-acetylene flame.* A Perkin-Elmer premix-type burner with nitrous oxide head was used. In addition to the 2 stage regulators on the gas tanks,

pressure gauges were used in the nitrous oxide lines and a flow meter was used in the acetylene line. A flame with atomizer  $N_2O$  pressure of 35 p.s.i., auxiliary  $N_2O$  pressure of 13 p.s.i. and acetylene flow of 5 l/min was found to be satisfactory in these studies. The radiation from the hollow-cathode tube was passed through the red reaction zone of the flame. While working with these flames all precautions as described in the operation manual were carefully observed.

## RESULTS AND DISCUSSION

### *Oxy-acetylene flame*

An aqueous solution containing 1 g/l vanadium gave a 6% absorption. However, a considerably higher absorption signal was obtained by the use of organic solvents. The effect of various organic solvents on the absorption signal for vanadium was studied and discussed in a separate publication<sup>5</sup>. A solvent mixture of MIBK and oleic acid (78:22, v/v) when used for extracting vanadium as the cupferrate was found to be the most useful system for atomic absorption studies. An oxygen flow rate of 3.5 l/min and acetylene flow rate of 3.3 l/min were found to give the maximum absorption signal.

### *Flame position*

The position of the burner was varied by means of the positioning mechanism. The tip of the burner when placed in the radiation beam was taken as the zero position.

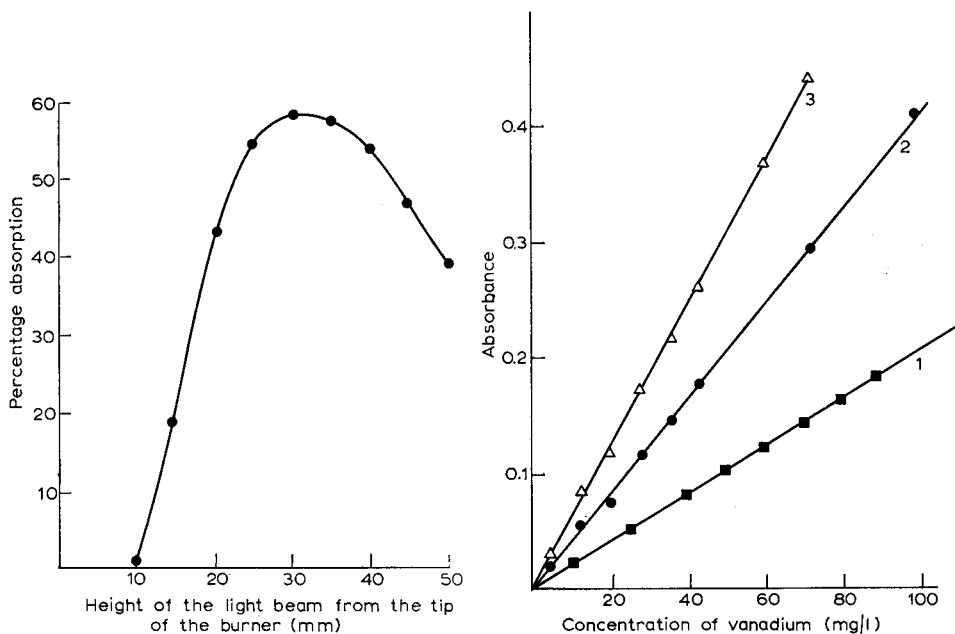


Fig. 1. Effect of variation of burner height on the absorption of 3183.9 Å line of vanadium. Concentration of vanadium = 200 mg/l; flow rates: oxygen 3.5 l/min, acetylene 3.3 l/min. V present as cupferrate.

Fig. 2. Calibration curves: ■, ●, △, obtained with one, two and three Beckman burners respectively. Sensitivity (for 1% absorption): 1, 2.1 mg/l; 2, 1.08 mg/l; 3, 0.72 mg/l.

The burner was moved downward in 5-mm steps and the absorption signal noted at each increment. The absorption was maximum when the tip of the burner was about 30 mm below the light beam (Fig. 1), at which point the radiation was passing through the upper part of the white luminous inner cone of the flame.

#### *Use of multiple burners*

Atomic absorption studies were made using 1, 2 and 3 burners respectively. Calibration curves obtained are shown in Fig. 2 where absorbance is plotted against concentration of vanadium in the organic phase. While using 2 or 3 burners, gas flow rates should be so adjusted that each burner consumes about 3.5 l/min of oxygen and 3.3 l/min of acetylene.

#### *Study of interferences*

The use of the extraction procedure eliminates a large number of potential interferences from cations as well as from anions. The following ions, however, may be extracted along with vanadium under the conditions described for extraction:  $\text{Sb}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{WO}_4^{2-}$ ,  $\text{Bi}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$  and  $\text{Zr}^{4+}$ . The effect of the presence of these ions on the adsorption signal for vanadium was studied. The concentration of interfering ions was 10 times that of vanadium.

To 2.5 ml of solution containing 1 g/l of vanadium, 2.5 ml of interfering ion solution containing 10 g/l of interfering ion, and 2.5 ml of concentrated sulfuric acid were added. The volume of the mixture was made up to 25 ml by adding distilled water. Vanadium from the resulting solution was extracted into 25 ml of a mixture of MIBK and oleic acid, and atomic absorption measurements of the extract were compared with that of a similar solution of vanadium containing 100 mg/l of vanadium but no interfering ion.

None of the ions mentioned earlier were found to interfere with the determination of vanadium. However, excess cupferron must be added if  $\text{Fe}^{3+}$ ,  $\text{Sb}^{3+}$  or  $\text{Zr}^{4+}$  are present because these ions are preferentially complexed under the described conditions. Zirconium forms a white precipitate which is not extractable with MIBK and can be easily filtered off.

#### *Nitrous oxide-acetylene flame*

Vanadium can be determined from an aqueous solution by the use of a fuel-rich nitrous oxide-acetylene flame. Although very little interference from diverse ions was expected, a study of interferences proved otherwise. The effect of the following potential interfering ions and compounds on the absorption signal for vanadium was investigated.

Group I.  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Ag}^+$ .

Group II.  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}_2^{2+}$  and  $\text{Hg}_3^{2+}$ .

Group III.  $\text{B}_4\text{O}_7^{2-}$ ,  $\text{Al}^{3+}$  and  $\text{Ce}^{4+}$ .

Group IV.  $\text{CO}_3^{2-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sn}^{4+}$  and  $\text{Pb}^{2+}$ .

Group V.  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{Sb}^{5+}$  and  $\text{Bi}^{3+}$ .

Group VI.  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cr}^{3+}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{TeO}_3^{2-}$ ,  $\text{WO}_4^{2-}$  and  $\text{UO}_4^{2-}$ .

Group VII.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{Mn}^{2+}$ .

Group VIII.  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$ .

Miscellaneous substances: citrate, tartrate, oxalate, EDTA, detergents,

hydrochloric acid, sulfuric acid, nitric acid, perchloric acid, acetic acid, and phosphoric acid.

The solutions tested contained 100 mg/l of vanadium and 500 mg/l of the respective interfering ion. The cations were added as chlorides or nitrates, or in certain cases, as sulfates. The anions were introduced as sodium or potassium salts. The effect of acids was examined by adding 5 ml of the appropriate concentrated acid to the solution followed by dilution to 100 ml with water.

Among the ions and compounds listed, the following ions and compounds were found to enhance the absorption signal:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ , detergents (Tide), acetic acid and phosphoric acid. The increase of absorption signal was noted to be 10% to 25% of its value depending upon the ions or compound present. The results are shown in Table II. The enhancement of the absorption by acetic acid may be similar to that of organic solvents and that of detergents may be

TABLE II  
INTERFERENCES

<i>Interfering ion or compound present (500 mg/l)</i>	<i>Absorption for vanadium in the presence of interfering ions (%)</i>	<i>Interfering ion or compound present (500 mg/l)</i>	<i>Absorption for vanadium in the presence of interfering ions (%)</i>
None	40.6	$\text{Cs}^+$	50.0
$\text{Al}^{3+}$	56.3	$\text{Ti}^{4+}$	56.2
$\text{Cr}^{3+}$	50.3	$\text{Bi}^{3+}$	48.7
$\text{Fe}^{3+}$	47.7	Acetic acid	45.1
$\text{Li}^+$	48.0	$\text{H}_3\text{PO}_4$	48.6
$\text{Na}^+$	48.0	Detergent (Tide)	47.6
$\text{K}^+$	48.2		

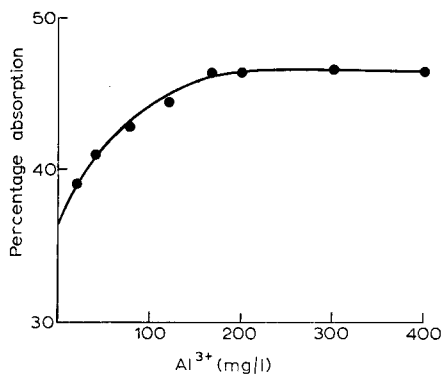
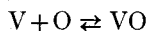


Fig. 3. The effect of addition of  $\text{Al}^{3+}$  on the absorption signal of vanadium. Concentration of V = 100  $\mu\text{g/ml}$ .

due to the lowering of the surface tension and viscosity of the solution. The effect of surfactants is discussed later in this paper. The enhancement of the absorption signal by ions such as  $\text{Al}^{3+}$  and  $\text{Ti}^{4+}$  may be due to competition with vanadium in the formation of oxides. The following equilibrium,



which exists in the flame, may shift in the favor of free vanadium atoms. In support

of the above reasoning is the fact that maximum enhancement of the absorption signal (about 25%) was noted by the addition of ions such as  $\text{Al}^{3+}$  and  $\text{Ti}^{4+}$  which readily form stable oxides. The effect of addition of increasing amounts of aluminum on the absorption signal for vanadium from a solution containing 100 mg/l of vanadium was studied. The results are shown in Fig. 3.

It can be seen that the absorption signal increased with the increasing amounts of  $\text{Al}^{3+}$  until the concentration of  $\text{Al}^{3+}$  was about twice that of the vanadium. Beyond this point, the increase in  $\text{Al}^{3+}$  concentration did not affect the absorption signal. Furthermore, in the presence of  $\text{Al}^{3+}$  and vanadium (2:1), the various other interfering ions no longer showed any effect.

#### *Effect of surfactants*

In a premix-type atomizer burner, only a small fraction (3–10%) of the total sample aspirated reaches the flame. Most of the sample is lost due to condensation on the walls of the mixing chamber. The fraction of the sample reaching the flame depends upon (a) the pressure and temperature of the atomizer gas, (b) temperature of the walls of the chamber, and (c) vapour pressure and surface tension of the solution aspirated.

Considerable enhancement in the absorption signal for vanadium was observed upon the addition of diethylene glycol and certain other similar surface-active compounds<sup>5</sup>. The effect of the addition of increasing amounts of diethylene glycol diethyl ether on the absorption signal was studied. It was found that the presence of about 6% diethylene glycol diethyl ether increased the absorption by 70%, but that higher concentrations did not yield further enhancement.

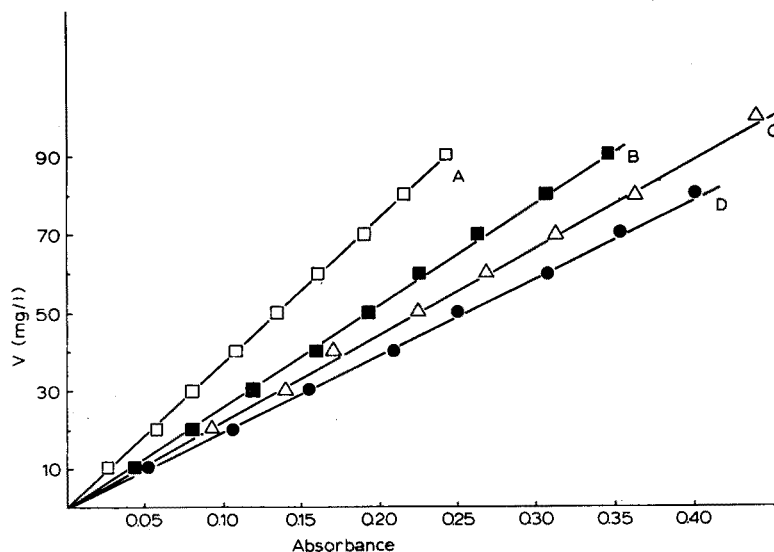


Fig. 4. Calibration curves for vanadium in  $\text{N}_2\text{O}$ -acetylene flame. (□) for aqueous vanadium solution; (■) for aqueous vanadium solution containing 200  $\mu\text{g}/\text{ml}$   $\text{Al}^{3+}$ ; (△) for aqueous solution of vanadium containing 200 mg/ml of  $\text{Al}^{3+}$  and 40 mg/ml of diethylene glycol diethyl ether; (●) for vanadium cupferrate in M.I.B.K.

Calibration curves for aqueous vanadium, aqueous vanadium in the presence of  $\text{Al}^{3+}$ , aqueous vanadium in the presence of  $\text{Al}^{3+}$  and diethylene glycol diethyl ether and vanadium as vanadium cupferrate in MIBK are shown in Fig. 4. Sensitivities for vanadium as shown in the 4 cases are 2 mg/l, 1.2 mg/l, 0.8 mg/l and 1.0 mg/l (for 1% absorption) respectively.

#### RECOMMENDED PROCEDURE

##### *For solutions containing 5–10 mg/l of vanadium*

Prepare standard solutions containing 10, 20, 30, 40, 50, 60, 80 and 100 mg/l of vanadium by diluting the stock solution of vanadium with a solution containing 300 mg/l of  $\text{Al}^{3+}$ . Add an appropriate amount of  $\text{Al}^{3+}$  to the unknown solution (about 9 mg of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  should be present in 10 ml of the unknown solution). Determine the absorbance for the standard solutions using nitrous oxide–acetylene flame under the conditions described under EXPERIMENTAL. Prepare the calibration curve (Fig. 4, Curve B). Feed the sample solution to the flame, determine the absorbance and determine the concentration of vanadium by reference to the calibration curve. Because flame conditions and position are critical factors, new calibration curves should be prepared for each set of experiments.

##### *For solutions containing 0.5–10 mg/l of vanadium*

To 100 ml of the unknown solution add 10 ml of concentrated sulfuric acid and cool to about  $10^\circ$ . Transfer the solution to a separatory funnel (200-ml capacity), add approximately 2 ml of 6% cupferron solution and 10 ml of methyl isobutyl ketone (MIBK). Shake the mixture for 1 min, and separate the phases. Feed the organic phase containing the vanadium cupferrate to a nitrous oxide–acetylene flame and note the absorbance. A calibration curve (Fig. 4, Curve C) should be prepared by using vanadium solutions in MIBK containing vanadium in the range 5–100 mg/l. These should be prepared by extracting vanadium from standard solutions containing 0.5, 1, 2, 3, 5, 7 and 10 mg/l, by following the extraction procedure described for the unknown solution. Alternatively, oxy–acetylene flames from a set of 3 total consumption burners, arranged in a row, may be used. In such a case vanadium should be extracted in a mixture of MIBK and oleic acid (78:22, v/v). The procedure for extraction and preparation of the calibration curve is exactly similar to the one described earlier.

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#### SUMMARY

Methods for the determination of vanadium, in the range 0.5–100 mg/l, by atomic absorption spectroscopy in an oxy–acetylene as well as in a nitrous oxide–acetylene flame are presented. For use with oxy–acetylene flames, vanadium is extracted as vanadium cupferrate into a mixture of methyl isobutyl ketone and oleic acid (78:22, v/v) and the organic phase is aspirated to the flame. The sensitivity is 0.7 mg/l of vanadium in the organic phase. For nitrous oxide–acetylene flames, an

aqueous solution of vanadium is aspirated directly. The sensitivity is further improved by the use of methyl isobutyl ketone, the addition of  $Al^{3+}$  and diethylene glycol diethyl ether. Many potential interferences were examined and methods to overcome those found are given.

#### RÉSUMÉ

On présente des méthodes pour le dosage du vanadium (0.5–100 mg/l) par spectroscopie par absorption atomique avec flammes oxy-acétylène et oxyde nitreux-acétylène. Dans le cas des flammes oxy-acétylène, le vanadium est extrait sous forme de cupferrate de vanadium dans un mélange méthylisobutylcétone-acide oléique (78:22, v/v); la phase organique est aspirée dans la flamme. Sensibilité 0.7 mg/l de vanadium dans la phase organique. Pour les flammes oxyde nitreux-acétylène, la solution aqueuse est aspirée directement dans la flamme. La sensibilité est améliorée par la méthylisobutylcétone,  $Al^{3+}$  et le diéthylèneglycoldiéthyléther.

#### ZUSAMMENFASSUNG

Es werden Methoden zur Bestimmung von Vanadin mit der Flammenabsorptionsspektralanalyse im Bereich von 0.5 bis 100 mg/l angegeben. Bei Verwendung der Sauerstoff-Acetylen-Flamme wird das Vanadin als Vanadinkupferrat mit einer Mischung aus Methylisobutylketon und Oleinsäure extrahiert und die organische Phase in die Flamme gesprüht. Die Empfindlichkeit beträgt 0.7 mg V/l in der organischen Phase. Bei Verwendung der Stickstoffoxyd-Acetylen-Flamme wird die wässrige Vanadinlösung direkt eingesprüht. Die Empfindlichkeit wird durch Zugabe von Methylisobutylketon,  $Al^{3+}$  und Diäthylenglykoldiäthyläther verbessert. Viele mögliche Störungen wurden geprüft; Methoden zu deren Beseitigung werden angegeben.

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## DETERMINATION OF COPPER, CADMIUM AND ZINC BY ATOMIC ABSORPTION SPECTROSCOPY

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Atomic absorption spectroscopy has found increasing use as a rapid means of determining trace quantities of metals in diverse materials. However, the application of this technique to studies of water and air pollution has been limited. WEST AND HERRIN<sup>1</sup> have demonstrated that a simple atomic absorption photometer can be used for determining the major cations in water. The determinations are essentially specific and they are rapid, simple and accurate. BIECHLER<sup>2</sup> recently reported the determination of certain heavy metals by atomic absorption spectroscopy in industrial waste waters; his method involved the use of Dowex A-1 resin for concentrating the metallic impurities. The preconcentration step was desirable because the concentrations of the metals in question were lower than the limits of sensitivity obtainable at that time by atomic absorption methods. CHAKRABARTI, ROBINSON AND WEST<sup>3</sup> have developed a very sensitive method for determining lead for studies of air and water pollution, based on a solvent extraction technique for concentrating the metal, followed by measurement by means of atomic absorption spectroscopy.

The purpose of the present investigation was to develop atomic absorption techniques capable of the direct determination of cadmium, copper and zinc in dilute systems such as drinking water, without prior concentration or treatment of the sample. According to the United States Public Health Service<sup>4</sup>, the maximum concentrations of these elements that may be present in drinking water are: cadmium—0.01 mg/l; copper—1.0 mg/l; and zinc—5.0 mg/l. Satisfactory quantitative procedures were developed by using a "T"-piece adapter to increase the sensitivity of the atomization process. Interference studies were carried out, and the results are indicated below.

### EXPERIMENTAL

#### *Equipment*

A Perkin-Elmer (Model 303) atomic absorption spectrophotometer fitted with a Beckman total-consumption burner for sample atomization was used. A "Hoke" gas flow meter was employed for measuring the flow rates of oxygen and hydrogen.

A quartz "T"-piece flame adapter was used to provide increased sensitivity. The ports through which the sample beam passed to enter the optical section of the instrument were covered with quartz plates to prevent damage by the flame products to the optical components. An air jet was also provided at each end of the adapter



to help prevent the hot products of the flame from entering the spectrometer. The adapter itself was cooled by circulating air around it as indicated in Fig. 1. These additions to the sample beam caused an imbalance between the sample and the reference beam. This was corrected by physically blocking part of the reference beam

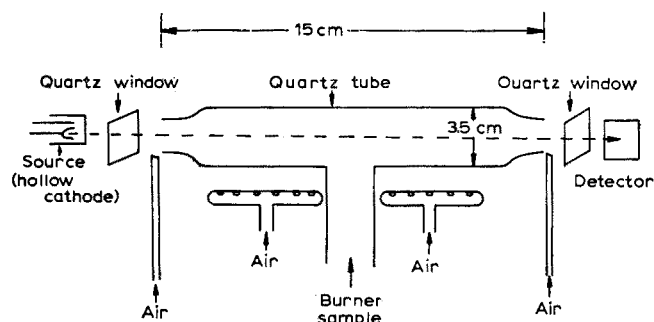


Fig. 1. Flame adapter (schematic).

TABLE I  
SENSITIVITY LIMITS FOR CADMIUM, COPPER AND ZINC  
(Optimum conditions)

Metal	Absorption wavelength (Å)	Lamp current (mA)	Slit (mm)	Oxygen flow rate (l/min)	Hydrogen flow rate (l/min)	Acetylene flow rate (l/min)	Sensitivity (mg/l for 1% absorption)	Sensitivity (mg/l for 1% absorption) with "T"-piece
Cd	2288	6	1.0	4.5	20	4.2	0.048	0.002
				4.5			0.020	
Cu	3247	8	1.0	4.5	20	5.5	0.25	0.008
				4.0			0.10	
Zn	2138	10	3.0	4.5	20	2.8	0.060	0.002
				4.0			0.025	

so that the 2 beams were approximately equal. The controls on the instrument were used for final adjustment.

For the radiation source, single-element Ransley hollow cathodes were employed.

#### Sensitivity limits

The sensitivity limits and the optimum flame conditions for each metal are listed in Table I. These were established with aqueous solutions of the metals under study. Both oxy-hydrogen and oxy-acetylene flames were investigated. Under the experimental conditions the sample uptake was about 4 ml/min.

#### Interference studies

*Oxy-hydrogen flame.* The interference effects of the following anions and cations on the spectral absorption of cadmium, zinc and copper were examined:

- Group I.  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$   
 Group II.  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Hg}^{2+}$   
 Group III.  $\text{B}_4\text{O}_7^{2-}$ ,  $\text{Al}^{3+}$ ,  $\text{Ce}^{4+}$   
 Group IV.  $\text{HCO}_3^-$ ,  $\text{SiO}_3^{2-}$ ,  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Pb}^{2+}$   
 Group V.  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{VO}_3^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{Sb}^{5+}$ ,  $\text{Bi}^{3+}$   
 Group VI.  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cr}^{3+}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{TeO}_3^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{UO}_4^{2-}$   
 Group VII.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{Mn}^{2+}$   
 Group VIII.  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$

Miscellaneous substances: citrate, tartrate, oxalate, EDTA, detergents (Dreft), hydrochloric acid, sulfuric acid, nitric acid, perchloric acid, and acetic acid.

Standard solutions containing 1 mg/l each of zinc and cadmium, and 5 mg/l of copper were prepared. To these, 100 mg/l of the interfering ion was added. The cations were added as chlorides or nitrates, or in certain instances, as sulfates. The anions were introduced as sodium or potassium salts. A solution of "Dreft" was used to study the effect of detergents. The effect of acids was examined by adding 5 ml of the appropriate concentrated acid to the metal under investigation followed by dilution to 100 ml with water.

No interferences were found from the cations on the absorption signal of cadmium, copper and zinc. Similarly, none of the anions interfered with the absorption of copper. However, slightly lower absorption values were obtained for zinc and cadmium in the presence of certain anions. The interferences were effectively overcome by acidifying or by adding EDTA to the solutions (Table II). The addition of EDTA was found to enhance the absorption of cadmium although no such effect was noticed in the case of copper and zinc.

TABLE II  
ANIONIC INTERFERENCES

Interferent	Percentage absorption			
	Cd (1 mg/l)	Cd (1 mg/l) + EDTA (4000 mg/l)	Zn (1 mg/l)	Zn (1 mg/l) + EDTA (4000 mg/l)
None	21.0	25.3	16.4	16.4
$\text{HPO}_4^{2-}$	—	—	14.0	16.4
$\text{SeO}_3^{2-}$	—	—	14.3	16.6
$\text{B}_4\text{O}_7^{2-}$	15.9	25.6	13.2	16.2
$\text{SiO}_3^{2-}$	19.9	25.4	10.7	16.8
$\text{CO}_3^{2-}$	19.1	25.4	12.2	16.4
$\text{HCO}_3^-$	18.5	25.3	10.5	16.3
$\text{HAsO}_4^{2-}$	19.8	25.3	14.8	16.4

None of the acids interfered in the determination of cadmium and zinc; but hydrochloric, sulfuric and perchloric acids caused a slight reduction in the absorption of copper. The results are shown in Table III.

*Oxy-acetylene flame.* A study in this flame was undertaken in order to find out if certain interferences noticed in oxy-hydrogen flame could be avoided by the use of an oxy-acetylene flame. Results showed that although the interferences on zinc, cadmium and copper were not eliminated, there was some enhancement in the degree of absorption by these metals as is evident from Table I.

*"T"-piece adapter*

With the possible exception of zinc, preliminary data indicated that a pre-concentration step involving solvent-extraction or ion-exchange column was essential for the determination of these elements in water. In order to avoid such a step it was decided to investigate the use of a "T"-piece adapter to enhance the sensitivity.

TABLE III

EFFECT OF HIGH ACID CONCENTRATION ON THE ABSORPTION OF COPPER

Acid (5%)	Percentage absorption of 5 mg Cu/l
None	24.5
Hydrochloric acid	21.9
Nitric acid	24.5
Sulfuric acid	20.7
Perchloric acid (70%)	23.6
Acetic acid	24.7

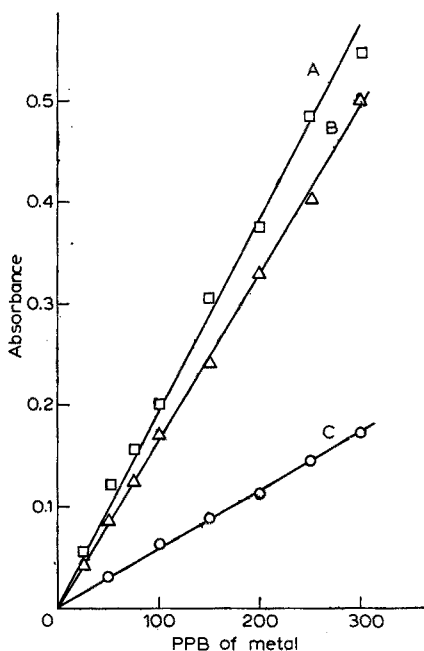


Fig. 2. Calibration curves with flame adapter. (A) Cadmium; (B) zinc; (C) copper.

The construction and use of a "T"-piece adapter has been described elsewhere<sup>5</sup>. CHAKRABARTI, ROBINSON AND WEST<sup>3</sup> have recently described its use for the determination of lead in air and water.

Calibration curves were obtained by using standard solutions of cadmium, copper, and zinc in an oxy-hydrogen flame. The conditions used were those listed in

Table I. Results shown in Fig. 2 indicate that a considerable enhancement in the absorption was obtained. No attempt was made to study the interferences with the "T"-piece adapter, since it was assumed that these would be the same as when the adapter was not used.

#### *Precision and accuracy*

Table IV summarizes the precision and accuracy data obtained with a Perkin-Elmer (Model 303) instrument using the recommended conditions.

TABLE IV  
PRECISION

<i>Metal</i>	<i>Amount taken (p.p.b.)</i>	<i>Number of determinations</i>	<i>Standard deviation, p.p.b. (95% confidence level)</i>
Cadmium	25	8	0.4
	50	8	0.4
Copper	50	10	2.2
	100	8	2.1
Zinc	25	8	1.2
	100	8	1.2

#### DISCUSSION

The present investigation showed that cadmium, copper and zinc could be determined directly in water samples by atomic absorption spectroscopy by taking advantage of a flame adapter which considerably enhances the absorption of these elements. The almost complete lack of interference associated with high sensitivity and reproducibility makes this method very attractive for the routine determination of these 3 pollutants. The effect of large excesses of the few anions which interfere in the determination of zinc and cadmium can be readily overcome if the determination is carried out in the presence of EDTA. When once the instrument is set, the operation of the apparatus is very simple, and all 3 metals can be determined in a matter of minutes with a high degree of accuracy.

Lastly, the method, although described from the point of view of water analysis, should be equally applicable for the determination of these 3 pollutants in the atmosphere. Depending upon the method of collection, the sample should be brought into solution by appropriate treatment. Since the few interferences noted in the case of cadmium and zinc are not likely to be present, the solution can be subjected directly to atomization.

#### RECOMMENDED PROCEDURE

##### *Reagents*

Prepare stock solutions of cadmium, copper and zinc containing 1 mg/ml of the metal by dissolving reagent-grade metals in a minimum amount of nitric acid. Boil off the excess acid, add distilled water and adjust the solution to the appropriate volume.

### *Equipment*

The equipment recommended is that described under EXPERIMENTAL.

### *Analytical procedure*

Turn on the instrument and allow about 30 min for it to warm up. Open the air jet and adjust the instrument settings to the optimum conditions for the element under investigation as listed in Table I. Aspirate distilled water into the flame and adjust the zero. Since the absorption for each element is sensitive to burner height, adjust the position of the burner while aspirating the metal solution of a suitable strength until maximum absorption is obtained. Aspirate distilled water and check zero again. This operation is repeated after each absorption measurement.

### *Calibration curve*

Transfer suitable aliquots of the stock solution to obtain 0.025 mg/l to 0.30 mg/l of metal into volumetric flasks and dilute to mark with double distilled water. Determine the percentage absorption as described under procedure. Convert the percentage absorption into optical density and plot a graph for each metal.

### *Determination of cadmium, copper and zinc*

*Cadmium.* Proceed as given under *Analytical procedure* to determine the percentage absorption. If silicate or bicarbonate are present in concentrations greater than 30 mg/l, add 0.4 g of the disodium salt of EDTA per 100 ml of sample. Since the presence of EDTA slightly enhances the absorption of cadmium, a separate calibration curve containing the same concentration of EDTA must be prepared. The concentration of cadmium is determined from the calibration curve after converting absorption values into optical density.

*Copper.* Proceed as under *Analytical procedure* and determine the copper content of the aqueous sample from the calibration graph. For samples other than drinking water, care must be exercised to avoid the presence of a large excess of hydrochloric, sulfuric or perchloric acid, which slightly suppress the absorption by copper.

*Zinc.* Determine the percentage absorption of zinc in the sample as given under *Analytical procedure*. In the presence of silicate or bicarbonate in concentrations above 10 mg/l, determine the percentage absorption in the presence of 0.4 g of disodium EDTA per 100 ml of sample. There is no need to modify the calibration curve procedure for the addition of EDTA. Convert the percentage absorption to optical density and the zinc concentration is then established from the calibration curve.

This investigation was supported by the United States Public Health Service Research Grant AP 00128.

### SUMMARY

A procedure for the direct determination of zinc, cadmium and copper in air and water has been developed. The possible interference effects of numerous anions and cations have been investigated. Few interferences were found, and these were eliminated by the addition of EDTA. The sensitivities found were 2 p.p.b. for cadmium, 8 p.p.b. for copper and 2 p.p.b. for zinc.

## RÉSUMÉ

On a mis au point une méthode de dosage direct du zinc, du cadmium et du cuivre, dans l'air et dans l'eau. L'influence de nombreux anions et cations a été examinée. Une addition d'EDTA permet d'éliminer les interférences. Sensibilité: 2 p.p.b. pour le cadmium, 8 p.p.b. pour le cuivre et 2 p.p.b. pour le zinc.

## ZUSAMMENFASSUNG

Eine direkte Bestimmung von Zink, Cadmium und Kupfer mit der Flammenabsorptionsspektroskopie in Luft und Wasser wurde entwickelt. Die möglichen Störungseffekte zahlreicher Anionen und Kationen wurden untersucht. Einige Störungen wurden durch Zugabe von AeDTE eliminiert. Die Empfindlichkeiten für Cadmium, Kupfer und Zink betragen 2, 8 bzw. 2 p.p.b.

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## THE DETERMINATION OF SILVER IN SULPHIDE MINERALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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For the determination of silver in sulphide ores fire assay is the conventional method; the need in this method for samples weighing several grams eliminates any effects of sample inhomogeneity, but makes the procedure unsuitable for geochemical studies of ore veins requiring silver determinations in separated minerals. Spectrophotometric determinations based on the formation of silver chelates with different reagents, *e.g.*, dithizone, diethyldithiocarbamate, tetraethylthiuramdisulphide, etc., have often been used<sup>1-4</sup>, but their accuracy is generally poor compared to that of the fire assay method. The atomic absorption spectrophotometry of silver seemed a more promising approach because of the high specificity and simplicity of the determination. The problems involved in its application to sulphide minerals are discussed below.

## EXPERIMENTAL

*Apparatus*

A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used; the silver line Ag 328.1 nm was measured. Initially, a Hilger hollow-cathode lamp for silver was used but was later replaced with a lamp of our own manufacture.

*Solutions*

A silver stock solution was prepared by dissolving 1 g of pure silver metal in nitric acid; the final concentration was 1000 p.p.m. of silver in 1 M nitric acid. Standard solutions were prepared by dilution, adding the same volume of acids as to the analysed samples. The standard solutions contained 0.5–8 p.p.m. of silver. Because even trace amounts of chloride ions made the standard solutions unstable, either re-distilled water and acids of highest purity were used or mercury(II) nitrate was added. Standard solutions containing 30 mg of mercury(II) in 100 ml stored in polyethylene flasks were stable for several months.

*Measurement*

The analytical conditions on the Perkin-Elmer Model 303 atomic absorption spectrophotometer were set as follows: wavelength 328.1 nm, slit 4, meter response 2, air flow 7, acetylene flow 4.5, lamp current 14 mA. The absorption of the standard solutions was measured and a working curve constructed. For measuring very low silver concentrations below 0.5 p.p.m., scale expansion is recommended.

## RESULTS

*Interfering effects*

The determination of silver by atomic absorption spectrophotometry is relatively free from interfering effects. Interferences may arise, however, by precipitation of silver compounds in the solution (*e.g.* with iodate and permanganate) or by the blocking effect of unevaporated oxides in the flame (*e.g.*  $\text{WO}_3$ ,  $\text{ThO}_2$ ,  $\text{Al}_2\text{O}_3$ )<sup>5,6</sup>. The effect of acids in the solution sprayed has also to be considered<sup>7-9</sup>. The effects of up to 10 ml of concentrated nitric acid, 3 ml of sulphuric acid and 1 g of tartaric acid in 50 ml were examined; sulphuric acid had the strongest depressing effect whereas tartaric acid had an enhancing effect. Although the differences did not exceed  $-3\%$  and  $+10\%$ , the concentration of these acids in the standard solutions used was kept at the same level as in the analysed samples. The flow-rates of acetylene and air had no influence on the results but a blue oxidizing flame was found preferable.

The Hilger silver lamp used emitted a fairly strong copper spectrum. When the slit setting 4 recommended for the silver determination<sup>10</sup> was used, the resonance copper line Cu 327.4 nm was partly included in the spectral bandpass of the monochromator and the copper content in the samples influenced the absorption measured. Samples of high copper content gave high results for silver, *e.g.*, the results for a tetraedrite containing 0.026% Ag and about 15% Cu with a slitwidth of 3 were about 0.007% high. This interference could be eliminated by using slitwidth 2, but measurements were then somewhat unstable. An argon-filled pure silver hollow cathode was therefore prepared and the copper interference was eliminated.

*Sample decomposition*

For the decomposition of the minerals, *i.e.* galenites, tetraedrites, sphalerites and antimonites, different decomposition methods had to be used.

*Galenites.* Galenites can be decomposed by hydrochloric acid provided that its concentration is at least 8 M so that silver remains in solution as  $\text{AgCl}_2^-$ . This decomposition has been used for atomic absorption determination of silver in ores<sup>11,12</sup>; however, on cooling any precipitated lead chloride may adsorb some silver chloride complex. GREAVES<sup>13</sup> exploited the finding of FORWARD *et al.*<sup>14</sup> that polyalkylamines form stable soluble chelates with lead and silver. For the analysis of lead concentrates, GREAVES dissolved 1-g samples with nitric and hydrochloric acids and then added 8 ml of diethylenetriamine so that the pH of the sprayed solution was about 1. Perchloric acid speeds up the dissolution and if the temperature is correctly controlled, the products are soluble in water<sup>15</sup>. However, small amounts of chloride ions may be produced and may cause precipitation of silver chloride which is retained by the residue. Sulphuric acid precipitates lead sulphate but silver is coprecipitated slightly.

For the dissolution of galenites only nitric acid was used in the present work. At room temperature (leaving the dissolution to proceed overnight) only small amounts of sulphur and lead sulphate resulted; when the decomposition was hastened by warming, considerable amounts of sulphur and lead sulphate were formed, which could adsorb some silver. The addition of sufficient tartaric acid prevented the hydrolysis of antimonite even during the subsequent heating of the solution; this would be important for samples of high antimony content (steinmanites). After this decomposition the solution was filtered and the undissolved residue was ashed and treated



with hydrofluoric and nitric acids and added to the main portion. The amount of silver retained in this residue varied for different galenite specimens but depended mainly on the purity of the reagents used; any traces of chloride increased the amount of silver retained. This effect was overcome simply by adding mercury(II) nitrate which forms less dissociated compounds with chloride than silver. The results shown in Table I prove that the effect of chloride impurities was best eliminated by adding mercury(II) nitrate at the beginning of the procedure. Under these conditions the relative amount of silver in the undissolved residue did not exceed 2%; in most cases it was considerably lower, and could often be disregarded.

TABLE I

AMOUNT OF SILVER RETAINED IN THE RESIDUE OF A GALENITE SAMPLE WITH DIFFERENT DECOMPOSITION CONDITIONS

Sample run	Conditions of decomposition <sup>a</sup>	Total amount of Ag found (%)	Amount of Ag in residue	
			$n \cdot 10^{-4}$ % Ag	% Ag of total content
1	I	0.341	55	1.6
2		0.343	20	0.6
3		0.344	58	1.7
4	II	0.343	36	1.05
5		0.342	69	2.0
6		0.342	78	2.3
7	III	0.344	114	3.3
8		0.339	102	3.0
9		0.338	65	1.9
10	Ia	0.343	35	1
11		0.342	21	0.6
12		0.342	25	0.7
13	IIa	0.340	179	5.2
14		0.341	120	3.5
15		0.337	93	2.8
16	IIIa	0.330	121	3.7
17		0.332	137	4.1
18		0.325	240	7.4

<sup>a</sup> I = HNO<sub>3</sub> high-purity grade, redistilled water, Hg(II) added before decomposition.

II = HNO<sub>3</sub> high-purity grade, redistilled water, Hg(II) added after decomposition.

III = HNO<sub>3</sub> high-purity grade, redistilled water, without Hg(II).

For decompositions marked with the suffix *a* only analytical grade HNO<sub>3</sub> and distilled water were used.

*Tetraedrites*. These could be decomposed in the same way as galenites, *i.e.* with a mixture of nitric and tartaric acids at room temperature, followed by heating for 2–3 h. However, since tetraedrites contain only minute amounts of lead, complete decomposition could be achieved more easily with a mixture of sulphuric and nitric acids; after dissolution and cooling the evaporated residue was leached with a 10% solution of tartaric acid.

When the concentrate contained only small amounts of pyrite, the sample could be decomposed by boiling with sulphuric acid alone for about 10 min. Because tetraedrites have a high mercury content, it is unnecessary to add more mercury(II).

*Antimonites.* Decomposition with nitric and tartaric acids was used by HAMPE<sup>16</sup> for antimony alloys and minerals, but the amount of tartaric acid recommended proved to be excessive for atomic absorption measurements. It was found that 2 g of tartaric acid sufficed to prevent precipitation of antimonite acid during dissolution. The decomposition was best achieved with nitric and sulphuric acids or sulphuric acid alone as described for tetradrites. However, sulphur salts of lead and antimony had to be decomposed by a mixture of nitric and tartaric acids as described for galenites. Perchloric acid precipitated antimonite acid immediately.

*Sphalerites.* These are very easy to decompose. All 3 procedures described could be used. The portion of silver retained in the insoluble residue was negligible (0.4–1.7% of the total silver content), provided that chloride-free acids were used or mercury(II) nitrate was added. When using only nitric acid mercury(II) nitrate must be added after decomposition of the sample. So that one set of standard solutions could be used throughout tartaric acid was also added.

Several hundred analyses showed that galenites and sulphur salts of lead and antimony were best decomposed with nitric and tartaric acids at room temperatures; tetradrites and antimonites were best decomposed with nitric and sulphuric acids, whereas sphalerites could be decomposed by any of the 3 methods.

#### *Blocking of chloride ions by addition of mercury*

If the solutions contain chloride as an impurity, colloidal silver chloride is formed. This is easily dissociated in the flame but a decrease in the signal is observed because silver chloride is adsorbed on the flask walls or sometimes on the undissolved residue of the ore sample. Accordingly, either silver or chloride ions must be bound in some sort of complex. Mercury(II) as a complexing agent for silver is the most satisfactory additive, since the reaction is quite selective and takes place in strongly acidic solutions. The addition of mercury(II) has no effect on the atomic-absorption determination of silver, in contrast to all spectrophotometric determinations based on the formation of silver complexes with organic dyes. Calculation by conventional methods shows that for the highest concentration of silver in the standard solutions (10 p.p.m. or *ca.*  $1 \cdot 10^{-4} M$ ) and for an estimated chloride concentration from distilled water and acids used, of  $5 \cdot 10^{-5} M$ , the amount of mercury(II) required is  $2.65 \cdot 10^{-5} M$ . For a chloride concentration of  $5 \cdot 10^{-4} M$ , the required amount of mercury(II) would be  $2.73 \cdot 10^{-4} M$ .

The concentration of mercury finally chosen was  $0.75\text{--}1.5 \cdot 10^{-3} M$  which ensured the presence of an excess. During decomposition of the sample, some mercury(II) was precipitated, but the amount left in solution sufficed to block the chloride present.

#### *Recommended procedures*

*Decomposition with nitric and tartaric acid.* To 0.1–0.3 g of powdered mineral, add 10 ml of 10% tartaric acid solution (for antimonites, 10 ml of a 20% solution), 10 ml of concentrated nitric acid and 30 mg of mercury as mercury(II) nitrate. Leave at room temperature for 12 h, and then heat on a steam bath for 2–3 h. Wash the undissolved residue and sulphur formed twice by decantation, filter on a dense filter paper and wash thoroughly with redistilled water. Collect the filtrate in a 100-ml measuring flask. Ash the filter in a corundum crucible and dissolve with nitric and

hydrofluoric acid. After fuming, dissolve any residue in the crucible in 2 ml of concentrated nitric acid and add to the main filtrate in the 100-ml flask which is then filled to the mark with redistilled water. The treatment of the insoluble residue may be omitted in most cases since the content of silver is negligible.

*Decomposition with nitric and sulphuric acid.* Dissolve 0.1–0.3 g of powdered sample in a mixture of 14 ml of 1:1 nitric acid and 3–4 ml of concentrated sulphuric acid. Cover the beaker with a watch glass and warm on a steam bath till dissolution is complete. Then evaporate on a sand bath until white fumes of sulphur trioxide appear. After cooling, add a few ml of water and dissolve the contents of the beaker in 10 ml of a 10% solution of tartaric acid by warming and thoroughly stirring. Filter off the insoluble residue and treat as described before.

*Decomposition with sulphuric acid.* Treat 0.1–0.3 g of powdered sample in a small Erlenmeyer flask with 5 ml of concentrated sulphuric acid. The mineral dissolves within 10 min on boiling. After cooling, dissolve the salts in the tartaric acid solution as described above.

#### DISCUSSION

In all several hundred analyses were performed. The precision of a determination depends strongly on the composition of the specimen analysed and on the decomposition. Some coefficients of variation found for different samples are given in Table II. The results were in general agreement with those found by the fire assay method, but the results of atomic absorption were 1–10% higher; this corresponds to earlier

TABLE II

PRECISION OF SILVER DETERMINATION AND COMPARISON WITH FIRE ASSAY RESULTS

<i>Mineral</i>	<i>Decomposition<sup>a</sup></i>	<i>Number of detns.</i>	<i>Coefficient of variation</i>	<i>Arithmetic mean (%)</i>	<i>Fire assay<sup>b</sup> (%)</i>
Tetraedrite 1	2	8	1.5	0.341	0.333
Tetraedrite 2	2	8	2.1	0.346	0.343
Tetraedrite 3	2	3	—	0.0271	0.0256
Sphalerite S	1,2	15	4.38	0.0308	0.0300
Sphalerite St	1,2	15	3.43	0.0499	0.0452
Antimonite	1,2,3	19	10.5	0.0105	—
Galenite G	1	6	1.7	0.344	0.330
Galenite Ga	1	8	6.95	0.111	0.110

<sup>a</sup> 1 = HNO<sub>3</sub> + tartaric acid; 2 = HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>; 3 = H<sub>2</sub>SO<sub>4</sub>.

<sup>b</sup> Arithmetic mean of 5 results.

findings<sup>12</sup> as well as to the fact that part of the silver is lost during cupellation<sup>17,18</sup>. The differences therefore do not indicate any bias in the atomic absorption method. For the determination of silver by atomic absorption much less sample is needed, and the method is less time-consuming and highly selective. A further advantage is that it is possible to determine several other elements in the same solution.

The authors wish to express their gratitude to Mr. V. SIXTA p. ch. for many fruitful discussions.

## SUMMARY

Silver can be determined in sulphide minerals by atomic absorption spectrophotometry after decomposition with nitric and/or sulphuric acid with addition of tartaric acid to prevent precipitation of antimonious acid. The amount of silver retained in the residue is negligible if the acids used are completely chloride-free or if mercury(II) nitrate is added.

## RÉSUMÉ

Une méthode est proposée pour le dosage de l'argent dans des minerais sulfurés, par spectrophotométrie par absorption atomique. L'échantillon est traité par l'acide nitrique et/ou l'acide sulfurique avec addition d'acide tartrique, afin d'éviter une précipitation d'acide antimonique. La quantité d'argent retenue dans le résidu est négligeable, si les acides utilisés sont exempts de chlorure ou si on ajoute du nitrate de mercure(II).

## ZUSAMMENFASSUNG

Silber kann in sulfidischen Mineralien mittels der Flammenabsorptionsspektroskopie bestimmt werden. Dazu wird die Probe vorher mit Salpeter- und/oder Schwefelsäure zerstört und Weinsäure zur Verhinderung eines Niederschlages von Antimonsäure zugegeben. Das vom unlöslichen Rückstand zurückgehaltene Silber ist vernachlässigbar, wenn die verwendeten Säuren völlig chloridfrei sind, oder Quecksilber(II)-Nitrat zugegeben wird.

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THE DETERMINATION OF COPPER IN ZINC MATERIALS BY NEUTRON ACTIVATION ANALYSIS USING THE  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  REACTION

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The optical and electrical properties of zinc sulfide phosphor are affected by the presence of trace copper. Therefore, the determination of copper is necessary to clarify the correlation between the physical properties and the presence of the element. For the determination of copper in various materials by neutron activation analysis, 2 nuclear reactions,  $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$  and  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  are considered.  $^{64}\text{Cu}$  with a half-life of 12.8 h from the former reaction emits a positron, 0.573-MeV  $\beta$ -ray, and 1.34-MeV  $\gamma$ -ray. The branching ratio of the  $\gamma$ -ray is only 0.43% and is not adequate for the determination of  $^{64}\text{Cu}$ . The annihilation radiation can hardly be distinguished from the 0.43-MeV  $\gamma$ -ray of 13.8-h  $^{69\text{m}}\text{Zn}$  in irradiated zinc materials. Nondestructive activation analysis using  $^{64}\text{Cu}$  therefore cannot be used. Moreover, even in activation analysis involving chemical separation, the method using  $^{64}\text{Cu}$  is seriously disturbed by the  $^{64}\text{Zn}(n,p)^{64}\text{Cu}$  reaction caused by fast neutrons in an atomic reactor. MELLISH *et al.*<sup>1</sup> reported that the interfering nuclear reaction gave rise to  $^{64}\text{Cu}$  activities equivalent to those produced from 708 p.p.m. of copper present as impurity even in the irradiation of pure zinc. Accordingly, the sample must be irradiated in a position with a minimum of fast neutrons in a high thermal flux reactor. BROSER AND FRANKE<sup>2</sup> reported that 0.5 p.p.m. of copper in zinc sulfide could not be determined even if the most highly moderated neutrons in the Berlin Reactor BER (the cadmium ratio (Au) : 8000) were utilized. Although COSGROVE AND MORRISON<sup>3</sup> analyzed single crystals of the phosphor weighing less than 500  $\mu\text{g}$  by destructive neutron activation using  $^{64}\text{Cu}$ , their study was at the level of 100 p.p.m. or greater copper concentrations.

The present authors investigated the possibility of utilizing the  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  reaction for the determination of copper in zinc materials from the consideration that the cross-section of the  $^{66}\text{Zn}(n,p)^{66}\text{Cu}$  reaction for fission neutrons is much smaller than that of  $^{64}\text{Zn}(n,p)^{64}\text{Cu}$ . Also,  $^{66}\text{Cu}$  with 5.1-min half-life emits 2.63 and 1.65 MeV  $\beta$ -rays, and a 1.044 MeV  $\gamma$ -ray which is probably useful for the nondestructive determination.

The technique which WAYMAN<sup>4</sup> used for the determination of phosphorus and sulfur in water samples was applied in this investigation to eliminate the interference of the (n,p) reaction. A sample and a standard were irradiated without cadmium foil wrappings, and the activities of  $^{66}\text{Cu}$  produced in the sample and the standard,  $A(X)$  and  $A(\text{Cu})$ , both in unit weight respectively, were measured. Another portion of the same sample and a standard were shielded with a cadmium foil, and irradiated under

the same conditions as the bare sample, and the activities produced in unit weight of the sample and the standard copper,  $A'(X)$  and  $A'(Cu)$  respectively, were measured. The  $^{66}Cu$  activities produced in 1 g of the sample by the  $^{66}Zn(n,p)^{66}Cu$  reaction,  $A(Zn)$ , do not change whether it is shielded or not. Hence, if the content of copper in the sample, per unit weight, is  $X$ , the activities produced in 1 g of the samples wrapped with cadmium and bare are,

$$A'(X) = A(Zn) + A'(Cu) \cdot X \quad (1)$$

and

$$A(X) = A(Zn) + A(Cu) \cdot X \quad (2)$$

respectively. From the 2 equations, we obtain the copper content as

$$X = \frac{A(X) - A'(X)}{A(Cu) - A'(Cu)} \quad (3)$$

The combination of the double irradiation technique and  $^{66}Cu$  formation permitted the determination of trace copper in zinc materials with poorly moderated neutrons in a relatively low power reactor.

Zinc dibenzylthiocarbamate was proposed as a suitable organic reagent for the spectrophotometric determination of copper in dyes and rubber chemicals by MARTENS AND GITHENS<sup>5</sup>, who reported that 0.5 g of zinc did not interfere in the determination. The reagent has also been used for the determination of copper in beers<sup>6</sup>. The spectrophotometric determination of the element in zinc materials with this reagent was employed in the present work for comparison with the results by neutron activation.

## EXPERIMENTAL

### *Apparatus*

Neutron irradiations were carried out in the 100-kW TRIGA Mark II Reactor of Rikkyo University in 2 positions—in the rotary specimen rack (thermal neutron flux:  $5 \cdot 10^{11}$  n/cm<sup>2</sup>/sec, the cadmium ratio (Au) : 3) and in the thermal column (thermal neutron flux:  $2.5 \cdot 10^{10}$  n/cm<sup>2</sup>/sec, the cadmium ratio for Au : 78). A 400-channel TMC pulse-height analyzer was coupled to a  $3 \times 3''$  NaI(Tl) crystal to detect  $\gamma$ -rays. A standard Geiger-Müller counter with a 0.9 mg/cm<sup>2</sup> thick mica end-window was used to detect  $\beta$ -rays. The spectrophotometer used in the colorimetric determination was a Hitachi model EPU 5.

### *Reagents*

Zinc sulfide phosphors containing various concentrations of copper, were prepared in the Government Chemical Industrial Research Institute, Tokyo. Highly purified zinc metal was prepared by Chisso Chemicals Co., Yokohama. Cadmium foils to shield thermal neutrons were 630 mg/cm<sup>2</sup> thick. All other chemicals were of reagent grade.

### *Preparation of copper standard*

A standard sample of copper was made by dropping 0.1 ml of copper(II) nitrate solution onto a 2.5-cm diameter filter paper while being dried with a blower. The filter

paper was sealed in a polyethylene sheet. A quantity of 102  $\mu\text{g}$  of copper was contained in the reference sample irradiated without the cadmium shield, and 2.30 mg of copper in the shielded sample.

#### *Sample irradiation*

About 0.2 g of zinc sulfide sample and the reference without the cadmium cover were put into a polystyrene capsule. The same sample and the reference shielded with cadmium were put at the center of the polystyrene capsule and the space was filled with boron powder. These polystyrene capsules were irradiated in the rotary specimen rack for 2 min. Highly purified zinc metal sample was irradiated in the thermal column for 2 min.

#### *Nondestructive determination procedure*

The irradiated sample and the reference were mounted separately on stainless steel dishes of 2.5 cm diameter. The  $\gamma$ -spectrum of the irradiated sample was measured for 4 min with a live-timer installed to correct the counting dead time. In addition to the live-timer an ordinary stop-watch was used to measure the true time of start and finish of the counting time, and the observed activities were corrected for decay to obtain the true activities at the end of bombardment. The sum of the measured activities around the 1.04-MeV peak of  $^{66}\text{Cu}$  was determined from the spectrum, and the Compton contribution from other nuclides was subtracted graphically. The counting of the reference was also made for 4 min and the activities of  $^{66}\text{Cu}$  at the end of bombardment were determined in the same manner as the sample. Subsequently, the irradiation and the activity measurements for the same sample and the reference shielded with cadmium were carried out under the same conditions as for the bare sample. Thus, the copper content was evaluated from the 4 observed activities by eqn. (3).

#### *Destructive determination procedure*

The irradiated sample was transferred into a beaker containing 20 mg of copper carrier as copper(II) nitrate solution; 10 ml of hydrochloric acid and a few drops of nitric acid were added and the sample was dissolved by heating. If any elemental sulfur appeared, it was removed. Some 10% sodium hydroxide was added to the solution until a precipitate appeared. After the precipitate was dissolved by addition of hydrochloric acid, about 5 g of sodium hydrogen sulfite powder were added. A precipitate of copper(I) thiocyanate was prepared by adding 10% ammonium thiocyanate solution. The precipitate was collected on a filter paper and washed with water containing a small amount of hydrochloric acid and ammonium thiocyanate, with pure water and finally with ethanol. After drying for 1 min under an infrared lamp, the precipitate was mounted on an aluminum planchet. The activities of the 2.63- and 1.65-MeV  $\beta$ -rays from  $^{66}\text{Cu}$  were measured for 4 min after placing a 212  $\text{mg}/\text{cm}^2$  thick aluminum absorber over the sample to absorb the 0.573-MeV  $\beta$ -rays from  $^{64}\text{Cu}$ . The chemical yield was obtained by weighing the thiocyanate after it was dried again by the infrared lamp and cooled in a desiccator containing phosphorus pentoxide. The irradiated standard was transferred to a beaker containing the copper carrier solution. Concentrated sulfuric acid was added while stirring, until the filter paper was dissolved and the solution became transparent. Copper(I) thiocyanate was

precipitated and the activities of  $^{66}\text{Cu}$  were measured in the same way as for the sample. The time required for chemical separation was about 10 min and the chemical yield was greater than 50%.

#### *Spectrophotometric procedure*

A zinc sulfide sample weighing 50–100 mg was dissolved in a minimum amount of nitric acid. After evaporating to dryness, the residue was taken up with a few ml of hydrochloric acid. The solution was again evaporated to remove nitric acid completely. The residue was dissolved with 0.1 *N* hydrochloric acid and the solution volume was adjusted to 25 ml with the acid solution in a volumetric flask. It was shaken with 10 ml of 0.01% zinc dibenzylthiocarbamate in carbon tetrachloride for 30 sec in a 50-ml separatory funnel. The absorbance of the carbon tetrachloride layer at 435  $m\mu$  was obtained using a 1-cm quartz cell. A calibration curve was obtained by carrying aliquots containing 0.8–40  $\mu\text{g}$  of copper through the extraction procedure in the same manner as the sample. Beer's law was obeyed in the above copper concentration range and no significant increase in absorbance occurred on the addition of 0.1 g of zinc.

#### RESULTS AND DISCUSSION

In order to compare the interference by (n,p) reactions in activation analyses using  $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$  and  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  reactions, pure metallic zinc wrapped with cadmium foil and copper without cadmium foil were irradiated for the same time interval in the same position and the activities of  $^{64}\text{Cu}$  produced in 1 g of the elements were compared. Subsequently, the activities of  $^{66}\text{Cu}$  in 1 g of zinc and copper were also compared in the same manner as  $^{64}\text{Cu}$ . These results are shown in Table I.

TABLE I

COMPARISON OF INTERFERENCE BY (n,p) REACTIONS IN ACTIVATION ANALYSIS USING  $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$  AND  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$

Irradiation position	Nuclide produced	Activities of radioactive copper	
		counts/min/g Zn	counts/min/g Cu
Rotary specimen rack	$^{64}\text{Cu}$	$7.98 \cdot 10^3$	$1.21 \cdot 10^7$
Rotary specimen rack	$^{66}\text{Cu}$	$5.89 \cdot 10^5$	$1.61 \cdot 10^{10}$
Thermal column	$^{66}\text{Cu}$	$6.31 \cdot 10^2$	$8.22 \cdot 10^8$

The activities of  $^{64}\text{Cu}$  and  $^{66}\text{Cu}$  produced by the (n,p) reactions in 1 g of zinc irradiated in the rotary specimen rack were equivalent to the activities produced by the (n, $\gamma$ ) reactions in 660 and 36.6  $\mu\text{g}$  of copper respectively. Therefore, the disturbance by (n,p) reaction in activation analysis using the  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  reaction was much less significant than using the  $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$  reaction. The activity of  $^{66}\text{Cu}$  from 1 g of pure zinc irradiated in the thermal column was equivalent to that from only 0.77  $\mu\text{g}$  of copper.

The cross-sections of the  $^{64}\text{Zn}(n,p)^{64}\text{Cu}$  and  $^{66}\text{Zn}(n,p)^{66}\text{Cu}$  reaction for fission spectrum neutrons were evaluated from the figures of rotary specimen rack irradiations in Table I and from the following data: cross-sections of  $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$



and  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  for thermal neutrons were 3.8 and 1.6 b (the cross-sections for neutrons at the velocity of 2200 m/sec were multiplied by  $\sqrt{\pi}/2$ )<sup>7</sup>; isotopic abundances of  $^{63}\text{Cu}$ ,  $^{65}\text{Cu}$ ,  $^{64}\text{Zn}$  and  $^{66}\text{Zn}$  were 69.1, 30.9, 48.89 and 27.81% respectively; thermal neutron flux was  $5.0 \cdot 10^{11}$  n/cm<sup>2</sup>/sec, and equivalent fission spectrum neutron flux was  $6.5 \cdot 10^{10}$  n/cm<sup>2</sup>/sec. The flux was calculated from the cross-section of  $^{31}\text{P}(n,p)^{31}\text{Si}$  reaction which was 31 mb<sup>8</sup>. These results and earlier cross-section values<sup>9</sup> are compiled in Table II.

Our result for  $^{64}\text{Zn}(n,p)^{64}\text{Cu}$  reaction cross-section agrees well with the previous data including PASSELL AND HEATH'S<sup>10</sup>. For the  $^{66}\text{Zn}(n,p)^{66}\text{Cu}$  reaction, no

TABLE II

CROSS-SECTION OF (n,p) REACTIONS FOR FISSION SPECTRUM NEUTRONS

Authors	Cross-section (mb)		
	$^{64}\text{Zn}(n,p)^{64}\text{Cu}$	$^{66}\text{Zn}(n,p)^{66}\text{Cu}$	$^{67}\text{Zn}(n,p)^{67}\text{Cu}$
This work	28	0.51	—
PASSELL AND HEATH (1959) <sup>10</sup>	28	—	0.57
MELLISH <i>et al.</i> (1958) <sup>1</sup>	44	—	0.54
DURHAM (1960) <sup>11</sup>	49	—	0.8
ROCHLIN (1959) <sup>12</sup>	35	—	—
HOGG AND WEBER (1962) <sup>13</sup>	26	—	—

other data for reference could be found. The observed cross-section value, 0.51 mb, was lower than the literature values for the  $^{67}\text{Zn}(n,p)^{67}\text{Cu}$  reaction. For a given element, the (n,p) reaction cross-section must decrease with increasing weight of the isotope, since the heavier isotopes are already neutron-rich, so that the reaction would carry them even further from the most stable neutron-proton ratio  $N/Z$ <sup>14</sup>. This contradictory result may be explained by considering that in the case of the  $^{67}\text{Zn}(n,p)^{67}\text{Cu}$  reaction the neutron which is being added is an even one and the proton which is displaced is an odd one. Therefore, the threshold will be much lower for  $^{67}\text{Zn}(n,p)^{67}\text{Cu}$

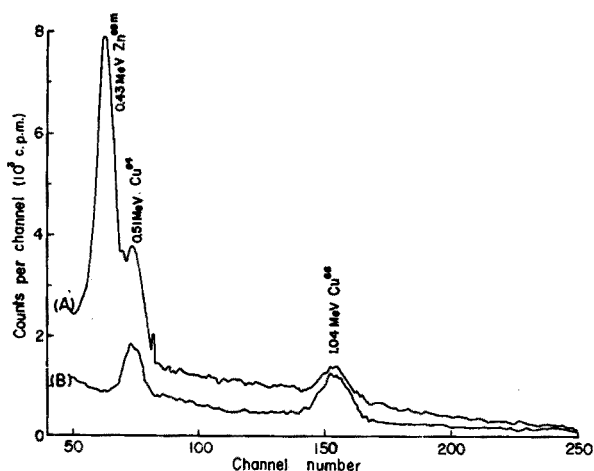


Fig. 1.  $\gamma$ -Ray spectra of the activated zinc oxide and copper. (A) 100 mg of ZnO containing 800 p.p.m. Cu, 7 min after irradiation. (B) 102  $\mu\text{g}$  of Cu, 8 min after irradiation.

reaction than  $^{66}\text{Zn}(n,p)^{66}\text{Cu}$  and the cross-section value of the latter reaction may be smaller.

To check the proposed methods, zinc oxide samples containing copper were prepared from pure zinc metal by adding a definite amount of copper, dissolving with nitric acid in a platinum dish, evaporating it to dryness and igniting at  $1000^\circ$  in an electric oven. Fig. 1 shows the  $\gamma$ -ray spectra obtained after irradiation from 0.1 g of the zinc oxide sample containing 800 p.p.m. of copper and from a 102- $\mu\text{g}$  copper standard; Fig. 2 shows the spectra from the same sample and the copper standard

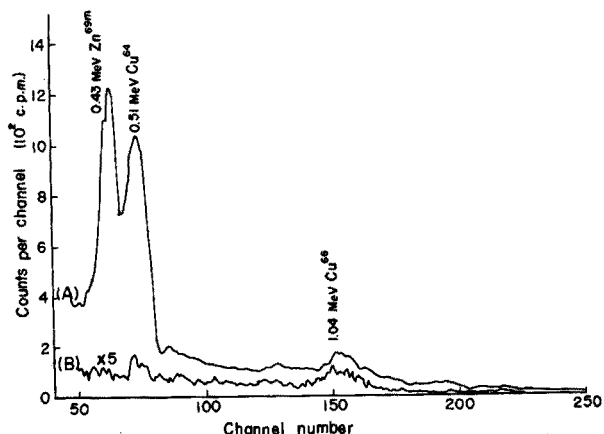


Fig. 2.  $\gamma$ -Ray spectra of activated zinc oxide and copper wrapped with cadmium foil. (A) 200 mg of ZnO containing 800 p.p.m. Cu, 8 min 45 sec after irradiation. (B) 2.30 mg of Cu, 11 min after irradiation.

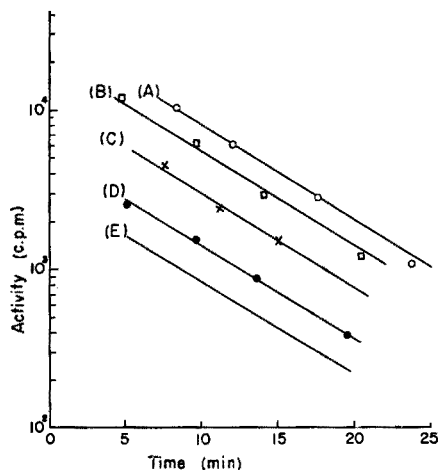


Fig. 3. Decay curves of 1.04-MeV peaks. (A) bare Cu; (B) bare ZnO; (C) Cu wrapped with Cd; (D) ZnO wrapped with Cd; (E) theoretical curve of 5.1-min half-life.

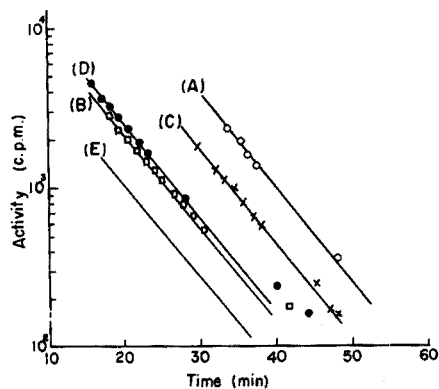


Fig. 4. Decay curves of copper(I) thiocyanates purified by the radiochemical procedure. (A) bare Cu; (B) bare Zn; (C) Cu wrapped with Cd; (D) Zn wrapped with Cd; (E) theoretical curve of 5.1-min half-life.

shielded with cadmium. As shown in Fig. 1, utilization of the 0.51-MeV annihilation radiation from  $^{64}\text{Cu}$  is impossible because of the interference by the predominant photopeak of 0.43-MeV  $\gamma$ -ray from  $^{69\text{m}}\text{Zn}$ . On the other hand, a tiny but sharp peak, probably due to  $^{66}\text{Cu}$  was found at 1.04 MeV in Fig. 1. This photopeak was also found in Fig. 2 for the sample shielded with cadmium, but the activity was much less than for the bare sample.

Fig. 3 shows that decay of the 1.04-MeV peaks corresponds to a half-life of 5.1 min and that the influence of the weak 1.09-MeV  $\gamma$ -ray<sup>15</sup> from 2.1-min  $^{71}\text{Zn}$  is insignificant.

Decay curves for copper(I) thiocyanate purified by the radiochemical proce-

TABLE III  
ACTIVITIES OF  $^{66}\text{Cu}$  PRODUCED IN 1 g OF ZINC SULFIDE SAMPLE AND COPPER

Procedure	Sample	Activity (counts/min)	
		Bare	Cd-shielded
Nondestructive	ZnS II	$2.10 \cdot 10^5$	$1.70 \cdot 10^4$
Nondestructive	Cu	$5.07 \cdot 10^8$	$9.10 \cdot 10^8$
Destructive	ZnS II	$6.72 \cdot 10^6$	$5.40 \cdot 10^5$
Destructive	Cu	$1.70 \cdot 10^{10}$	$3.26 \cdot 10^8$

TABLE IV  
COMPARATIVE RESULTS BY SPECTROPHOTOMETRY AND ACTIVATION ANALYSES (p.p.m. Cu)

Sample	Spectrophotometric	Nondestructive	Destructive
ZnO I	775, 784, 829 Av. 796	704, 710, 731, 737, 756, 762, 839, 857 Av. $762 \pm 57$	737, 782, 847, 979 Av. 836
ZnO II	203, 210 Av. 207	171, 190, 190, 192, 203, 213, 215, 219 Av. $199 \pm 17$	190
ZnO III	32.5, 33.3, 39.0 Av. 34.9	—	31.1, 33.0, 35.0, 40.4, 43.2 Av. $36.5 \pm 5.1$
ZnS I	698, 719 Av. 709	632, 662, 669, 693, 701 Av. $671 \pm 28$	—
ZnS II	377, 383 Av. 380	375, 387, 409 Av. 390	370
ZnS III	76.4, 76.7, 78.3 Av. 77.1	98.4	83.8
ZnS IV	19.5, 21.2 Av. 20.4	—	30.2, 30.9 Av. 30.6
Zn I	—	—	0.42, 0.49, 0.51 Av. 0.47
Zn II	—	—	0.74, 0.93, 1.13 Av. 0.93

ture from the irradiated zinc metal and copper standard, are shown in Fig. 4. All the curves corresponded to the half-life of  $^{66}\text{Cu}$ .

$^{66}\text{Cu}$  activities obtained by  $\gamma$ -ray spectrometry and by the radiochemical procedure were corrected to those at the end of bombardment and to 100% chemical yield. Examples of the activities thus obtained for a zinc sulfide sample are shown in Table III. The copper contents obtained by substitution of these figures into eqn. (3) were 387 and 370 p.p.m. by nondestructive and destructive activations respectively.

Typical results of the copper concentration in zinc oxides, zinc sulfide phosphors and zinc metals by the activation analyses and spectrophotometry are shown in Table IV. No significant difference was found among the values for the 3 procedures except for the ZnS IV sample. Although fairly good agreement was obtained between the spectrophotometric and destructive activation method for zinc oxide samples of low copper concentrations, the destructive activation result was slightly higher than the spectrophotometric one for ZnS III and IV. This might have arisen from incomplete decontamination from 5.1-min  $^{37}\text{S}$  which was produced by a  $(n,\gamma)$  reaction (cross-section: 0.14 b) on  $^{36}\text{S}$  (isotopic abundance: 0.016%) and which might have been exchanged with sulfur atoms in thiocyanate. Results by activation analysis for highly purified zinc metals could not be compared with spectrophotometric results, so that no discussion of accuracy is possible; however, the results show that the proposed activation method is satisfactorily precise for samples of such low concentrations of copper.

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#### SUMMARY

The nondestructive and destructive determinations of copper in zinc materials by neutron activation using  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  reaction are described. Observed cross-sections of  $^{64}\text{Zn}(n,p)^{64}\text{Cu}$  and  $^{66}\text{Zn}(n,p)^{66}\text{Cu}$  reactions for fission spectrum neutrons were 28 and 0.51 mb respectively. A double irradiation technique with one sample wrapped in cadmium foil and another bare, was employed for the correction of the concurrent formation of  $^{66}\text{Cu}$  by  $(n,p)$  reaction. 100 p.p.m. of copper in zinc sulfide was determined nondestructively by  $\gamma$ -ray spectrometry using a thermal flux of  $5 \cdot 10^{11}$  n/cm<sup>2</sup>/sec, while 0.5 p.p.m. of copper in zinc was determined by a thermal flux of  $2.5 \cdot 10^{10}$  n/cm<sup>2</sup>/sec, and by a rapid chemical separation involving copper(I) thiocyanate precipitation. The proposed activation procedures were compared with the spectrophotometric dibenzylthiocarbamate procedure.

#### RÉSUMÉ

Les auteurs décrivent les dosages non-destructifs et destructifs du cuivre dans le zinc, par activation au moyen de neutrons, en utilisant la réaction  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$ . On a dosé ainsi 100 p.p.m. de cuivre dans un sulfure de zinc par spectrométrie gamma, en utilisant un flux thermique de  $5 \cdot 10^{11}$  n/cm<sup>2</sup>/sec, tandis que 0.5 p.p.m. de cuivre dans le zinc sont dosés avec un flux thermique de  $2.5 \cdot 10^{10}$  n/cm<sup>2</sup>/sec, et par sépara-

tion chimique rapide avec précipitation de thiocyanate de cuivre(I). Les procédés par activation, proposés, sont comparés avec la méthode spectrophotométrique au dibenzylthiocarbamate.

## ZUSAMMENFASSUNG

Die Bestimmung von Kupfer in Zinkmaterialien mit der Neutronenaktivierungsanalyse unter Verwendung der Reaktion  $^{65}\text{Cu}(n,\gamma)^{66}\text{Cu}$  wird beschrieben. Für Neutronen des Spaltspektrums werden Einfangsquerschnitte für  $^{64}\text{Zn}(n,p)^{64}\text{Cu}$  und  $^{66}\text{Zn}(n,p)^{66}\text{Cu}$  von 28 bzw. 0.51 mb beobachtet. Zur Korrektur der konkurrierenden Bildung von  $^{66}\text{Cu}$  durch die (n,p)-Reaktion wurde eine doppelte Bestrahlungstechnik entwickelt, bei der eine von zwei Proben in eine Cadmiumfolie gewickelt wurde. Ohne Zerstörung der Probe wurden 100 p.p.m. Cu in Zinksulfid mit der  $\gamma$ -Spektrometrie bestimmt bei einem thermischen Fluss von  $5 \cdot 10^{11}$  n/cm<sup>2</sup>/sec. Durch schnelle Fällung von Kupfer(I)-thiocyanat wurden 0.5 p.p.m. Kupfer bei einem thermischen Fluss von  $2.5 \cdot 10^{10}$  n/cm<sup>2</sup>/sec bestimmt. Die vorgeschlagenen Aktivierungsverfahren wurden mit der spektralphotometrischen Bestimmung mittels Dibenzylthiocarbamat verglichen.

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## RAPID DETERMINATION OF MAGNESIUM IN THE PRESENCE OF CALCIUM AND PHOSPHATE BY TITRATION WITH CDTA

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A very large number of compleximetric titration methods for the determination of magnesium have been published in which magnesium is determined as the difference in 2 titrations. None of these methods has found widespread usage for extremely low levels of magnesium oxide and wide ranges of calcium oxide to magnesium oxide ratios in the presence or absence of large quantities of phosphate because of the non-reproducibility of the titration at the higher ratios of calcium to magnesium and the positive interferences from trace metal concentration for which empirical corrections must be made. The work described here presents a procedure whereby high or extremely low levels of magnesium are determined at wide ranges of calcium to magnesium ratios and without prior removal of phosphate.

The fundamental concepts of compleximetry have been extensively discussed in the literature<sup>1-5</sup>. VAN THIEL AND TUCKER<sup>6</sup> investigated the titration of magnesium in the presence of phosphates; phosphate interfered and was removed by precipitation with iron(III) at a low pH. LOTT AND CHENG<sup>7</sup> substituted calcon for murexide in the calcium titration and completed the titration with EDTA using eriochrome black T indicator after adjusting to pH 10. CARLSON AND JOHNSON<sup>8</sup> removed phosphate and interfering metals on a cyclohexanediaminetetraacetate (CDTA) anion-exchange column. This is both time-consuming and cumbersome for day-to-day usage. SCHMID AND REILLY<sup>9</sup> and RINGBOM *et al.*<sup>10</sup> discuss the theoretical aspects of titrating magnesium and calcium selectively in pure solutions, but the effects of known interfering ions and wide ranges of calcium to magnesium ratios are not discussed and the work is of little practical use for actual sample conditions.

Many proposals for masking or removing interfering metals before the combined magnesium and calcium titration at pH 10 have been described<sup>3-5,11,12</sup>. None of them fully mask or otherwise eliminate interferences even in the simplest matrices where the magnesium oxide level is extremely low, *i.e.*, *ca.* 0.05%. Rather, the interfering metal ions are only reduced to a minimum level whereby the higher values of magnesium oxide, *i.e.*, > 1.0%, can be determined within a fairly narrow range of calcium to magnesium ratio. In addition, all proposed masking techniques checked in this laboratory on typical phosphate samples resulted in either or both inactivation of the indicator or interference between the masking agents and phosphate.

Magnesium was determined by REDMOND<sup>13</sup> in the presence of large quantities of calcium by preferentially precipitating and titrating as magnesium 8-quinolinolate in the presence of calcium oxalate. The method was not precise for very low levels of magnesium because of the probable coprecipitation of some magnesium as magnesium

oxalate and because of the low solubility of magnesium ammonium phosphate. Later<sup>14</sup> it was theorized that removal of ammonium ions and substitution of sodium ions would greatly improve the stability and reliability of the procedure at very low magnesium levels. This method proved to be reliable under very precise conditions which are extremely difficult to define properly for general usage from laboratory to laboratory.

In the work described here, cyclohexanediaminetetraacetic acid (CDTA) was substituted for EDTA, thus increasing the pertinent equilibria of the metal-CDTA complexes by the order of  $10^2$  compared to the same metal-EDTA complexes. It was proved that this increased stability was necessary to bring about consistently sharp complex formation and end-point detection. Interfering metals are complexed with CDTA in acid solution. The pH is then adjusted to 5.0 and the excess CDTA determined by titration with standard zinc solution using xylenol orange indicator. Total metal ion concentration is determined on a separate aliquot in the same manner except the pH is adjusted to 10.0 and the excess CDTA is titrated with standard magnesium solution using eriochrome black T indicator. Calcium is determined with calcein II modified indicator under UV light by titration with CDTA at a pH > 12. Magnesium is calculated from these titrations with an unequivocal linear correction for interferences. The titrations, although so-called back-titrations, require little, if any, more time to complete since the complexes are actually formed more rapidly in excess CDTA than if a direct titration were used, *i.e.*, aluminum and iron.

#### EXPERIMENTAL

##### *Apparatus and reagents*

Ultraviolet titration assembly, Fisher Scientific Co. No. 15-182-600V2, 10-ml microburets; magnetic stir light Thermolyne, Fisher Scientific Co. No. 14-511-100VI.

*CDTA (hexaver, Hach Chemical Co., Ames, Iowa)*. Dilute a known volume of a saturated solution of CDTA to 0.05 M. Standardize at pH 5 using xylenol orange indicator against 0.0500 M zinc chloride solution prepared from pure zinc metal.

*Calcium chloride 0.02 M*. Add excess of hydrochloric acid to 4 g of primary standard calcium carbonate, boil to expel all CO<sub>2</sub>, cool and dilute to 2 l with CO<sub>2</sub>-free distilled water. Standardize against CDTA.

*Zinc metal*, 20-mesh Fisher certified, Fisher Scientific Co. No. Z-15.

##### *Recommended procedure*

*General*. Accurately weigh 2.5–2.6 g of sample into a 250-ml pyrex beaker. Add 15–20 ml of 72% perchloric acid and 10–15 ml of water. Digest to strong fumes of perchloric acid, *i.e.*, until the liquid is 5 ml or less. Remove from the heat, partially cool, and dilute to about 50 ml with water, adding the first 10–20 ml cautiously. Heat gently to dissolve all the perchlorates, then filter and wash the residue acid free with hot water, catching the filtrate and washings in a 250-ml volumetric flask.

*Caution*. Do not use perchloric acid on any samples containing appreciable quantities of organic solvents or organic matter of any kind. Either fuse them or make a preliminary acid digestion with nitric acid. Then add perchloric acid and digest until all the nitric acid is gone; usually two additions of perchloric are required, fuming the first strongly, cooling, then adding a few milliliters of water and the second, then again fuming. Under no circumstance use any hood connected with a hood system

that might contain organic vapors. Use a separate hood with a separate vent to the atmosphere, or better a hood specially designed for digestion with perchloric acid.

*Total metals.* Pipet an aliquot of the same size as that used for calcium into a 250-ml beaker. Add an 8- to 9-ml excess of 0.05 *M* CDTA. Dilute to about 100 ml with distilled water and adjust to pH  $10.0 \pm 0.03$  using 10% sodium hydroxide and saturated boric acid solution. Add 0.25–0.30 ml of eriochrome black T indicator solution (0.15 g of dye and 0.5 g of sodium borate in absolute methanol). Titrate the excess CDTA with 0.05 *M* magnesium sulfate solution to the first discernible tinge of violet.

*Interfering metals.* Pipet the same size of aliquot as that used for the calcium determination into a 250-ml beaker. Add an 8- to 9-ml excess of CDTA and dilute to about 100 ml with distilled water. Adjust the solution to pH  $5.0 \pm 0.1$  with 10% sodium hydroxide solution. Then add 10 ml of sodium acetate buffer solution (70 g of sodium acetate per l adjusted to pH 5.0 with glacial acetic acid). Add 0.2 ml of aqueous 0.4% xylenol orange indicator. Titrate the excess of CDTA with 0.05 *M* zinc sulfate solution to the first perceptible change from yellow to orange yellow.

*Calcium.* Pipet a 5- or 10-ml aliquot into a 250-ml beaker. Dilute to about 100 ml with distilled water. Adjust to pH  $> 12$  with potassium hydroxide (pellets or 45% (w/w) solution). Add 0.01 g of modified calcein II; or if desired, add 0.15 ml of calcein W solution (0.5 g of dye dissolved in 25 ml of 0.5 *N* potassium hydroxide and diluted to 50 ml with water), and 0.25 ml of aqueous 0.2% bromothymol blue. Place the beaker in the chamber of the ultraviolet titrator assembly and add excess CDTA with stirring. Stir the reaction mixture for 6–8 min, and then titrate the excess CDTA with 0.02 *M* calcium chloride solution to the first permanent fluorescence. Very carefully discharge the fluorescence with 0.05 *M* CDTA.

*Calculation.*

$$\% \text{Mg}^{2+} = \frac{[A - (B + C)] (24.31 \text{ mg Mg/mM CDTA})(100)}{\text{sample in the aliquot (mg)}}$$

where A = net millimoles of total metals; B = net millimoles of calcium; C = net millimoles of interfering metals.

## DISCUSSION

Although a perchloric acid digestion for all samples is recommended, it is only necessary for wet process phosphoric acid samples and products derived therefrom. It was found that in the presence of both chloride and/or ammonia, results for magnesium were quite inconsistent and low in commercial phosphoric acid samples, though they were not apparently affected in phosphate rock samples. From a study of the pertinent equilibria expected at both pH 5 and pH 10, it was surmised that the M–CDTA complexes formed in acidic solution with excess CDTA were stable to chloride, and ammonia at pH 5 when excess CDTA was discharged with zinc. However, the same complexes were not totally stable to chloride and ammonia at pH 10, and competing equilibria occurred among some of the known metal ammonia, chloride and/or hydroxide complex formers and the M–CDTA complexes. Excess CDTA prevents the formation of the competing magnesium ammonium phosphate. Thus it, as well as hydroxyl ion concentration, had no apparent effect on the results. When the suspected



interfering ions were removed from the system by using only perchloric acid for digestion and a sodium or potassium borate buffer system, the competing equilibria as well as spurious results were eliminated.

The direct titration of calcium with CDTA involves a partition equilibrium with calcium phosphate, calcium hydroxide and CDTA, each competing for the calcium. This leads to a slow and tedious titration, especially near the end-point. In order to circumvent this, excess of CDTA is added to the calcium solution to force the reaction to completion. Then, when excess CDTA is discharged, the titration proceeds rapidly. This technique enabled more accurate and precise results to be obtained in about one-third of the time ordinarily required for a direct titration. Adsorption of the calcium hydroxide described by POVONDA AND PRIBIL<sup>11</sup> was not observed even in systems where the magnesium concentration exceeded the calcium concentration. The pH was adjusted with potassium hydroxide instead of sodium hydroxide because of residual fluorescence and hydration that can occur with sodium hydroxide.

None of the many attempts to mask or remove interfering metals in the combined calcium and magnesium determination has been totally adequate even under nearly ideal conditions. In the complex system described here it was apparent that a successful method had to include an absolute method of determining interfering metals. A study of the metal-complex stability characteristics showed that in addition to the preferential chelation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at pH 10 a partial chelation of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ , etc. also occurred. By addition of excess of standard CDTA in acid solution, followed by adjustment to pH 5.0, all the metals except calcium and magnesium were chelated. Excess CDTA was titrated with standard zinc solution and the concentration of interfering metals calculated. Then addition of excess CDTA to another sample under the same conditions followed by adjustment to pH 10 resulted in chelation of all the metals including calcium and magnesium. Again the excess CDTA was titrated with standard magnesium solution and the total metal concentration calculated. The preferential formation of the metal chelates in acid solution eliminated any competing equilibria from metal-hydroxide or hydrous oxide formation as the solution was adjusted to pH 10. Thus, the difference between the pH 10 and the pH 5 determinations truly represented combined calcium and magnesium.

Phosphate did not interfere in this analysis even when the ratio of phosphate to either calcium or magnesium was 2500 : 1. Magnesium phosphate precipitation was prevented both by preferential chelation and elimination of ammonia from the system. Calcium phosphate as well as calcium hydroxide precipitate above pH 12, but the technique used for titration circumvented any phosphate interference. End-point detection using CDTA in the presence of phosphate was as sharp and sensitive as in its absence. In the presence of murexide indicator, phosphate did interfere with the calcium titration but not when calcein W was used. Metal-phosphate compounds as well as metal-hydrous oxides and possible chloride and ammonia complexes were of course included in the pertinent equilibria studies. Likewise, these were also selectively eliminated by the removal of offending ions and preferential chelation in acid solution.

It must be emphasized that this procedure requires care to accomplish a successful analysis. The pH adjustments must be done on a reliable pH meter using symmetrical electrodes. Duplicate titrations should agree within  $\pm 0.001$  and  $\pm 0.005$  mmole at the 0.5 and 0.05 mmole level, respectively, or the results will be inconsistent.

Microburets are suggested for all the titrations.

Although this work specifically covered phosphatic materials, the procedures described can also be used for non-phosphatic materials. This procedure has been used in our laboratory for all types of inorganic and many organic compounds containing both extremely low and large amounts of calcium and magnesium for several months. Thus far no limiting interferences have been observed after proper conversion of the samples to the perchlorate system.

## RESULTS

Data in Table I represent the recovery of different levels of magnesium added to several phosphate rock samples. The calcium oxide and phosphate levels in the samples ranged from 45 to 48% CaO and 28 to 34% P<sub>2</sub>O<sub>5</sub>. The magnesium content of the samples was determined classically in 2 laboratories and by the described method

TABLE I  
RESULTS OF MAGNESIUM RECOVERY FROM PHOSPHATE ROCK

Sample	No. of replicates	MgO (mg)			Recovery of added MgO (Av. %)	% Rel. std. dev.	% MgO in sample
		Added	Recovered	Range			
1	6	None	1.34	1.34-1.35	103.9	0.34	0.67
	4	1.85	3.26	3.23-3.29			
2	2	None	3.08	3.07-3.07	96.7	1.31	1.63
	2	1.85	4.87	4.87-4.87			
3	2	None	0.14	0.12-0.15	102.3	0.75	0.07
	4	1.85	2.03	1.99-2.07			
4	2	5.55	5.54	5.49-5.58	97.4	0.98	1.01
	2	None	0.84	0.81-0.86			
5	6	5.55	6.14	6.11-6.22	95.6	0.45	2.77
	5	None	0.22	0.20-0.25			
	5	9.30	9.04	9.22-9.32	97.2		0.42
							3.07
							0.11
							4.52

in this laboratory. Recovery of added magnesium was determined by the described procedure. All the data were good, ranging from 95.6 to 103.9% for recovery of magnesium added to the various samples with the percent relative standard deviation ranging from 0.45 to 1.31% of the recovered magnesium. The precision of the method at levels of 0.11% and 0.67% magnesium oxide ranged from 0.98 to 0.34% relative standard deviation. It is difficult to predict the accuracy of magnesium and calcium determinations at extremely low levels of 0.005 to 0.02% MgO and 0.005 to 0.05% CaO because the classical methods are not sufficiently accurate to rely on the results. Likewise, flame emission is wrought with interferences in this system. Flame absorption methods, however, are very promising for low levels of magnesium oxide. By the described procedure, precision is about  $\pm 4\%$  with an estimated accuracy of  $\pm 6\%$  for magnesium oxide which is currently better than flame absorption techniques.

Table II shows the results obtained by classical and the described chelation procedures for magnesium in typical phosphate rock and wet process phosphoric acid samples. Calcium oxide values are included to show the CaO/MgO ratios covered. The values for magnesium cover a wide range with the calcium:magnesium ratios ranging

TABLE II

DETERMINATION OF CALCIUM AND MAGNESIUM BY CLASSICAL AND THE PROPOSED CHELATION PROCEDURES

Sample	CaO (%) Chelation	MgO (%)		Type
		Classical <sup>a</sup>	Chelation	
1	45.20	0.30	0.42	Phosphate rock
2	46.61	0.20	0.23	
3	46.10	0.45	0.38	
4	45.52	0.67	0.67	
5	45.35	0.70	0.68	
6	47.96	0.38	0.40	
7	46.16	0.49	0.42	
8	45.82	0.75	0.77	
9	48.26	0.21	0.07	
10	0.24	0.05	0.02	Phosphoric acid
11	0.06	0.04	0.03	
12	0.13	0.53	0.56	
13	0.06	0.48	0.52	
14	0.23	0.66	0.60	

<sup>a</sup> Double pptn. as  $Mg(NH_4)PO_4$  after separating magnesium sulfate from calcium sulfate with methanol.

from 1:9 to 850:1. The magnesium results for phosphate rock by classical procedures are based on data obtained from the Agrico Chemical Company Laboratory at Pierce, Florida, and our own laboratory. Phosphoric acid samples were all analyzed in our laboratory and range from 42 to 73%  $P_2O_5$ . Comparison of the magnesium results shows essentially no significant difference between the methods except for sample No. 9 for which we have no explanation. The absolute difference in magnesium results for phosphoric acid by the 2 different methods appears to be quite large; however, the significance of this variation must be questioned since the reliability of the classical and chelation as well as flame absorption methods at these low levels is not known.

## SUMMARY

A method is presented for the accurate determination of magnesium in phosphate rock and phosphoric acid down to 0.03% magnesium oxide in the presence of 0-70% phosphorus pentoxide by titration with cyclohexanediaminetetraacetic acid (CDTA). Interference from heavy metals for which inaccurate empirical corrections have previously been made in the combined magnesium and calcium titration are linearly and unequivocally determined and subtracted from the combined titration. Magnesium oxide is determined in less than 20 min after sample digestion for Ca:Mg ratios from 1:9 to 850:1.

## RÉSUMÉ

Une méthode est présentée pour le dosage du magnésium dans des roches phosphatées et dans l'acide phosphorique (0.03% MgO en présence de 0-70%  $P_2O_5$ ).

On procède par titrage au moyen d'acide cyclohexanediaminotétracétique (ACDT). On tient compte des interférences des métaux lourds. L'oxyde de magnésium est dosé en moins de 20 min après digestion de l'échantillon (rapports Ca:Mg de 1:9 à 850:1).

#### ZUSAMMENFASSUNG

Es wird eine Methode angegeben zur genauen Bestimmung von Magnesium in Phosphatmineralien und Phosphorsäure. Es können noch 0.03% Magnesiumoxid in Gegenwart von 0-70% Phosphorpentoxid durch Titration mit Cyclohexandiamin-tetraessigsäure (CDTE) bestimmt werden. Störungen durch Schwermetalle, für die früher ungenaue empirische Korrekturen bei der kombinierten Magnesium- und Calciumtitration durchgeführt werden mussten, werden eliminiert. Nach der Probenzubereitung kann das Magnesiumoxid in weniger als 20 Minuten bestimmt werden für Ca:Mg-Verhältnisse von 1:9 bis 850:1.

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## "PALLADIAZO" A NEW SELECTIVE METALLOCHROMIC REAGENT FOR PALLADIUM

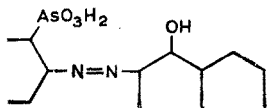
### PART I. THE MAIN CHARACTERISTICS OF THE PURE REAGENT AND ITS REACTION WITH PALLADIUM(II)\*

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Since the synthesis of the reagent arsenazo I, reported in 1941 by KUZNETSOV<sup>1</sup>, a great deal of attention has been given to the analytical possibilities of chromogenic reagents derived from the coupling of chromotropic acid with *o*-phenylarsonic acid. The great sensitivity of the metallochromic reactions of such reagents with many metallic cations results from chelate formation; this is especially favoured by the presence of the molecular grouping



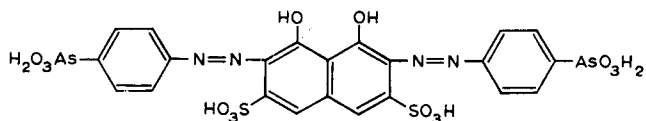
which possesses both salt-forming and chelating functional groups.

A further improvement of considerable interest was introduced by the synthesis of the reagent "arsenazo III" reported by SAVVIN<sup>2</sup> in 1959, which represents a bis-diazoarsenazo containing all the analytical functional groups of "arsenazo I" duplicated. Since then, a good deal of synthesis and analytical work has been done on derivatives of "arsenazo III" by introducing different functions at different substitution sites in its basic molecular structure, in attempts to improve its selectivity properties<sup>3-8</sup>. Such investigations have proved fruitful and the analytical stock of organic reagents has been enriched by many valuable new bis-diazoarsenazo spectrophotometric reagents which possess both great sensitivity and enhanced selectivity for a number of elements. The theoretical aspects involved in the complex formation between such reagents and cations have also been widely investigated in recent years<sup>4,5,7,9-16</sup>; the pertinent reaction mechanisms are fairly well understood at the present time.

Nevertheless, it is interesting to notice that the general trend of investigation has kept on the line of essentially *o,o'*-substitution, since the basic complexing properties both of "arsenazo I" and "arsenazo III" are ascribed to the diazo group(s) and the arsonic radical(s) present as *o*- or *o,o'*-substituent(s).

The above facts made it seem of interest to attempt the synthesis of an isomer of "arsenazo III" with substitution in the *p,p'*-sites instead of the *o,o'*-positions.

\* Paper presented at the XIIth Biennial Meeting of the Spanish Royal Society of Physics and Chemistry, Salamanca, Spain, June 1965.



Such a reagent would allow a comparative study of the properties of the new reagent and its main complex-formation characteristics and a correlation with the *o,o'*-isomer ("arsenazo III"). This correlation might throw new light on the role of the arsonic acid groups as substituents in the molecular structure considered, and might lead to a better understanding of such basic analytical requirements as those constituted by the sensitivity, selectivity, and strength of the complexes involved.

#### EXPERIMENTAL

##### *Instruments and chemicals*

Gamma and Pye pH-meters accurate to 0.05 pH units. Beckman DU spectrophotometer with 4 glass cells of 10-mm path-length. Glass and plastic columns to carry out ion-exchange experiments. Afora type 5208 semimicro Kjeldahl apparatus.

The following chemicals were used: *p*-phenylarsonic acids (Fluka, B.D.H., Schuchardt and Austranal), chromotropic acid (Fluka, B.D.H., Merck, Hopkins-Williams, Schuchardt and Austranal), calcium oxide (May & Baker), palladium chloride (Schuchardt and Fluka), dimethylglyoxime (Merck), cetyldimethylbenzylammonium chloride (F. Berk and Co., Ltd.), Dowex 21K, 20–50 mesh, anion-exchange resin, and Dowex 50W, 50–100 mesh, cation-exchange resin. All the chemicals used were of p.a. quality, or the best quality available unless otherwise stated.

##### *Synthesis of the reagent*

The reagent was prepared following essentially SAVVIN's instructions<sup>2,5,9</sup> for arsenazo III. Further purification was done by repeated reprecipitation–dissolution cycles and finally an aqueous solution of the reagent was passed through a layer of cation-exchange resin in the hydrogen form in order to obtain the free acid form of the bis-diazoarsenazo.

*p*-Phenylarsonic acid (10 g) was dissolved in 50 ml of an aqueous solution containing 12 ml of concentrated hydrochloric acid cooled to 0–4°. This solution was diazotized by slowly adding about 10 ml of 5 *M* sodium nitrite solution controlling the end of the process with starch–iodide paper\*. The solution of the diazonium salt at 4° was added slowly and under constant stirring to 125 ml of an aqueous suspension cooled at 4° containing 5 g of chromotropic acid (obtained in the free acid form by passing an aqueous solution of the disodium salt through a cation-exchange resin in the H-form) and 10 g of calcium oxide. The reaction mixture was kept at *ca.* 4° during the whole process by using an ice-jacket and by addition of ice pieces to the suspension as needed and was stirred at 4° for 1 h after the end of the coupling process. Then

\* In some cases—in connection with other syntheses—attempts were made to eliminate the excess of nitrous acid at the end of the diazotization by adding small portions of solid sulphamic acid. As stated in detail elsewhere<sup>17</sup>, this procedure led to a massive "thermal degradation" of the reagent on drying at 100–110°, which makes the reagent completely unsuitable for analytical purposes. The involved mechanism of decomposition is not known with certainty.

100 ml of concentrated hydrochloric acid were added, and the mixture was diluted with distilled water to about 1 l. The mixture was left standing for 24 h at 4° (freezing chamber) and was subsequently vacuum-filtered through a No. 4 sintered-glass filter. The filtrate was discarded and the retained solid was first washed with 100 ml of hot 1:1 hydrochloric acid, discarding the filtrate, and then dissolved on the filter with 250 ml of a solution containing 10 g of sodium carbonate and 25 g of sodium hydroxide. The filtrate was precipitated with 100 ml of concentrated hydrochloric acid, diluted to 1 l, let stand for 24 h at 4°, filtered as before, etc. The filtration–washing–dissolution–reprecipitation process was repeated 3 times, rejecting all the filtration–washing filtrates and the solid product was finally dried at 100–110° to constant weight. The yield obtained of the solid product amounted to 5.3 g (43.6% of the theoretical yield).

Finally, 5 g of the solid product were dissolved in 1 l of distilled water and the solution was slowly percolated through a 200 × 14 mm column loaded with Dowex 50-X16, 50–100 mesh cation-exchange resin in the H-form to obtain the free acid form of the reagent. The reagent was precipitated by addition of 100 ml of concentrated hydrochloric acid and after standing at room temperature for 24 h the suspension was filtered and washed as before, sucking dry the precipitate. After a short wash of the precipitate with absolute ethanol on the filter, the solid product was dried at 100–110° to constant weight.

#### *Determination of elemental As and N contents of the reagent*

Arsenic was successfully determined by the method of TUCKERMAN *et al.*<sup>18</sup> which is based on decomposition of the samples with chloric acid ( $d=1.28$ ) followed by a iodimetric titration, and nitrogen was determined by suitably modifying the standardized alternative to Kjeldahl's method as described by OGG<sup>19</sup>. The experimental details of these modified methods together with the analytical results obtained for the 9 different products synthesized will be published in due course<sup>20, 21</sup>.

The reagent synthesized has the empirical formula  $C_{22}H_{18}O_{14}N_4S_2As_2$  (m.w. 776.37); the results obtained were 18.54% As (average of 4 determinations) and 7.07% N (average of 10 determinations) compared with the theoretical values of 19.30% and 7.22%, respectively. The purity of the reagent, established from these figures, ranged from 96.06 to 97.90%, thus being quite satisfactory.

#### RESULTS AND DISCUSSION

##### *Physico-chemical properties of the new reagent*

The product obtained was a dark-red powder with greenish iridescence in the finely ground state. It was readily soluble in water, giving a violet-purple solution, slightly soluble in ethanol and quite insoluble in most organic solvents. On heating it decomposed with partial sublimation; decomposition proceeded rapidly between 300 and 425° as established thermogravimetrically. It was slightly soluble in hydrochloric acid, the minimum solubility being located in the 2–5 *M* acid range; in more concentrated hydrochloric acid solutions it underwent visible protonization accompanied by sharp, progressive, stable and reversible color changes passing from violet-purple (slightly acid medium), through deep-blue (6–7 *M* HCl) to a final deep emerald-green colour (7–13 *M* HCl). The progressive protonization in 0–13 *M* hydrochloric acid, or 0–12 *M* perchloric acid was shown to proceed over neatly defined isosbestic points<sup>17</sup>,

thus proving the existence of simple stepwise protolytic and protonization equilibria to give proton complex(es) of the general type  $[H_{s+n}R]^{n+}$ . The reagent was very soluble in alkaline solutions, its color becoming deeper and shifted towards the violet. In concentrated sodium hydroxide solution (0.5–4 M) important color changes were again apparent, a deep-blue color being formed in the more concentrated solutions<sup>17</sup>. Aqueous solutions of the reagent were very stable, being practically unchanged for years for analytical purposes, although some small and definite variations were found<sup>17</sup>. The thermal stability of the solid reagent on heating at 100–110° to constant weight was also excellent; no decomposition was found even when the drying process was extended over long periods of time, except for very small and progressive changes, attributed to phenolic oxidation<sup>17</sup>.

The absorption spectrum of an aqueous solution of the reagent at pH 4.15 (Fig. 1) shows the presence of a wide absorption band exhibiting a principal maximum at 540 m $\mu$  together with a less pronounced absorption band characterized by a secondary maximum located at 625 m $\mu$ . The molar absorptivities of these maxima

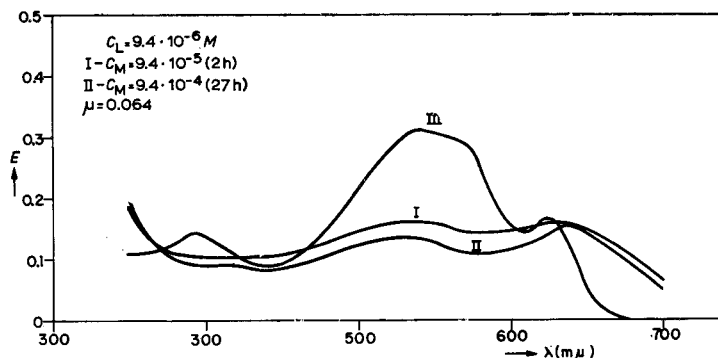


Fig. 1. Absorption spectra of the pure reagent and of the Pd(II) complex (formed with a large excess of cation).

were calculated as  $3.3 \cdot 10^4$  and  $1.75 \cdot 10^4$ , respectively. Surprisingly, this reagent shows 2 different absorption maxima in the visible region whereas practically all the reported mono- or bis-diazoarsenazos are characterized by a single maximum located in the 500–550 nm region. One exception appears to be chlorophosphonazo III, which seems to have 2 absorption maxima located at about 540 and 640 nm<sup>22</sup>. Another similarity shown by chlorophosphonazo III and the new reagent lies in its protonization in concentrated acid media<sup>23</sup> (see above). Such differences, found by correlating the optical properties of *p,p'*- and *o,o'*-arsonic-substituted bisdiazo-derivatives of chromotropic acid, are most probably the direct result of the varying degree of conjugation between the 2 symmetrical halves of the basic molecular structure, this being intimately related to the very different planarity of the molecules in the 2 isomers<sup>17</sup>. The planarity of the arsenazo III molecule is greatly distorted by steric hindrances created by the  $-AsO_3H_2$  groups substituted in *o,o'*-positions, which would not apply to the new reagent.

#### *Alkalimetric titration of the reactive*

Figure 2 shows the results of the potentiometric titration of palladiazos with



0.1000 *N* sodium hydroxide. Curve I was obtained with a sample of the purified reagent without further treatment, while curve II refers to a sample of the free acid form. Both titration curves show the presence of 2 equivalence points located at pH *ca.* 6.5 and *ca.* 9.1, respectively. From the much sharper first equivalence point, it is inferred that curve I corresponds to the titration of the reagent in the form  $\text{NaH}_7\text{R}$

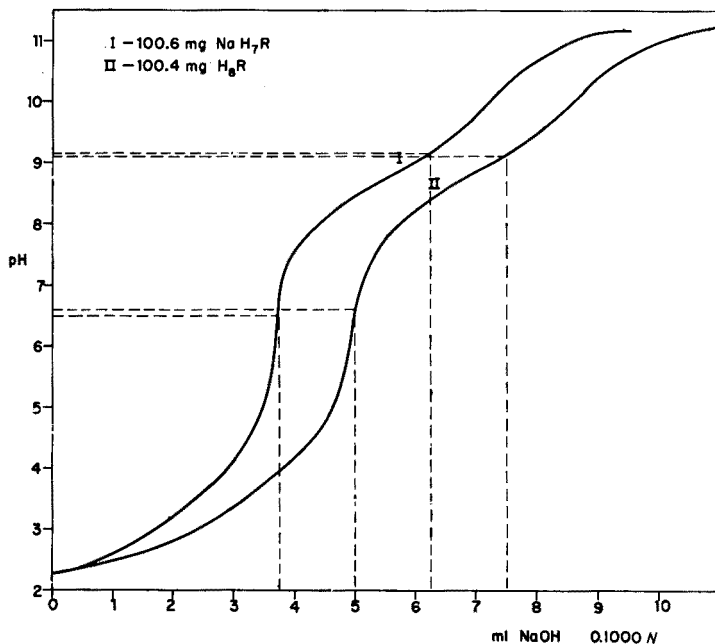


Fig. 2. Potentiometric titration of the reagent dried to constant weight. (I) Reagent in purified form. (II) Reagent treated with cation-exchange resin.

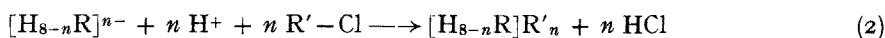
while curve II corresponds to the form  $\text{H}_8\text{R}$ . In the first case, 2.98 equiv. $\text{H}^+$ /mole of reagent were titrated while in the second the equivalence point was located at about 3.88 equiv. $\text{H}^+$ /mole. It is concluded that the main equivalence point corresponds to the neutralization of the 4 more acidic groups (sulfonic and second protolytic step of the arsonic groups). These data indicate a purity degree of about 97.05% for the reagent which is in excellent agreement with the data obtained from elemental analyses.

The second equivalence point was located at a 6:1 ratio of  $\text{H}^+$ :mole of reagent, indicating the neutralization of 2 further acid groups. These acid groups may correspond to the third protolytic step of both arsonic groups or possibly to the titration of the first phenolic and any one of the arsonic groups. The possibility of the titration of both phenolic groups is ruled out, since a remarkably stable chelate originates between the 2 phenolic groups of chromotropic acid upon splitting of the first proton from any of the 2 groups considered<sup>24</sup>.

#### *Determination of the mean number of dissociated groups in aqueous solution*

The ion-exchange technique was selected for determining the number of groups spontaneously protolyzed by the new reagent dissolved in neutral distilled

water; 50 ml of a  $1.25 \cdot 10^{-3} M$  aqueous solution of the reagent were percolated at a very slow flow-rate (6–10 ml/h) through a  $100 \times 10$  mm Dowex 21K, 20–50 mesh resin layer quantitatively transformed to the Cl-form. The effluent together with the wash liquors was then titrated with 0.1000 *N* sodium hydroxide using an alcoholic solution of bromocresol green–methyl red as indicator to determine the number of protons liberated per mole of reagent. The process may be represented by the reactions:



(R=totally deprotonized anionic residue of the reagent; R'=monovalent resin matrix positively charged). The titration required 2.54 ml of sodium hydroxide compared with a theoretical value of 2.58 ml, assuming that 4 of the 8 acid groups potentially available were titrated. These data indicate a 98.45% degree of purity for the reagent, which compares satisfactorily with the above purity data.

#### *Reactions of palladiazole with different cations*

An extensive preliminary investigation of the reactivity of the new arsenazo was carried out by studying its behaviour with 56 different cations using the spot-test technique. The investigation was carried out both in aqueous and in 2–10 *M* hydrochloric acid media. In strong hydrochloric acid solution the new arsenazo seemed to react with Ce(III), the rare-earth elements, Th(IV), Fe(II), and Fe(III), although some of these reactions were strongly masked by the reagent's own color, which depended on the acidity of the medium (see above). Only the reactions in weakly acidic aqueous solution (pH 2–4) are considered in detail here. Under these conditions palladiazole showed a very limited reactivity; blue colors were formed with lead(II) and bismuth(III), precipitates being formed after a few hours. The presence of nitrate ions was shown completely to inhibit the reaction with lead(II). Strong reducing and oxidizing ions quickly produced extensive or total discoloration of the reagent, and the rare-earth elements formed bluish solutions of varying tints.

Special consideration must be given to the reaction with palladium(II); a very characteristic and stable pale-blue or greyish-blue color is formed depending on the formation pH. The reaction is not instantaneous and may take from 2–4 h to about one month to reach complete equilibrium in the 0–13 pH range, as described in detail elsewhere<sup>17</sup>. The high selectivity of the new reagent towards palladium(II) suggested a suitable trivial name PALLADIAZO, which summarizes its 2 basic features (bis-diazo-arsenazo selective for palladium). This denomination will be used in all further reference to the new reagent in order readily to differentiate it from other arsenazos. The reaction with palladium(II) was found so interesting that a very detailed study of the system palladiazole–Pd(II)–H<sub>2</sub>O<sup>17</sup> was made.

#### *Study of the properties of the palladiazole–Pd(II) complex*

A stock solution containing ca. 1 mg Pd(II)/ml was prepared by dissolving PdCl<sub>2</sub> in an aqueous 0.5 *M* hydrochloric acid solution; this solution was standardized gravimetrically by precipitation with an ethanolic 0.5% dimethylglyoxime solution at 60–70°. This stock solution was used throughout this investigation to prepare the different Pd(II) working solutions by suitable dilution.

A stock aqueous  $1.25 \cdot 10^{-3} M$  palladiazole solution was prepared by dissolving 1.000 g of the solid reagent in the free acid form in 1 l of distilled water. The working solutions were again prepared by suitable dilution of this solution. No buffer solutions were used in this initial study of the system. The visible absorption spectra of a pure palladiazole and a palladiazole-Pd(II) solution prepared with a large excess of the cation over the ligand concentration are reproduced in Fig. 1. The spectra I and II, corresponding to the solution of the complex, show that the principal maximum of palladiazole (spectrum III) located at 540 nm is considerably reduced, while the secondary maximum located at 625 nm is shifted towards 640 nm, giving rise to a wide absorption band. The complex formation results in the disappearance of the initial violet-purple color of the reagent solution, which becomes grayish-blue after the formation of the complex. It is interesting to observe that the complex formation does not cause any hyperchromic effect—as is the case for most reactions of other arsenazoles with different cations—and that the bathochromic effect is rather small. The slow formation kinetics of the complex become apparent by comparing spectra I and II where the main changes are observed in the absorption region characteristic of the principal absorption band of the pure reagent, while the absorption maximum of the complex remains practically unchanged. Thus complicating factors would undoubtedly appear in the spectrophotometric study of the complex because of the proximity of the second absorption maxima of the reagent and the complex, and because of their similar apparent molar absorptivity values. In the initial work it was therefore decided to study the complex formation of the system only under conditions of excess cation concentration.

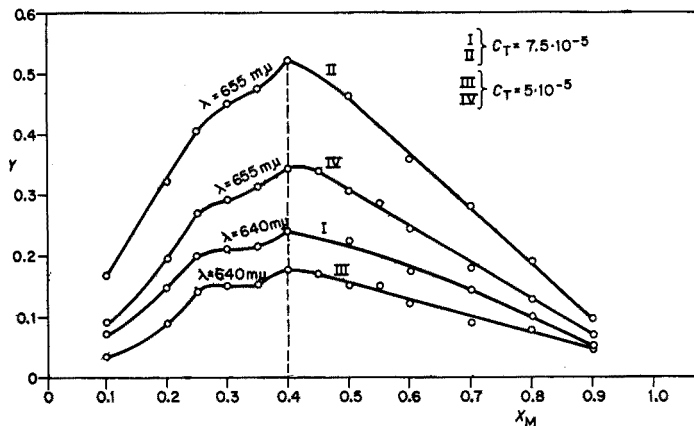


Fig. 3. Study of the composition of the palladiazole-Pd(II) complex by the isomolar continuous variations method.

#### *Composition of the palladiazole-Pd(II) complex compound*

The application of the isomolar continuous variations method of JOB<sup>25</sup> to determine the composition of the complex compound investigated is reproduced in Fig. 3. Absorbance measurements were carried out at 640 and 655 nm, corresponding to the absorption maximum of the complex (Fig. 1) and to the wavelength furnishing the greatest absorbance difference between the complex and ligand in excess. This second wavelength of 655 nm was chosen because of the slight bathochromic effect

brought about by the complex formation which results in a serious interference of the excess ligand at the wavelength of 640 nm. A correction for the absorbance of the free ligand itself was made as suggested by VOSBURGH AND COOPER<sup>26</sup>. The optimum of the represented function was located in all cases at  $x_M = 0.4$ , thus indicating the forma-

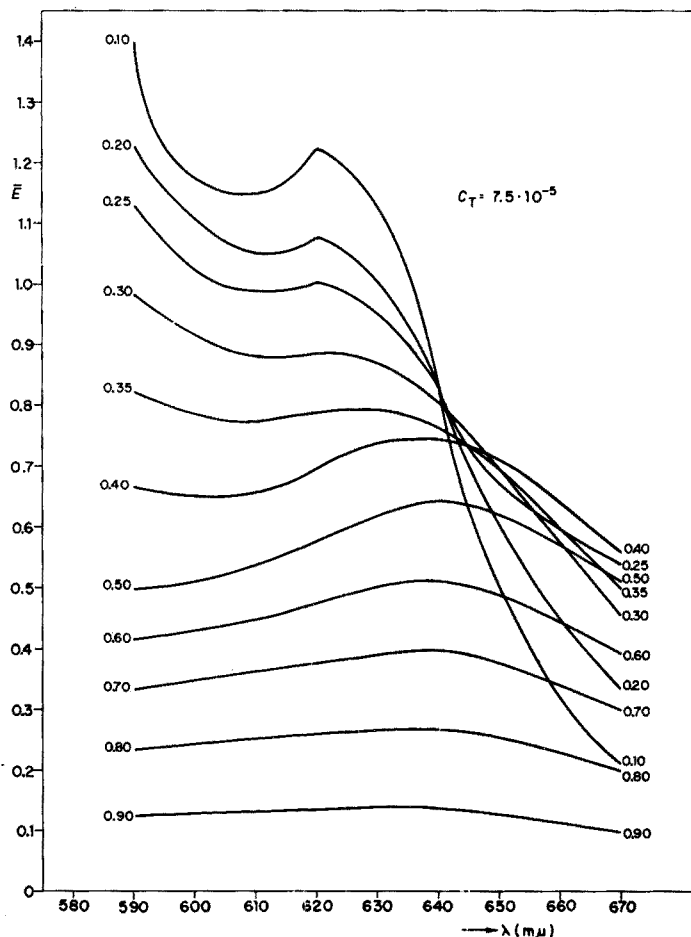


Fig. 4. Application of the isosbestic point method to the determination of the composition of the palladiazole-Pd(II) complex. The numbers at each side of the spectra refer to the molar fraction  $x_M = c_M / (c_M + c_L)$ .

tion of a complex of type  $M_2L_3$  (only metal:ligand ratios are considered here, ignoring the absolute correct formulation of the complex species formed, which would involve the protolytic and solvolytic species). The important discontinuities which are clearly observed in the  $x_M$  0.25–0.40 interval, made it necessary to carry out further investigation by other spectrophotometric methods. These discontinuities probably derived from the coincidence observed for the wavelengths corresponding to the complex absorption maximum and to the isosbestic point characteristic of the isomolar series

investigated, both being located at 640 nm (Figs. 1 and 4). This disturbance is more clearly shown by the absorbance measurements carried out at 640 nm, as could be expected.

The application of the isosbestic point method of ASMUS<sup>27</sup> (Fig. 4) shows the apparent existence of a complex of type  $ML_3$  as deduced from the occurrence of an isosbestic point for the limiting value  $x_M = 0.25$ . However, it is believed that this result can be ascribed only to the inapplicability of the ASMUS method to the present rather unusual case, which could be a serious argument against the general applicability of the isosbestic point method.

From the small slope values of the functions represented in Fig. 3 in the  $x_M$  0.4–0.9 interval, it is possible to suggest that the  $M_2L_3$  species is not a strong complex.

Figure 5 shows the application of the molar ratio method<sup>28</sup> to the system. The existence of a  $M_2L_3$  species of presumably low stability is confirmed, judging by the curvature observed for the interval covered by the 2 extrapolated lines. The absorbance values were again systematically corrected for the absorbance of the free ligand<sup>26</sup>. The results furnished by this method are less ambiguous for the measurements made at 660 nm than for those at 640 nm, because of the reduced interference of the free ligand absorption; the measurements at 640 nm show unexpected discontinuities.

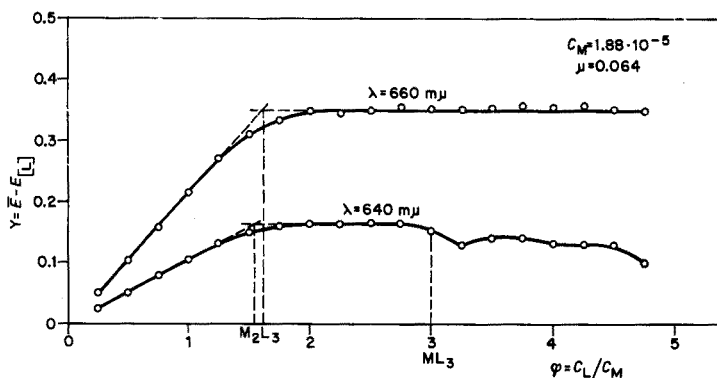


Fig. 5. Application of the molar ratio method to the determination of the composition of the palladiaz-Pd(II) complex system.

In order to obtain further information about the possible existence of other complex species, in addition to the  $M_2L_3$  complex, the absorption spectra of the different solutions used in connection with the molar ratio method were examined in the 610–700 nm wavelength interval. The spectra obtained (Fig. 6) seem to confirm the earlier results. As a result it is definitely concluded that a single  $M_2L_3$  complex with a molar absorptivity of *ca.*  $5.7 \cdot 10^4$  at 640 nm is formed in the palladiaz-Pd(II)- $H_2O$  system at  $pH\ 3.0 \pm 0.5$ .

An analysis of Fig. 6 shows clearly the important interference brought about by the absorbance of the free ligand itself which becomes negligibly small at 675 nm. This would considerably reduce the potential analytical sensitivity of the palladiaz-Pd(II) reaction, and makes it difficult to select optimum conditions for a fundamental spectrophotometric study of the system.

*Sign of the charge of the  $M_2L_3$  complex*

A solution of the complex compound prepared by adding a large excess of palladium(II) to a palladiazole solution, based on the 2 : 3 stoichiometry, was percolated through 2 small columns loaded with cation- and anion-exchange resins in the H- and Cl-forms, respectively. Sorption of the colored solution was quantitative on a thin

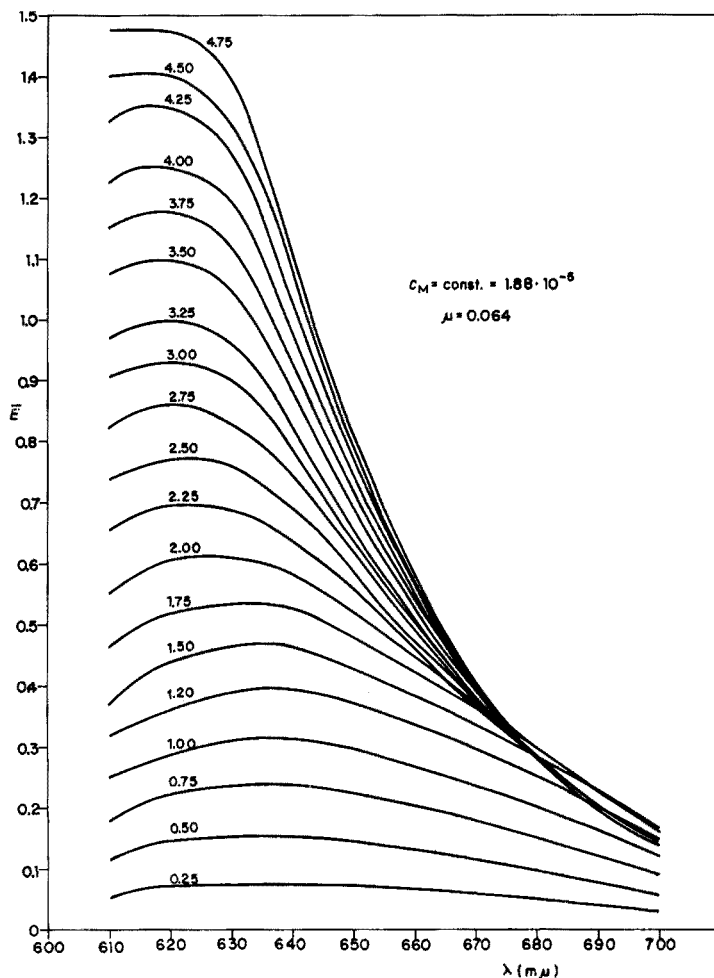


Fig. 6. Absorption spectra of the more significant solutions used in connection with the molar ratio method (the numbers above each spectrum refer to the  $c_L/c_M$  molar ratio).

layer of the anionic resin while no sorption was found on the cationic layer. It was therefore concluded that the  $M_2L_3$  complex is probably a highly charged anionic complex of type  $[Pd_2H_{24-n}R_3]^{4-n}$ .

*Extractability of the  $M_2L_3$  complex into organic phase*

A large number of organic solvents, including alcohols, ethers, ketones, hydrocarbons and different solvents (TBP, MIK, TTA, TLA) etc. as well as various mix-

tures of these solvents were tested for the extraction of the complex, but no positive results could be achieved.

Since the complex is of anionic nature it seemed more promising to attempt its extraction with voluminous cations dissolved in organic solvents, such as guanidine<sup>29</sup> and quaternary ammonium salts<sup>30</sup>. These extractants have already been successfully employed, *e.g.* by KUZNETSOV<sup>29</sup> and by SARDIÑA *et al.*<sup>30</sup>, for the extraction of  $\text{UO}_2^{2+}$ -arsenazo III and  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$  complexes, respectively.

The extraction of the  $\text{M}_2\text{L}_3$  complex was accomplished with varying degree of success by using cetyldimethylbenzylammonium chloride (CDBA) dissolved in methyl isobutyl ketone, carbon tetrachloride, octane or *n*-butanol mixed with kerosene, *o*-dichlorobenzene, cyclohexane, TBP, petroleum ether and mixtures of benzene and diisobutyl ketone. Diphenylguanidine chloride could be used instead of CDBA with the organic solvents cited.

Best results were obtained when the extraction both of the pure palladiazole and  $\text{M}_2\text{L}_3$  complex aqueous solutions with palladiazole: Pd(II) molar ratios ranging from 0.1-5 was done with CDBA and diphenylguanidine chloride dissolved in *n*-butanol. The experiments were carried out in graduated 20-ml test tubes by adding 2 ml of the aqueous pure reagent or complex phase, 10 ml of *n*-butanol and 1 ml of 10% diphenyl-

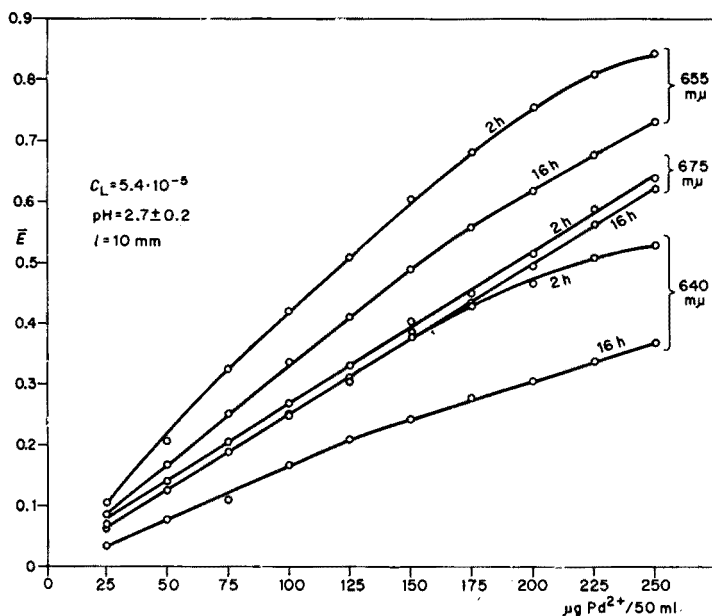


Fig. 7. Conformance to Beer's law by the  $\text{M}_2\text{L}_3$  palladiazole-Pd(II) complex as a function of the wavelength and time elapsed since the formation of the complex.

guanidine chloride; in the case of CDBA 10 ml of 0.5% CDBA in *n*-butanol were added to the aqueous phase. The test tubes were then stoppered and shaken for 1 min. Almost complete extraction of the pure reagent and complex compound or both into the organic phase was attained, the aqueous phase remaining either completely color-

less or slightly colored in the case of very high ligand : metal ratios. The separation of the phases proceeded rapidly without emulsion formation.

The simplicity of the extraction of the  $M_2L_3$  complex should offer advantages in connection with the potential analytical value of the reaction.

#### *Conformance to Beer's law by the $M_2L_3$ complex*

The results shown in Fig. 7 confirmed the prediction (Fig. 6) that Beer's law is obeyed by the  $M_2L_3$  complex at 675 nm or longer wavelengths. The sensitivity (0.65 absorbance units for 250  $\mu\text{g}$  Pd(II)/50 ml using 10-mm cells, measured against a reagent blank) and the time-dependence of the absorbance of the complex are quite satisfactory. Accordingly, the successful utilization of the complex for the spectrophotometric determination of trace amounts of palladium(II) in connection with a variety of practical problems appears quite feasible, particularly since possible interferences could be eliminated or considerably diminished by the extraction process.

The authors wish to express their warmest thanks to the "Dow Chemical Company" (Midland, Michigan), "Fluka" (Buchs, Switzerland), and "Loba-Chemie" (Vienna, Austria) for their kindness in supplying us with free samples of different products used in this investigation. The authors are also indebted to the Directorate of Chemistry and Isotopes of the Spanish Atomic Commission which prepared all the diagrams connected with this work.

#### SUMMARY

The synthesis and purification of 2,7-bis(4-azophenylarsono)-1,8-dihydroxynaphthalene 3,6-disulphonic acid is reported. Because of its selectivity for palladium(II), the name palladiazoo is suggested for the reagent. Aqueous solutions of palladiazoo are very stable and exhibit 2 absorption maxima located at 540 and 625 nm, the molar absorptivities being  $3.3 \cdot 10^4$  and  $1.7 \cdot 10^4$ , respectively. Palladiazoo changes color stepwise and reversibly with increase in hydrochloric acid concentration from 0 to 13 *M*. A negatively charged complex of type  $M_2L_3$  is formed with Pd(II) at pH 2.5-3.5, and shows an absorption maximum at 640 nm with a molar absorptivity of  $(5.7 \pm 0.1) \cdot 10^4$ ; the complex can be readily extracted with diphenylguanidine chloride or quaternary ammonium salts dissolved in *n*-butanol or higher alcohols. The complex obeys Beer's law at 675 nm in the concentration range 10-250  $\mu\text{g}$  Pd(II)/50 ml. Pb(II), Bi(III), Ce(III) and the rare-earth elements are the only expected cationic interferences.

#### RÉSUMÉ

On décrit la synthèse et la purification de l'acide 2,7-bis(4-azophénylarsono)-1,8-dihydroxynaphthalène-3,6-disulfonique. Les auteurs proposent d'appeler ce réactif "palladiazoo" en raison de sa sélectivité pour le palladium. Les solutions de ce composé sont très stables. Il se forme un complexe du type  $M_2L_3$  avec le palladium à pH 2.5-3.5, avec maximum d'absorption à 640 nm et absorption molaire de  $5.7 \pm 0.1 \cdot 10^4$ . Ce complexe peut être extrait avec le chlorure de diphénylguanidine ou des sels d'ammonium quaternaires dissous dans le *n*-butanol ou des alcools supérieurs. La loi de Beer



s'applique à 675 nm pour des concentrations de 10–250  $\mu\text{g Pd(II)}/50\text{ ml}$ . Seuls Pb(II), Bi(III), Ce(III) et les terres rares gênent.

## ZUSAMMENFASSUNG

Über die Synthese und Reinigung von 2,7-Bis(4-azophenylarsono)-1,8-dihydroxynaphthalin-3,6-disulfonsäure wird berichtet. Wegen der grossen Selektivität dieser Verbindung für Palladium(II) wird der Name Palladiazoo vorgeschlagen. Wässrige Lösungen von Palladiazoo sind sehr stabil und zeigen 2 Absorptionsmaxima bei 540 und 625 nm ( $\epsilon=3.3 \cdot 10^4$  bzw.  $1.7 \cdot 10^4$ ). Palladiazoo wechselt seine Farbe schrittweise und reversibel mit steigender Salzsäurekonzentration. Ein negativ geladener Komplex des Typs  $M_2L_3$  wird mit Pd(II) beim pH 2.5 bis 3.5 gebildet und zeigt ein Absorptionsmaximum bei 640 nm ( $\epsilon=5.7 \pm 1 \cdot 10^4$ ). Der Komplex wird schnell extrahiert mit in *n*-Butanol oder höheren Alkoholen gelöstem Diphenylguanidinchlorid oder quarternären Ammoniumsalzen. Das Beersche Gesetz wird befolgt bei 675 nm für Konzentrationen von 10–250  $\mu\text{g Pd(II)}/50\text{ ml}$ . Pb(II), Bi(III), Ce(III) und die Elemente der Seltenen Erden sind erwartungsgemäss die einzigen störenden Kationen.

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## ANALYTICAL APPLICATION OF ARSENAZO III TO THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

PART I. PRELIMINARY INVESTIGATION OF THE COMPLEX FORMATION IN THE ARSENAZO III-Pd(II)-H<sub>2</sub>O SYSTEM\*

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Since the synthesis of arsenazo III, first reported by SAVVIN<sup>1</sup> in 1959, this reagent has been widely investigated because of the great sensitivity of its reactions with a number of cations in neutral, weak acidic or strongly acidic media. The great stability of the reagent in hydrochloric and nitric acid media even as strong as 10 *M* is advantageous since the selectivity of the reagent for some cations can be increased considerably and classical anionic interferences from polyprotic acid radicals—such as those commonly used in buffer solutions—which can pose complex formation problems, are greatly decreased or even completely eliminated.

The literature over the past 7 years is rich in information on the analytical application of arsenazo III for the spectrophotometric determination of many elements, especially Sc(III)<sup>2-7</sup>, Y(III)<sup>2</sup>, La(III)<sup>8-10</sup>, the rare-earth elements<sup>2,3,5,6,8,11-14</sup>, Pa(III)<sup>6,7,15,16</sup>, Ti(IV)<sup>17</sup>, U(IV) and U(VI)<sup>1,3,6,7,18-30</sup>, Th(IV)<sup>1,3,6,7,9,30-50</sup>, Zr(IV) and Hf(IV)<sup>3,6,11,19,30,50-58</sup>, Pu(IV)<sup>59-61</sup>, and Np(V)<sup>62,63</sup>.

The general features of the reaction mechanism accounting for the complex formation of the metallochromic reagents known under the trivial name of arsenazos with metallic cations have been summarized in a previous contribution<sup>64</sup>. The most representative arsenazo reagents are included in Fig. 1 for illustrative purposes.

Surprisingly, such a typical complex-forming cation as palladium(II) has not been as yet considered with regard to its possible interaction with arsenazo(III), despite the fact that it reacts very characteristically with thorin<sup>65</sup> and arsenazo I<sup>66</sup>. In a previous paper<sup>64</sup>, the reaction of a new homologue of arsenazo III, trivially named "palladiazo", with palladium(II) was shown to take place very selectively. In order to complete the reaction picture of palladium(II) with metallochromic reagents of the arsenazo type, a study of its reaction with arsenazo III seemed to be of considerable interest. Aside from its intrinsic interest, such a study might yield comparative data to explain the different reaction mechanisms involved in the reaction of a metal cation with the *o,o'*- and *p,p'*-arsonic-substituted isomers of arsenazo III.

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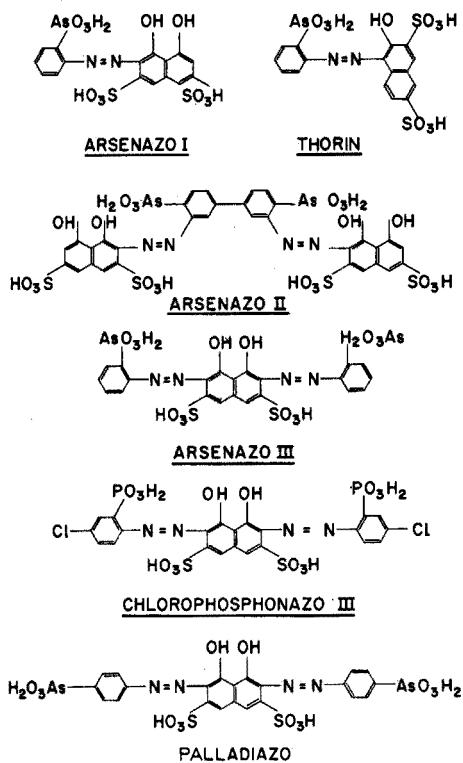


Fig. 1. Molecular structure of typical arsenazo reagents.

## EXPERIMENTAL

### *Instruments and reagents*

The instruments and chemicals used were the same as described previously<sup>64</sup> except that *p*-phenylarsonic acid was replaced by *o*-phenylarsonic acid in carrying out the synthesis of the reagent.

### *Synthesis and analysis of arsenazo III*

Arsenazo III was prepared following essentially SAVVIN's prescriptions<sup>1,3,67</sup>; it was further purified and then treated with cation-exchange resin in order to obtain the pure acid form of the reagent, as described previously<sup>64</sup>. The yield of the final purified product was 39.3%; this practical yield was low, mainly because considerable losses resulted from the repeated purification process.

Elemental analyses for arsenic and nitrogen were carried out exactly as described previously<sup>64</sup>. Average values of 17.64% As (mean of 4 determinations) and 7.12% N (mean of 19 determinations) were obtained (theor. 19.30% and 7.22%, respectively) for the pure acid form of the reagent, which has the empirical formula C<sub>22</sub>H<sub>18</sub>O<sub>14</sub>N<sub>4</sub>As<sub>2</sub> (m.w. 776.37).

## RESULTS AND DISCUSSION

*Physico-chemical properties of the reagent*

The general properties of arsenazo III are well established and reported in the abundant literature.

The visible absorption spectrum of an aqueous solution of the reagent prepared is shown in Fig. 2 (spectrum I), showing an absorption maximum at 540 nm characterized by a molar absorptivity of  $(3.5 \pm 0.1) \cdot 10^4$ . The aqueous solution thus pre-

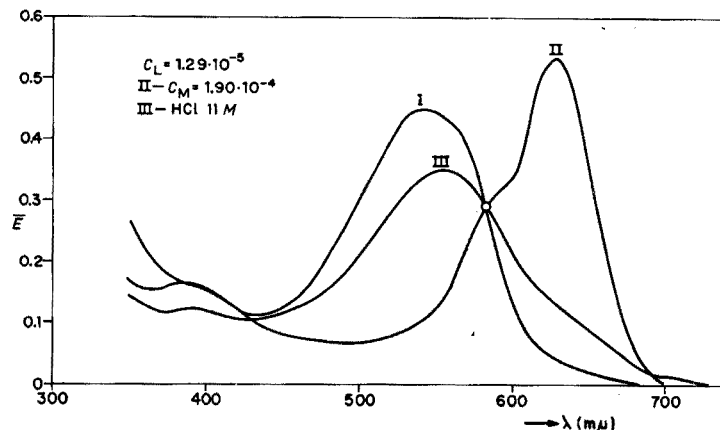


Fig. 2. Absorption spectra of arsenazo III in aqueous and 6 N HCl media and of the complex species formed in aqueous medium with a large excess of cation.

pared showed an intense red-crimson colour and remained unchanged for years. In contrast to the palladiazoreagent<sup>64</sup>, arsenazo III solutions showed no sign of undergoing visible protonization in a medium as acid as 11 N hydrochloric acid (Fig. 2, spectrum III), the process involved being accompanied in this case by a shift of about 20 nm of the absorption maximum towards longer wavelengths. The occurrence of an isosbestic point located at 585 nm indicates the existence of simple protolytic equilibria. Aqueous solutions of arsenazo III are a blue-violet colour of varying intensity in alkaline media, depending on the pH. The solid product seems to be quite stable when dried at 100–110° to constant weight. Thermogravimetric analysis showed that arsenazo III does not melt on heating, but decomposes in the 300–550° interval, with partial sublimation; the thermal stability appears to be slightly increased compared with its *p,p'*-isomer palladiazoreagent<sup>64</sup>.

*Potentiometric titration of the reagent*

Figure 3 shows the result of titrating a sample of arsenazo III with 0.1000 N sodium hydroxide; the corresponding titration curve of palladiazoreagent is included for comparative purposes. Both curves exhibit 2 well-defined equivalence points, especially the first one which is located at pH *ca.* 6.4 in both cases. For both reagents, this point corresponds to the neutralization of the 4 more acidic groups (2 sulfonic groups and the second dissociation step of the 2 arsonic groups). With regard to the second equivalence point, substantial differences become apparent for the titration of the 2 isomers. Thus, while this second point corresponds to the titration of 6 acid groups

for palladiazo (curve I), only 5 acid groups are titrated in the case of arsenazo III (curve II). This fact, together with the considerably less steep shape exhibited by curve I after the first equivalence point, shows that considerable buffering effects occur in this region, and it can be concluded that the  $pK$  values of palladiazo between

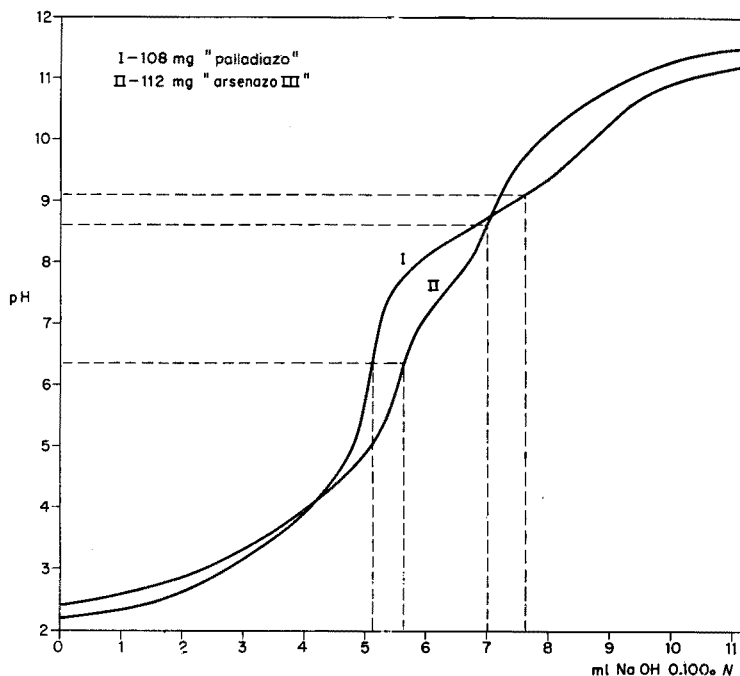


Fig. 3. Comparative potentiometric titration of the palladiazo and arsenazo III isomers.

the fourth and the seventh protolytical dissociation steps are considerably closer to each other than the corresponding values of arsenazo III. The second equivalence point is attributed in the case of arsenazo III to the titration of the first phenolic group, while the interpretation of this point remains considerably less clear in the case of palladiazo<sup>64</sup>.

The purity degree of arsenazo III, on the basis of the experimental data obtained for the first equivalence point, was calculated to be 97.5%, which compares satisfactorily with the data obtained from elemental As and N analyses (91.4 and 98.6%, respectively).

These potentiometric titrations of the 2 isomers (Fig. 3) indicate that *o,o'*-substitution of the fundamental arsenazo III structure by arsonic groups enhances the acid character of the first phenolic proton compared to the case of the *p,p'*-substituted isomer (palladiazo).

#### *Determination of the average number of acid groups dissociated from arsenazo III in aqueous solution*

The experimental details of the determination of the average proton number split off by arsenazo III on dissolution in pure distilled water were essentially the same as described earlier<sup>64</sup>; 2.90 ml of 0.1000 N sodium hydroxide (average value

from 4 experiments) were needed for the neutralization of the effluent obtained by passing 50 ml of an aqueous arsenazo III solution (1.000 mg reagent/ml) through a column loaded with Dowex 21K, 20–50 mesh, anion-exchanger in the Cl form. The theoretical alkali consumption should be 2.575 ml for these conditions, assuming that 1 acid groups were dissociated per mole of arsenazo III, hence it appears that an average of 4.5 acid groups were dissociated by arsenazo III on dissolution in water, compared with 4 groups dissociated by palladiazole under similar conditions<sup>64</sup>. These data provide additional confirmation that the differences noted between the reagents can be ascribed basically to the influence of the arsonic acid substitution sites.

#### *Reactivity of arsenazo III with different cations*

The spot-test technique was used to study the reactivity of a  $1.25 \cdot 10^{-3}$  M solution of arsenazo III, both in aqueous and 6 M hydrochloric acid media, towards 58 different metallic ions.

Arsenazo III exhibits a much greater reactivity than its isomer palladiazole<sup>64</sup>, since in aqueous solution it forms strongly colored violet solutions with Be(II), Ni(II) and Cu(II), weakly colored violet solutions with Al(III), Ca(II), Ti(IV), Mo(VI), Os(VIII), Co(II), Rh(III), Pt(IV) and Cd(II), very characteristic moderate-blue colored solutions with Pb(II) and Pd(II), while Y(III), the rare-earth elements and Th(IV) give rise to initially intense bluish-green colored solutions, which were shown to precipitate after some hours. The uranyl cation forms an intense bluish-green solution which is quite stable with time. Strongly reducing and oxidant cations totally or partially decolorize the reagent very quickly.

In 6 M hydrochloric acid solution, arsenazo III is much more selective, forming violet solutions with La(III), Ce(III), the rare-earth elements, U(VI), Ti(III), Nb(V) and Ta(V); with Th(IV) and U(IV) emerald-green solutions are formed while Zr(IV) yields a moderate-blue solution. The reactions with Th(IV) and U(IV) were shown to yield a precipitate after some hours.

These data show that arsenazo III exhibits a much greater reactivity towards metallic ions than palladiazole; the latter reagent is more selective, especially for palladium(II).

Since both reagents were shown to react readily and very characteristically with palladium(II), it was thought interesting for comparative purposes to carry out a parallel investigation of the complex formation in the system arsenazo III–Pd(II)–H<sub>2</sub>O. A very detailed study of this system was carried out in the 0–13 pH-interval<sup>68</sup>, but here the special case of the complex formation in aqueous solution in the pH interval 2.5–3.5 will be considered. No buffer solutions were used in this investigation.

#### *Spectrophotometric properties of the arsenazo III–Pd(II) complex*

Figure 2 (spectrum II) shows the visible absorption spectrum of an arsenazo III–Pd(II) solution prepared with a large excess of cation over the ligand concentration. A comparison of spectra I and II, referring to the same uncomplexed (I) and complexed (II) ligand concentrations, shows the favourable spectrophotometric characteristics of the complex-formation process involved; a considerable bathochromic shift is observed (90 nm) as well as a considerable hyperchromic effect. The small molar absorptivity of the ligand at the wavelength of maximum absorbance of the complex (630 nm) is, of course, also very favourable for spectrophotometric pur-

poses. It is interesting to observe how the spectrum of the complex passes through an isosbestic point at 685 nm, characteristic for the protolytic equilibria of the pure reagent.

*Determination of the composition of the complex species formed in the arsenazo III-Pd(II)-H<sub>2</sub>O system*

The results obtained by the application of JOB's<sup>69</sup> isomolar continuous variations method are shown in Fig. 4. Absorbance measurements were made at different wavelengths selected as the result of preliminary experiments. A very well-defined maximum is observed in all cases for a  $x_M = 0.65$  metal/ligand molar ratio, thus proving

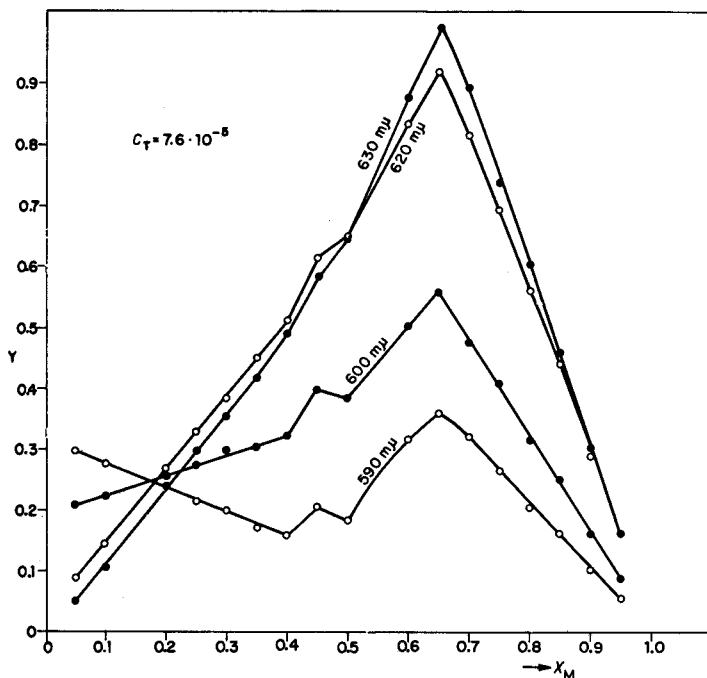


Fig. 4. The molar composition of the complexes formed in the arsenazo III-Pd(II)-H<sub>2</sub>O system by the isomolar continuous variations method.

the existence of a  $M_2L$ -type complex. In addition, the absorbance measurements carried out at 590 and 600 nm\* disclose the unequivocal existence of a second, less pronounced maximum at a  $x_M = 0.45$  molar ratio, indicating the formation of a second complex of the  $ML$ -type. In the plots at 620 nm and, less clearly, at 630 nm, the existence of the second complex can be deduced from the marked slope variation observed in the interval considered. Curiously enough, the only series of measurements showing a negative slope in the  $x_M$ -interval 0.0-0.4 are those carried out at 590 nm; this

\* Although the absorbance measurements carried out at 590 and 600 nm resulted in systematically negative absorbance values, it is felt that their inclusion together with the measurements carried out at 620 and 630 nm—characterized by positive absorbance values—constitutes no major inconvenience.

probably derives from the molar absorptivity of the ML-complex being smaller than that of arsenazo III at this wavelength.

ASMUS'<sup>70</sup> isobestic point method was also applied to a series of isomolar solutions to establish the composition of the system considered (Fig. 5). Analysis of this figure confirms the existence of more than one complex species in the system. The isobestic point, located at  $x_M = 0.40$  seems to indicate the existence of a complex species of the  $M_2L_3$  type while the absorbance maximum is placed at  $x_M = 0.65$ , thus confirming the existence of the  $M_2L$  complex detected by JOB's method whose absorption maximum is located at 630 nm. On the other hand, definite evidence of the presence of a second, less pronounced absorption maximum at 620 nm, is disclosed in the  $x_M$ -interval 0.4–0.55. Since the system seems to give rise to the formation of at least 2, possibly more, complex compounds, it becomes difficult to draw unambiguous conclusions from Fig. 5. Complicating factors arise from the closeness of the 2 reported

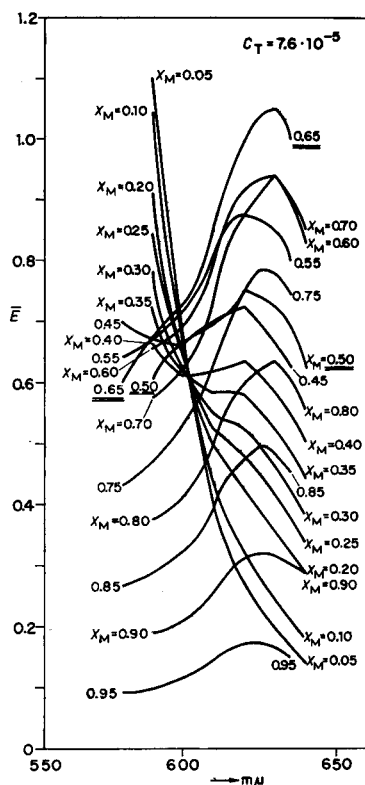


Fig. 5. The molar composition of the complexes by the isobestic point method.

absorption maxima, located at 620 and 630 nm, and from the presumably very different instability constants and molar absorptivities characteristic of the  $M_2L$  and  $ML$  complexes. In addition, stepwise complex-formation, rare as it may be in systems involving metallochromic reagents, cannot be completely ruled out.

The application of the isobestic point method confirms in any case the conclusions arrived at by JOB's method concerning the existence of an additional  $ML$



complex; owing to the very small molar absorptivity of the ligand at 620 nm, the appearance of a maximum at this wavelength could not be explained otherwise.

These conclusions were further confirmed by the application of the YOË-JONES<sup>71</sup> molar ratio method (Fig. 6). The absorbance measurements carried out at different wavelengths of special interest again showed the unequivocal existence of at least 2 complexes of the  $M_2L$  and  $ML$  types. As mentioned before, the measurements carried out at 500, 540, and 570 nm resulted in systematically negative absorbance values, but for the sake of clarity, the absolute sign of the absorbance values was ignored in the graphical representation.

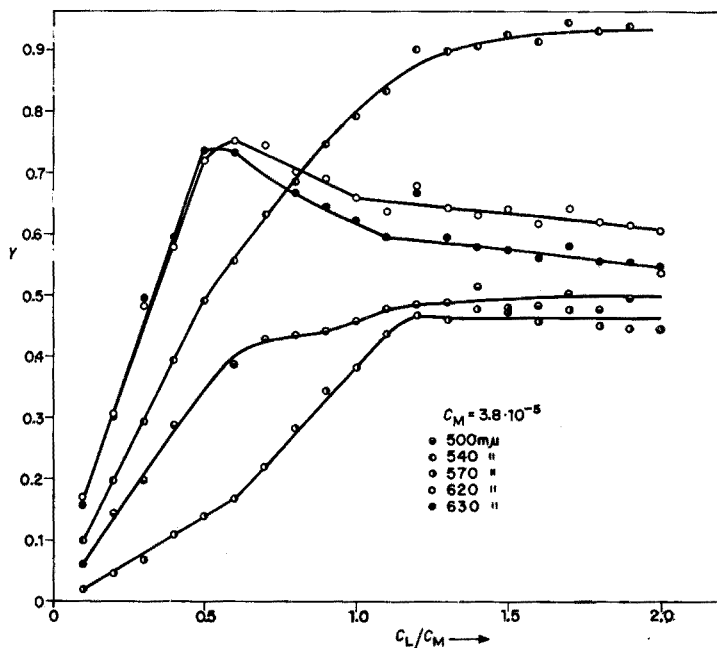


Fig. 6. The molar composition of the complexes by the molar ratio method.

The absorbance values shown in connection with the use of the 3 spectrophotometric methods were corrected in all cases for the absorption of the free ligand itself, by VOSBURGH AND COOPER'S method<sup>72</sup>.

Figure 7 shows the absorption spectra obtained for 3 of the solutions employed in connection with the molar ratio method exhibiting ligand/cation concentration ratios between 0.5 and 1.3. Spectrum III, together with the molar absorptivity calculated for its maximum (630 nm) completely agrees with the facts established for spectrum II of Fig. 2, thus proving the great stability of the  $M_2L$  complex. Spectrum II of Fig. 7 provides further evidence for the existence of the  $ML$  complex, characterized by an absorption maximum at 620 nm; its absorbance is somewhat lower than that of the  $M_2L$  complex, the overall cation concentration being identical in both cases. The maximum at 620 nm observed for spectrum I of Fig. 7 further confirms the  $ML$  complex. In this case, the wide absorption band located in the 520–570 nm region results from the presence of an excess of free ligand over the 1:1 stoichiometry.

In order to obtain more information about the spectral characteristics of the ML complex, an arsenazo III–Pd(II) solution containing a large known excess of ligand was prepared and its spectrum was recorded against a blank solution containing the same concentration of free ligand (calculated by subtracting the ligand con-

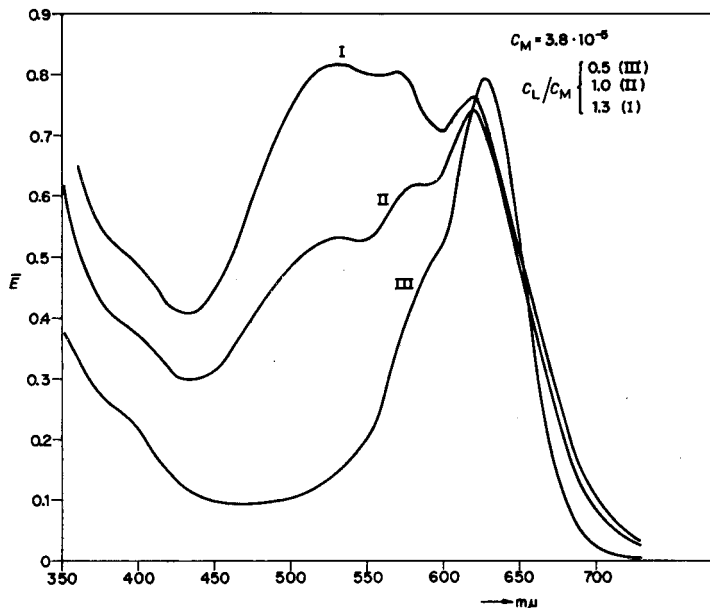


Fig. 7. Absorption spectra corresponding to 3 representative solutions employed in connection with the molar ratio method.

centration needed to build the 1:1 complex for the known amount of metallic ion, from the total ligand concentration present in the solution of the complex). Under the conditions selected, both the  $M_2L$  complex and free ligand concentration in equilibrium with the ML species can be assumed to be negligibly small compared with the ML complex concentration, owing to the great excess of added ligand.

The absorption spectrum of the ML complex showed a wide absorption band with a maximum at 500–510 nm together with a much sharper second absorption band with a maximum at 620 nm, as could be expected from the earlier observations. The molar absorptivities characteristic of the absorption maxima of the  $M_2L$  ( $\lambda_{max} = 630$  nm) and ML ( $\lambda_{max} = 620$  nm) complex species were calculated to be  $(4.2 \pm 0.1) \cdot 10^4$  and  $(1.6 \pm 0.2) \cdot 10^4$ , respectively.

A comparison of the functions shown in Figs. 4 and 6 with similar data obtained for the palladiazole–Pd(II) system<sup>64</sup> indicates that the arsenazo III–Pd(II)  $M_2L$  complex must be considerably stronger than the corresponding  $M_2L_3$  palladiazole–Pd(II) complex. Further, it is interesting to note that arsenazo III builds at least 2 different complexes with palladium, whereas palladiazole forms only one. This increased complex-forming capacity is ascribed in the case of arsenazo III to the remarkable facility of the reagent in forming rings between the metal cation, the azo group(s), and

the arsonic group(s) in the *o*-position(s); the molecular structure of palladiaz<sup>64</sup> is incompatible with such a reaction mechanism because of the substitution of the arsonic groups in the *p,p'*-sites.

*Conformance to Beer's law by the ML complex*

Since only the ML complex is of analytical interest with regard to the spectrophotometric determination of palladium(II), the pertinent experiments were carried out under experimental conditions guaranteeing the exclusive formation of the ML complex.

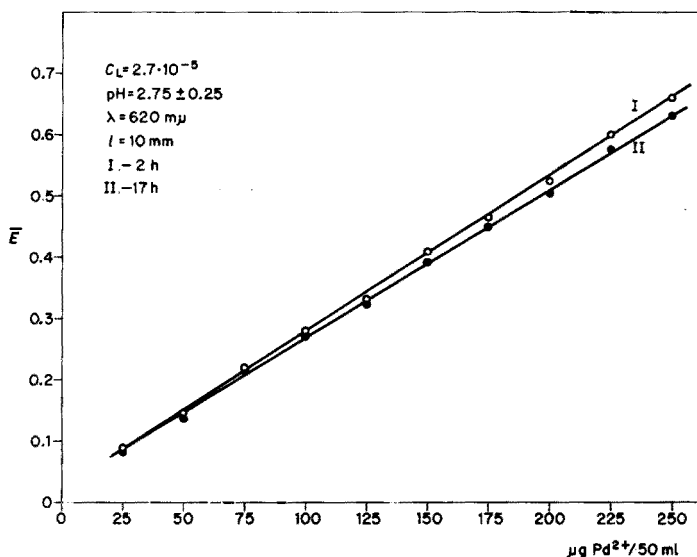


Fig. 8. Conformance to Beer's law by the complex species of 1:1 stoichiometry.

The results of this investigation, together with the colour evolution of the complex formed as a function of time, are shown in Fig. 8. This figure indicates the favourable characteristics of the 1:1 arsenazo III-Pd(II) complex in regard to its suitability for the spectrophotometric determination of palladium traces in aqueous solutions. Both the sensitivity and time-stability characteristics of the reaction are quite similar to those found for the palladiaz<sup>64</sup>-Pd(II) complex. In the latter case, however, the reaction might prove considerably more convenient from a practical analytical point of view, because of the much greater selectivity shown by the palladiaz<sup>64</sup> reagent.

The authors wish to express their warmest thanks to the "Dow Chemical Company" (Midland, Michigan), "Fluka" (Buchs, Switzerland), and "Loba-Chemie" (Vienna, Austria) for their kindness in supplying us with free samples of different products used in this investigation. The authors are also indebted to the Directorate of Chemistry and Isotopes of the Spanish Atomic Commission, which prepared all the diagrams connected with this work.

## SUMMARY

The reaction of arsenazo III with palladium(II) was investigated. Complex species of types  $M_2L$  and  $ML$  are formed at pH 2–4; the complex  $M_2L$  shows a very sharp maximum at 630 nm while the  $ML$  species shows maximum absorption at 620 nm. The molar absorptivities of the complexes are  $4.2(\pm 0.1) \cdot 10^4$  and  $1.6(\pm 0.2) \cdot 10^4$ , respectively. The complex  $ML$  conforms to Beer's law at 620 nm in the range 10–250  $\mu\text{g Pd(II)}/50$  ml. The sensitivity of the reaction of Pd(II) with arsenazo III is about the same as that of a new reagent, palladiazoo, but the latter is more selective for Pd(II). Serious interferences might be caused by  $UO_2^{2+}$ ,  $U^{4+}$ ,  $Th^{4+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Y^{3+}$  and the rare-earth elements.

## RÉSUMÉ

Les auteurs ont examiné la réaction de l'arsenazo III avec le palladium(II); il se forme les deux types de complexes  $M_2L$  et  $ML$  aux pH 2–4. Pour la forme  $ML$ , la loi de Beer s'applique de 10–250  $\mu\text{g Pd}/50$  ml à 620 nm. La sensibilité de cette réaction est à peu près la même que celle obtenue avec le nouveau réactif "palladiazoo", mais ce dernier est plus sélectif pour Pd.  $UO_2^{2+}$ ,  $U^{4+}$ ,  $Th^{4+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Y^3$  et terres rares gênent.

## ZUSAMMENFASSUNG

Die Reaktion von Arsenazo III mit Palladium(II) wurde untersucht. Komplexe des Typs  $M_2L$  und  $ML$  werden beim pH 2 bis 4 gebildet. Der Komplex  $M_2L$  zeigt bei 630 nm ein sehr scharfes Maximum, während der Komplex  $ML$  ein Absorptionsmaximum bei 620 nm besitzt ( $\epsilon = 4.2 \pm 0.1 \cdot 10^4$  bzw.  $1.6 \pm 0.2 \cdot 10^4$ ). Der Komplex  $ML$  gehorcht bei 620 nm dem Beerschen Gesetz im Bereich von 10 bis 250  $\mu\text{g Pd(II)}/50$  ml. Die Empfindlichkeit der Reaktion von Pd(II) mit Arsenazo III ist etwa gleich der des neuen Reagenzes Palladiazoo, jedoch ist das letztere selektiver. Ernsthafte Störungen werden vermutlich verursacht durch  $UO_2^{2+}$ ,  $U^{4+}$ ,  $Th^{4+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Y^{3+}$  und die Elemente der Seltenen Erden.

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## DETERMINATION OF TRACE QUANTITIES OF SCANDIUM IN SILICATE ROCKS BY A COMBINED ION EXCHANGE-SPECTROPHOTOMETRIC METHOD

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The determination of trace quantities of scandium in ores and rocks has generally been done by spectrographic<sup>1-6</sup> or neutron activation methods of analysis<sup>7-13</sup>. EBERLE AND LERNER<sup>14</sup> used alizarin red S for the spectrophotometric determination of scandium, which was previously isolated from all interferences by a stepwise process involving cupferron-chloroform extraction, iodate precipitation in nitric acid, tributyl phosphate extraction, precipitation with ammonium tartrate and a further tributyl phosphate extraction. This procedure provides a sound basis for the separation of scandium, but requires considerable time and effort. SHIGEMATSU *et al.*<sup>15</sup> determined scandium in rocks and ores by a spectrophotometric method involving 5,7-dichloroxinate-chloroform extraction. After the decomposition of samples with hydrofluoric acid, scandium was separated by coprecipitation with calcium oxalate, followed by extraction with thenoyltrifluoroacetone (TTA); in this procedure, thorium appears to interfere with scandium, because both elements behave similarly in the separation steps. So far, few selective reagents have been proposed for the spectrophotometric determination of scandium, so that the separation of scandium from interfering ions would be of primary importance before the successive determination of scandium in complex matrix materials like rocks and ores.

HAMAGUCHI *et al.*<sup>16</sup> developed an useful anion-exchange chromatographic method in ammonium sulfate media and applied it for radiochemical separation in neutron activation analysis of scandium in silicate rocks, cassiterite, and meteorites<sup>12</sup>. KURODA *et al.*<sup>17</sup> worked out a selective cation-exchange method for scandium in ammonium sulfate media. None of these ion-exchange methods, however, isolates trace quantities of scandium in a sufficiently pure state for direct spectrophotometric determination of scandium.

This work centered on the establishment of a complete ion-exchange procedure for scandium in silicate rocks and the subsequent spectrophotometric determination of scandium with arsenazo<sup>18</sup>.

## EXPERIMENTAL

*Reagents and apparatus*

*Scandium stock solution.* An appropriate amount of Sc<sub>2</sub>O<sub>3</sub> (99.9% purity) was dissolved in a minimum amount of hydrochloric acid, and evaporated to dryness.

The residue was finally taken up in 100 ml of 0.1 *M* hydrochloric acid. Scandium was determined by titration with 0.01 *M* EDTA solution standardized previously against zinc metal of primary standard quality. The stock solution contained 0.860 mg Sc/ml of 0.1 *M* hydrochloric acid and was used after appropriate dilution.

*Cation-exchange column (A)*. A conventional column, 1.0 cm i.d. and 20 cm long, was used. A strong acid cation exchanger, Dowex 50W-X8, 100–200 mesh, in the hydrogen form, was used; 5 g of dried resin was slurried with water and poured into the column. The resulting bed was usually 10 cm high.

*Anion-exchange column (B)*. A conventional column, 1.0 cm i.d. and 30 cm long, was used. A strong base anion exchanger, Dowex 1-X8, 100–200 mesh, sulfate form, was purified as described previously<sup>16</sup>; 10 g of the dried resin was slurried with water and filled into the column. Before use the column was washed with several column volumes of 0.1 *M* ammonium sulfate–0.025 *M* sulfuric acid solution. The resulting bed height was usually 18 cm.

*Anion-exchange column (C)*. A column, 1.0 cm i.d. and 6 cm in height, was used. Dowex 1-X8, 100–200 mesh, chloride form, was used; 2 g of dried resin was slurried with water and transferred to the column. Before use the column was washed with several column volumes of 6 *M* hydrochloric acid. The resulting bed was usually 3 cm long.

To each column the eluant was introduced through a 100-ml separatory funnel whose stem was attached to the top of the column with rubber tubing. All the other chemicals used were of G. R. grade purity.

A Hitachi FPW-4 type photoelectric colorimeter with 1-cm cells was used for absorbance measurements.

### *Procedure*

Add 5 ml of water, 3 ml of perchloric acid and 5 ml of hydrofluoric acid to 0.5–1.5 g of a rock sample placed in a platinum dish. Warm on a hot plate. Repeat the hydrofluoric acid treatment several times to ensure complete decomposition. Expel the excess of perchloric acid. Add a few drops of perchloric acid to the residue and evaporate to dryness to remove the hydrofluoric acid. Treat the residue with 3 ml of hydrochloric acid and 40 ml of water, and heat near the boiling point with stirring until a complete or almost complete solution has been obtained. Add a slight excess of 1:1 ammonium hydroxide solution to the hot solution. Keep the mixture near the boiling point for a few min and then filter through a 9-cm coarse filter paper. Wash the precipitate with hot 2% ammonium chloride solution. Transfer the precipitate to a beaker. Dissolve the precipitate in a minimum amount of hydrochloric acid and evaporate to dryness. Take up the residue in 20 ml of 3 *M* hydrochloric acid. Load the solution on to the top of the column (A) and wash with 10 ml of water. Remove foreign ions by elution with 20 ml of 0.3 *M* ammonium sulfate–0.025 *M* sulfuric acid solution at a flow rate of 0.7 ml per min. Strip the scandium by elution with 15 ml of the same solution. Add 30 ml of 0.025 *M* sulfuric acid to the effluent so that the resulting solution is 0.1 *M* in ammonium sulfate and 0.025 *M* in sulfuric acid. Load the solution on to the top of the column (B). Remove foreign ions by elution with 45 ml of 0.1 *M* ammonium sulfate–0.025 *M* sulfuric acid solution at a flow rate of 0.5–1 ml per min. Elute scandium with 130 ml of the same solution. Add 1 ml of iron(III) collector (10 mg Fe(III)/ml) to the effluent and heat to boiling. Precipitate



iron(III) hydroxide by dropwise addition of 1:1 ammonium hydroxide solution. Filter off through a coarse filter paper. Wash the precipitate with hot 2% ammonium chloride solution. Transfer the precipitate along with the filter paper to a beaker and dissolve in 10 ml of 6 *M* hydrochloric acid. Filter the mixture through a filter paper. Pass the filtrate through column (C). Wash the column 3 times with 2-ml portions of 6 *M* hydrochloric acid. Collect all the hydrochloric acid solution and evaporate to dryness. (When organic materials are present, they must be destroyed with a few drops of perchloric acid and nitric acid.)

Dissolve the residue in 1 ml of 0.1 *M* hydrochloric acid. Add 4 ml of water, 2 ml of aqueous 0.1% arsenazo solution, 2.5 ml of 1 *M* acetate buffer pH 6.1 and 1 ml of 0.1 *M* ammonium hydroxide. Transfer the colored solution to a 25-ml volumetric flask and dilute to the mark with water. Measure the absorbance at 570 nm, using a reagent blank as the reference and compute the quantity of scandium from a calibration curve.

#### RESULTS AND DISCUSSION

Many sensitive organic reagents have been reported for scandium, including alizarin red S<sup>14</sup>, arsenazo<sup>18</sup>, chlorophosphonazo III<sup>19</sup>, 5,7-dichloroxine<sup>20</sup>, eriochrome cyanine R<sup>21</sup>, 8-hydroxyquinoline<sup>22</sup>, pontachrome azure blue B<sup>23</sup>, 4-(2-pyridylazo)-resorcinol<sup>24</sup>, quercetin<sup>25</sup>, tiron<sup>26</sup>, and xylenol orange<sup>27</sup>. Because of the effective removal of interfering ions by the 3 steps of ion exchange, a choice of organic reagents is rather arbitrary. Based on considerations of color stability, sensitivity, availability, and simplicity, arsenazo was chosen for the present work.

The arsenazo method is sensitive (molar absorptivity  $1.7 \cdot 10^4$  at 570 nm) and conforms to Beer's law up to at least 50  $\mu\text{g}$  of scandium per 25 ml of solution. Al, Cr(III), Cu(II), Fe(III), rare earths, Th, Ti, U(VI) and Zr interfere strongly but Al, rare earths, Th, U(VI), Zr and Sc are strongly adsorbed on column (A) from 3 *M* hydrochloric acid solution, while Cr(III), Cu(II), Fe(III) and Ti(IV) are not adsorbed. Scandium is quantitatively recovered by elution with 0.3 *M* ammonium sulfate-0.025 *M* sulfuric acid solution from column (A). When the sample contains an excessive amount of aluminum or iron(III), the eluted scandium tends to be slightly contaminated. Thorium and uranium(VI) behave like scandium in column (A). These difficulties can be eliminated by introducing an additional anion-exchange step in acid sulfate medium. Unless excessive amounts of iron(III) and aluminum accompany scandium they can easily be removed from column (B) by eluting with 0.1 *M* ammonium sulfate-0.025 *M* sulfuric acid solution. Thorium and uranium(VI) are strongly adsorbed on column (B).

The volume of the effluent from column (B), which contains scandium, is inconveniently large hence scandium must be concentrated with 10 mg of iron(III) by ammonium hydroxide. The separation of scandium from iron(III) can easily be effected by column (C); iron(III) is strongly adsorbed, while scandium comes through. Scandium is thus effectively concentrated in a moderate amount of 6 *M* hydrochloric acid.

Five synthetic samples, which resembled the average composition of gabbro and contained known quantities of scandium, were analyzed for scandium by the above procedure. The results are shown in Table I; as can be seen, scandium was

TABLE I

RECOVERY OF SCANDIUM IN A SYNTHETIC SAMPLE<sup>a</sup>

<i>Sc taken</i> ( $\mu\text{g}$ )	<i>Sc found</i> ( $\mu\text{g}$ )
20.6	23.5
41.3	41.0
43.0	39.0
43.0	40.0
43.0	44.0

<sup>a</sup> Each synthetic mixture employed here contains:  $\text{Al}_2\text{O}_3$  75.58 mg,  $\text{Fe}_2\text{O}_3$  57.18 mg,  $\text{MgO}$  33.16 mg,  $\text{TiO}_2$  3.83 mg,  $\text{MnO}$  1.29 mg,  $\text{ThO}_2$  1.19 mg.

TABLE II

DETERMINATION OF SCANDIUM IN SILICATE ROCKS

<i>Sample</i>	<i>Sample taken</i> (g)	<i>Sc added</i> ( $\mu\text{g}$ )	<i>Sc found</i> ( $\mu\text{g}$ )	<i>Sc content in</i> <i>original sample</i> (p.p.m.)
Basalt	0.51796	—	17.5	33.8
Basalt	0.51697	—	19.0	36.7
Basalt	0.53181	—	18.5	34.8
Basalt	0.51064	—	18.5	36.2
Basalt	0.50845	—	17.0	33.4
Basalt	0.57230	15.5	36.0	35.8
Basalt	0.53822	10.3	28.5	33.8
Basalt	0.50419	5.2	22.0	33.3
				Av. $34.7 \pm 1.2$
Andesite	0.75813	—	14.0	18.5
Andesite	0.61285	—	14.0	22.8
Andesite	0.62507	—	13.5	21.6
Andesite	0.63541	—	14.0	22.0
Andesite	0.63489	—	12.5	19.7
Andesite	0.61042	—	12.5	20.5
Andesite	0.70001	—	13.0	18.6
Andesite	0.71686	15.5	30.5	20.9
Andesite	0.64021	15.5	29.0	21.1
Andesite	0.63903	10.3	24.5	22.2
Andesite	0.61215	10.3	23.5	21.6
Andesite	0.60049	5.2	17.0	19.7
Andesite	0.67375	5.2	17.5	18.6
				Av. $20.7 \pm 1.3$
Quartz diolite	1.06723	—	14.0	13.1
Quartz diolite	1.13207	—	14.0	12.3
Quartz diolite	1.05508	—	12.5	11.8
Quartz diolite	1.18530	—	13.0	11.0
Quartz diolite	1.16061	15.5	27.5	10.3
Quartz diolite	1.07787	10.3	24.5	13.1
Quartz diolite	1.05594	5.2	16.0	10.2
Quartz diolite	1.03141	5.2	19.0	13.3
				Av. $11.9 \pm 1.2$
W-1 (diabase)	0.45464	—	15.0	33.0
W-1 (diabase)	0.46061	—	15.5	33.7
W-1 (diabase)	0.41816	—	14.5	34.7
				Av. $33.8 \pm 0.7$

recovered within 90–110%. The results of the determination of scandium in some representative rock samples are shown in Table II. In order to obtain information about the accuracy of the present method, a known amount of scandium was added to each analyzed sample and overall recovery was obtained. The results are also quoted in Table II. Precision given indicates the standard deviation based on all determinations including the addition test. The results of the determination of scandium in the rock standard W-1 are also listed in Table II. For comparison earlier literature values for scandium in W-1 are quoted in Table III. The results of determination of scandium in W-1 by the present method indicate satisfactory agreement with values by neutron activation methods.

TABLE III  
PREVIOUS DATA FOR THE CONTENT OF SCANDIUM IN W-1

Sc (p.p.m.)	No. of detns.	Method	Reference
43 <sup>a</sup>		Spectrographic	AHRENS AND FLEISCHER <sup>1</sup>
25	10	Spectrographic	WEBER AND MIDDLETON <sup>2</sup>
38	21	Spectrographic	ROOKE AND FISHER <sup>3</sup>
40	2	Spectrographic	CLARKE AND SWAINE <sup>4</sup>
120	22	Spectrographic	GOVINDARAJU <sup>5</sup>
33	2	Neutron activation	DESAI <i>et al.</i> <sup>8</sup>
34	4	Neutron activation	KEMP AND SMALES <sup>9</sup>
34	3	Neutron activation	HAMAGUCHI <i>et al.</i> <sup>11</sup>
36	3	Neutron activation	HAMAGUCHI <i>et al.</i> <sup>12</sup>

<sup>a</sup> Value recommended by AHRENS AND FLEISCHER based on data before 1960; range 5–70 p.p.m.

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#### SUMMARY

A spectrophotometric determination of scandium in silicate rocks has been developed with arsenazo as the color reagent. After the decomposition of samples with a hydrofluoric–perchloric acid mixture, traces of scandium are separated from interferences by cation- and anion-exchange in acid sulfate media and anion exchange in hydrochloric acid solution. The successive 3 steps, with an intermediate concentration step, yield scandium in a sufficiently pure state for spectrophotometric determination.

#### RÉSUMÉ

On propose une méthode spectrophotométrique pour le dosage du scandium dans des roches silicatées, au moyen d'arsenazo comme réactif. Après décomposition des échantillons à l'aide d'un mélange acide fluorhydrique–acide perchlorique, des traces de scandium sont séparées par échangeur de cations et d'anions, en milieu sulfate acide, et par échangeur d'anions en milieu acide chlorhydrique. On obtient ainsi un scandium suffisamment pur pour un dosage spectrophotométrique.

## ZUSAMMENFASSUNG

Es wurde eine spektralphotometrische Bestimmung von Scandium in Silikaten unter Verwendung von Arsenazo entwickelt. Nach der Zerstörung der Probe mit einem Gemisch aus Fluorwasserstoff und Perchlorsäure werden Spuren Scandium von störenden Elementen durch Kationen- und Anionenaustausch abgetrennt.

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## THE EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM WITH TETRAPHENYLARSONIUM CHLORIDE

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Among the colorimetric methods that have been published for the determination of niobium, the thiocyanate methods are probably the most popular. A review of methods for niobium has been published which includes both the ether extraction and homogeneous method, which is dependent upon the addition of acetone for color development<sup>1</sup>. The former method is subject to interference by hydrolysis of the tantalum and niobium, which results in an incomplete extraction of the niobium. These sources of error make necessary a special treatment of the sample before analysis. Furthermore, the ether extract must be left for 30 min or more before the absorbance is measured. The homogeneous method has many interferences from metals which are difficult to reduce or mask under the conditions necessary for the determination and consequently require a time-consuming prior separation of the niobium. An interference with the determination of niobium has also been reported to occur from the polymerization products of thiocyanic acid. Moreover, it appears that the concentration of reagents must be closely controlled since the color intensity of the niobium complex is sensitive to any changes in reagent concentration.

Tetraphenylarsonium ion (TPA) forms a water-insoluble ion-pair with the thiocyanate complex of niobium which may be extracted from water into chloroform, 9:2 chloroform-acetone solution, other partially halogenated hydrocarbons, and some ketones. It appeared that the ion-pair type of extraction would allow a great improvement in the thiocyanate method for the determination of niobium since many of the difficulties of the acetone method as well as those encountered in the extraction of the free acid may be overcome by extracting with tetraphenylarsonium chloride (TPACl) and an inert solvent. This extraction of the TPA metal complex ion-pair with chloroform has been used successfully for the determination of gold, cobalt, palladium, and tungsten<sup>2-5</sup>. These methods indicate that the conditions for successful extraction of the arsonium ion-pair are usually much less critical than those for the free acid. Moreover, the arsonium ion-pair extract in inert solvents is usually more stable than extracts of the free acids in reaction solvents. Hence, a method for the analysis of niobium was investigated which was based on the chloroform extraction of the salt formed with the TPA ion and the niobium-thiocyanate complex. Approximately 70% of the niobium could be extracted in one extraction and a molar absorptivity of 27,500 was observed. Additional investigations revealed that more than 90% of the niobium could be extracted in one extraction using a 9:2 chloroform-acetone

solution and the molar absorptivity was increased to 36,000. Excellent results were obtained from the analysis of 5 NBS samples of steels and heat-resisting alloys with the new method. When little difficulty is encountered in the dissolution of a sample, an analysis can be completed in less than an hour. The interferences of molybdenum and tungsten are eliminated by a preliminary separation procedure where these elements are extracted as thiocyanate complexes, and the simultaneous extraction of niobium is prevented by masking as the fluoride complex. The fluoride complex is then destroyed with boric acid and the niobium is extracted as the thiocyanate complex.

The composition of the thiocyanate complexes of niobium has been investigated by radio-tracer techniques in aqueous and nonaqueous media. WERNER studied the extraction of radioactive niobium-95 in methyl isobutyl ketone and assigned to the species extracted, the formula  $\text{Nb}(\text{SCN})_6^-$  associated with oxonium ions of the type  $(\text{R}_2\text{OH})^+$  where R is an alkyl group<sup>6</sup>. TROITSKII studied the mechanism of the extraction in butyl alcohol, and concluded<sup>7</sup> that the extracted species is  $\text{HNbO}(\text{SCN})_4$ . GOLUB AND SYCH studied the thiocyanate complexes in methanol, butanol, and dimethylformamide (DMF) using conductance techniques, spectrophotometry, and precipitation of the niobium salts by evaporation of the solvent<sup>8</sup>. Spectrophotometric results indicated complexes with a thiocyanate/niobium ratio of 1:1, 2:1, and 3:1 in methanol; 1:1, 2:1, and 4:1 in butanol; and 1:1, and 7:1 in DMF. Precipitated niobium salts were isolated with a thiocyanate/niobium ratio of 2:1 and 7:1 in the methanol and DMF systems, respectively. An application in the present work of the modified variations method reported earlier<sup>9</sup> gave a thiocyanate/niobium ratio of 2:1.

## EXPERIMENTAL

### *Apparatus and materials*

Beckman Model DU, DB, and DK-1 spectrophotometers were used for absorption spectra measurements. The DU was operated at a mechanical slit width of 0.06 mm; 1-cm ground glass-stoppered quartz cells were used for all measurements.

A buret funnel and 2.5-cm filter paper were used to filter the chloroform extracts.

Standard niobium solutions were prepared from niobium pentoxide obtained from K and K Laboratories, Jamaica, New York. The oxide was dissolved by means of a bisulfate fusion, cooled, and then diluted to volume using 12 M hydrochloric acid and the minimum amount of water necessary to keep the potassium sulfate salts in solution. The niobium pentoxide was analyzed by means of an ion-exchange method and its purity was found to be 99.04%<sup>1,10</sup>.

Tetraphenylarsonium chloride, recrystallized from ethanol-ether solutions if discolored or if it gave colored solutions, was used to prepare 0.05 M solutions.

Potassium fluoride solutions, 4 M, were prepared from Mallinckrodt Analytical Reagent potassium fluoride dihydrate, filtered, and stored in a polyethylene bottle.

The mercaptoacetic acid, 80% in water (analytical grade), was obtained from Eastman Organic Chemicals, Rochester, New York.

A 9:2 by volume chloroform-acetone solution was used as the extracting solvent.

All other solutions were prepared from salts of analytical reagent quality.

### Absorption spectra

The absorption spectrum of the niobium complex was obtained in the following manner. A 2-ml aliquot of  $1.14 \cdot 10^{-4}$  M solution of niobium, in 12 M hydrochloric acid, was added to a 60-ml separatory funnel equipped with a Teflon stopcock, followed by 3 ml of water, 5 ml of 6 M hydrochloric acid, and 3 ml of 3 M potassium thiocyanate solution. Upon addition of 1.0 ml of 0.05 M TPACl, a yellow precipitate formed, as well as a white precipitate of TPASCN. The aqueous phase was then extracted with 13 ml of the chloroform-acetone solution by shaking vigorously for 1.5–2 min. The two phases separated quickly and well, the organic layer showing the bright yellow color of the niobium complex. The chloroform solution was filtered into a 25-ml volumetric flask in order to remove suspended water droplets. After the addition of 1 ml of TPACl, the aqueous phase was extracted a second time with 13 ml of 9:2 chloroform-acetone. The second extract, usually colorless, was combined with the first. The spectrum of the thiocyanate complex of niobium in 9:2 chloroform-acetone (Fig. 1) was obtained with a Beckman DB spectrophotometer using chloroform in the reference cell.

A blank extract was prepared by substituting a 2-ml aliquot of 12 M hydrochloric acid for the niobium aliquot in the above procedure. The spectrum of the blank is also shown in Fig. 1.

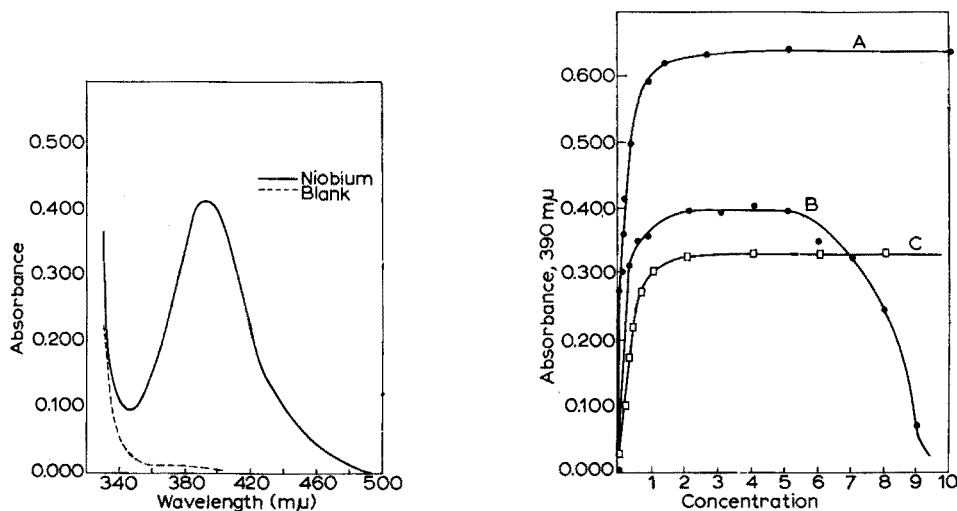


Fig. 1. Absorption spectrum of the niobium complex in 9:2 chloroform-acetone solution.

Fig. 2. Extraction efficiency as a function of reagent concentration in the aqueous phase. (A) (millimoles TPACl added)  $\cdot 100$ . (B) Molar concentration of HCl. (C) (Molar concentration of KSCN)  $\cdot 0.1$ .

### Extraction variables

The effect of various reagents on the efficiency of extraction was investigated by varying the concentration of the reagents, one at a time, and noting the absorbance of the extract. The following procedure was used to determine the extraction efficiency as a function of hydrochloric acid concentration. A 2-ml aliquot of standard niobium solution was added to a separatory funnel;  $(10-x)$  ml of cold 6 M hydrochloric

acid,  $x$  ml of cold water and 2 ml of 3 *M* potassium thiocyanate were also added. After the addition of 1 ml of 0.05 *M* TPACl, the aqueous solution was extracted with 15 ml of chloroform–acetone by shaking for 2 min. A small portion of the extract was filtered into a cell for measurement of the absorbance. The results are shown in Fig. 2. Procedures similar to that outlined above were used to study the effect of TPACl and thiocyanate on the extraction efficiency.

### Calibration

A series of standard solutions was prepared by dilution of aliquots of the stock solution with concentrated hydrochloric acid. Aliquots were analyzed by the *Analytical procedure* described below. The separation and masking steps were included, but the addition of tin(II) chloride after the second extraction was omitted. The absorbance of the extract was measured at 390 nm *vs.* chloroform in the reference cell.

TABLE I

INTERFERENCES IN THE EXTRACTION AND DETERMINATION OF NIOBIUM WITH TPACl  
(Taken: 21.3  $\mu\text{g}$  Nb; absorbance at 390 nm = 0.336)

Diverse element	Quantity ( $\mu\text{g}$ )	Ratio of diverse element to niobium	Absorbance ( $\pm 0.002$ )	Percentage error
—	21.3	—	0.336	$\pm 0.596$
Co	479	22.4	0.336	0.000
Mn	400	18.8	0.333	-0.892
Cr	400	18.8	0.336	0.000
Ni	482	22.6	0.334	-0.596
Cu	1000	47.0	0.335	-0.298
Ti	79.3	3.72	0.336	0.000
Ti	396	18.8	0.414	+23.2
V	204	9.6	0.334	-0.596
Sn	1000	46.9	0.179	-53.0
Ta	2520	118	0.341	+1.49
Mo <sup>a</sup>	998	45.8	0.336	0.000
W	18.4	0.9	0.337	+0.298
W	92	4.3	0.337	+0.298
Fe	2280	107	0.336	0.000

<sup>a</sup> Two extractions, each consisting of 0.25 ml of TPACl and 7 ml of chloroform–acetone, were required to move the molybdenum.

### Interferences

Interference studies were made on most of the elements that commonly occur in steels and niobium ores. The effect of each diverse element was checked by adding the element in the appropriate oxidation state to an aliquot of the standard niobium solution and then extracting the niobium as described in the *Analytical procedure*. The results are summarized in Table I.

### Analytical procedure

Samples are dissolved by heating in concentrated hydrochloric acid, to which 1-ml portions of concentrated nitric acid are added occasionally to assure complete



solution and oxidation. When dissolution is complete, the solution is boiled for 10–20 min to remove most of the nitrogen oxides. It is not necessary to remove completely the nitric acid. After boiling, the solution is transferred and diluted to volume with concentrated hydrochloric acid. The solution should be tested for the presence of oxides of nitrogen by making an extraction on a portion of the sample with chloroform. If the extract has a yellow-brown color, the aliquot of sample should be repeatedly extracted until the chloroform layer is colorless.

A suitable aliquot, usually 2 ml, of the sample is placed in a 60-ml separatory funnel for analysis. Dilute with 3 ml of cold water, add 1 ml of cold 3 M potassium thiocyanate, followed by 1 ml of 80% mercaptoacetic acid; swirl and leave for 1–3 min, or until the red color of the iron(III) thiocyanate complex is bleached. Add 0.5 ml of 4 M potassium fluoride solution and 0.5 ml of 0.05 M TPACl. Extract with 9–10 ml of chloroform–acetone by shaking for 1 min. Discard the extract and rinse the aqueous phase with 4–5 ml of solvent in order to remove remaining droplets of the first extract. Add 2–3 g of boric acid to demask the niobium, 5 ml of cold 6 M hydrochloric acid and 2 ml of cold 3 M potassium thiocyanate solution. Swirl frequently and leave for 2–3 min so that the boric acid may have time to dissolve. Add 1 ml of 0.05 M TPACl and swirl to mix. Extract with 13 ml of chloroform–acetone by shaking for 2 min. Filter the extract into a 25-ml volumetric flask. Repeat the extraction by adding both TPACl and chloroform–acetone solution. Two extractions are sufficient to remove all of the niobium. If necessary, add 1–2 drops of 10% tin(II) chloride to the volumetric flask in order to reduce any iron(III) present.

#### *Composition of tetraphenylarsonium thiocyanato–niobate(V)*

In order to determine the composition of the extracted complex with respect to thiocyanate and TPA the following investigations were made. For the determination of the TPA/niobium ratio, 2 ml of  $1.14 \cdot 10^{-4}$  M niobium in concentrated hydrochloric acid were transferred to a 25-ml ground glass-stoppered graduated cylinder containing 4 ml of cold 6 M hydrochloric acid. An aliquot ( $x$  ml) varying in volume from 0.5 to 5 ml of 0.05 M, 0.0025 M, or 0.00025 M TPACl was added, followed by 2 ml of 3.0 M potassium thiocyanate and  $(7-x)$  ml of cold distilled water, and the mixture was swirled to mix. Then, 15 ml of chloroform–acetone solution were pipetted in, the mixture was shaken for 2 min, the layers were allowed to settle, and the absorbance of the extract was measured at 390 nm. The absorbance,  $A_0$ , obtained if the niobium extraction was complete was 0.646. All absorbance measurements were corrected for the absorbance of the blank.

The experiment was repeated using 2 ml of  $2.30 \cdot 10^{-4}$  M niobium, for which the value of  $A_0$  was 1.295.

The determination of the thiocyanate/niobium ratio was carried out as follows: 5 ml of  $2.3 \cdot 10^{-5}$  M niobium in concentrated hydrochloric acid were pipetted into a graduate, and 1 ml of 0.05 M TPACl,  $x$  ml of cold water, and  $(9-x)$  ml of standard 3 M or 0.3 M potassium thiocyanate were added ( $x$  was 0.5, 1, 2, 3, 4 for the 3 M solution and 0.5, 0.7, 1, 1.5, 2, and 3 for the 0.3 M solution). The complex was then extracted with 15 ml of chloroform–acetone.  $A_0$  was 0.328.

The experiment was repeated using 2 ml of  $1.14 \cdot 10^{-4}$  M niobium as well as 6 ml of 6 M hydrochloric acid,  $(6-x)$  ml of water and  $x$  ml of 0.3 or 0.06 M potassium thiocyanate. In this experiment  $A_0$  was 0.647.

## TREATMENT OF DATA

The composition of the complex was deduced by means of a method previously described<sup>9</sup>. The basic equations, (2) and (4), which relate the absorbance,  $A$ , to the TPA/niobium ratio,  $n$ , or the thiocyanate/niobium ratio,  $r$ , which were used are written in the following manner:

$$\log \left( \frac{A}{A_0 - A} \right) = \log K_5 + r \log [(SCN)_t - rA/a] + n \log [(TPA)_t - nA/a] \quad (1)$$

$A_0$  is the expected absorbance for complete extraction of the niobium taken and  $a$  is 41,600. If the thiocyanate concentration,  $(SCN)_t$ , is large compared to the niobium concentration, and is held constant for a series of extractions in which the TPA concentration,  $(TPA)_t$ , is varied, then

$$\log \left( \frac{A}{A_0 - A} \right) = \log K_6 + n \log [(TPA)_t - nA/a] \quad (2)$$

As a first approximation, a plot of  $\log A/(A_0 - A)$  versus  $\log (TPA)_t$  or  $\log$  (total millimoles TPA) produces a straight line of slope  $n$ .

When the TPACl concentration is held constant and the thiocyanate concentration is varied, then

$$\log \left( \frac{A}{A_0 - A} \right) = \log K_7 + r \log [(SCN)_t - rA/a] \quad (3)$$

$$\text{Since } rA/a \ll (SCN)_t, \log \left( \frac{A}{A_0 - A} \right) = \log K_8 + r \log V_{KSCN} \quad (4)$$

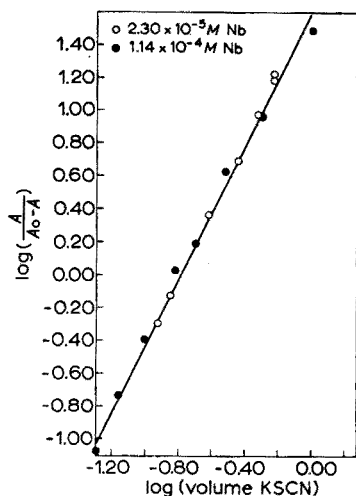


Fig. 3. Plot for determining stoichiometric molar ratio of thiocyanate to niobium.

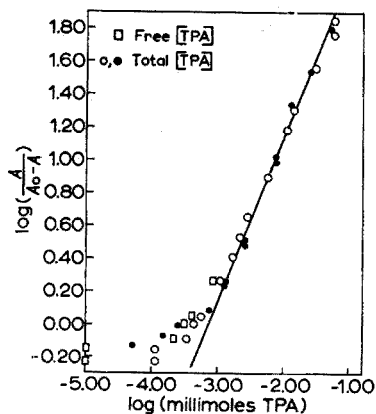


Fig. 4. Plot for determining stoichiometric molar ratio of TPA to niobium.

The data were plotted according to eqns. (4) and (2), and are presented in Figs. 3 and 4, respectively. The data from the experiments for higher concentrations

of niobium were corrected in the log concentration values by adding  $-0.250$  and  $-0.925$  respectively to each value for the TPA/niobium and thiocyanate/niobium ratios in order to reduce all the values to a single plot.

## RESULTS AND DISCUSSION

### *Composition of tetraphenylarsonium thiocyanato-niobate(V)*

In Fig. 3 the points are experimental and the line is drawn through the points with a slope of 2 which indicates a thiocyanate/niobium ratio of 2. The TPA graph (Fig. 4) is more complicated to interpret since a positive deviation occurs at very low TPA concentrations. Neglecting the lower portion of the curve, a line of slope unity is drawn through the data points. The agreement between the experimental points and the line of slope unity indicate a TPA/niobium ratio of one. The results indicate that the formula for the extracted species is  $(\Phi_4As)^+[Nb(SCN)_2X]^-$ , where X may be chloride, oxo, or hydroxy ligands, and niobium is present as niobium(V).

The positive deviation at very low TPA concentrations is caused by coextraction of niobium as the free thiocyanatoniobic acid along with the arsonium ion-pair. The presence of the free thiocyanatoniobic acid was verified by performing an extraction on a niobium solution in the absence of TPACl. The absorbance of the extract was 0.440 at 390 nm, and the shape of the spectrum was identical to that of the TPACl extract. At higher TPACl concentrations the extraction of the thiocyanatoniobic acid is negligible since the partition coefficient of the TPA complex is much greater, as inferred from the solubilities of the 2 species in water and the organic solvent. Corrections for simultaneous extraction of the free acid were not applied since quantitative values for the partition coefficients of the 2 complexes are not available.

The extraction of the free thiocyanatoniobic acid does not occur when commercial chloroform is used as the extraction solvent. A value of 0.95 was obtained for the slope of the line for the determination of the TPA/niobium ratio in the chloroform system. A continuing investigation of the nature of the complex and evaluation of the partition coefficients is in progress and the results will be reported later.

### *Analytical procedure*

The analysis consists of 4 parts: the dissolution of the sample, reduction of iron and separation of molybdenum and tungsten, formation and extraction of the thiocyanate complex of niobium followed by a spectrophotometric measurement of the concentration. The conditions must be carefully controlled in the final extraction step in order that a constant quantity of thiocyanic acid will be extracted in each analysis; however, the concentration of thiocyanate before extraction is not critical. It is recommended that the potassium thiocyanate, hydrochloric acid and water be chilled to  $3-5^\circ$  in an ice bath before use. (An ideal ice bath is a polystyrene shipping container used for shipping  $1/2$  gallon bottles of acid.) The use of cold solutions minimizes the decomposition of thiocyanate to the extent that the extracts are stable for several hours.

Curve B (Fig. 2) shows that the concentration of hydrochloric acid in the aqueous phase is not critical; however, it is kept within the range  $3-5 M$ . At lower acid concentrations hydrolysis of tantalum and tungsten is likely to occur, whereas

at concentrations above 5 *M* the decomposition of thiocyanate is more likely. Curve A (Fig. 2) indicates that for a minimum number of extractions 0.025 to 0.05 mmoles of TPACl should be used per extraction. Curve C (Fig. 2) indicates that the aqueous phase should be at least 0.2 *M* in thiocyanate ion. In the analytical procedure, a thiocyanate concentration of 0.6 *M* was used.

A calibration curve of absorbance as a function of concentration was prepared, assuming complete extraction of the niobium. Beer's law was followed over the entire concentration range investigated, 0.17 to 3.2 mg niobium/liter. The specific absorptivity of  $388 \pm 2$  was determined by a least squares fit of 35 data points on the calibration curve. The intercept of the line at zero niobium concentration occurred at an absorbance of 0.005. The absorbance of the blank is caused by the excess TPASCN present in the extract.

Preliminary investigations of diverse ions were conducted with the procedure outlined in the *Absorption spectra* section. Iron(III), molybdenum(V,VI), and tungsten(V,VI) interfered strongly, forming thiocyanate complexes that were extracted with the niobium complex. The interference of iron is removed by reduction and the interferences of molybdenum and tungsten are eliminated by a prior extraction with TPACl and potassium thiocyanate. The extraction of niobium is prevented by masking as a fluoride complex.

The separatory extraction not only removed molybdenum and tungsten, but also a large quantity of the mercaptoacetic acid reductant. Additional mercaptoacetic acid is not added to prevent the re-oxidation of iron(II) after niobium is demasked for: (1) this would cause slow reduction of any remaining tungsten(VI) to occur, and (2) iron(III)-thiocyanate complexes are not readily reduced by mercaptoacetic acid. Hence, in the analysis of steels, any iron that is oxidized and coextracted with niobium is reduced after extraction of the niobium. This is accomplished by adding 2 drops of 10% tin(II) chloride to the separatory funnel after the second extraction of the niobium, but before removal of the organic phase. The two phases are equilibrated for about 5 sec in order to transfer the tin(II) chloride to the organic phase. In some cases insufficient tin(II) chloride is extracted to reduce all the iron in the combined extracts containing the niobium complex; if the niobium extract is lemon yellow in appearance the iron is completely reduced, but if the extract is orange or brown-red, it is necessary to add 1 drop of tin(II) solution to the volumetric flask and invert a few times. A portion of the extract is then filtered into a spectrophotometer cell and the absorbance is measured at 390 nm. An alternative method for checking on the possibility of iron interference is to scan the spectrum in the vicinity of 500 nm and compare with the spectrum of a standard niobium extract.

The analytical procedure is adequate to prevent the interference of molybdenum, tungsten, and iron when they are present in ratios of 45:1, 4:1, and 107:1, respectively, compared to niobium on a gram/gram basis. When larger quantities of tungsten are present, it will be necessary to use a strong reductant to reduce the tungsten(VI) completely to tungsten(V) before its removal in the separation step.

When titanium is present a precipitate of a thiocyanate complex forms with the TPA ion. Prolonged shaking will cause the precipitate to decompose due to the preferential extraction of TPASCN from the aqueous phase.

Oxidizing agents such as nitrogen oxides interfere with the determination of niobium by causing the oxidation of thiocyanate ion. The absorbance of the extract

rapidly increases as a function of time, especially in the spectral region of 350–360 nm, which is characteristic of the thiocyanate decomposition products. For this reason it is mandatory to remove all nitrogen oxides from the solutions before making an analysis. It is not necessary to remove nitric acid, as no interference from small quantities has been observed.

The nature of this new method for niobium is such that the method can be easily modified for the analysis of niobium in special material, as the use of alternative reducing agents and masking agents for eliminating the interference of diverse ions will permit many modifications. For example, the determination of traces of niobium in tungsten can be made using a zinc amalgam to reduce the tungsten before its extraction from the masked niobium. Also, niobium can be determined in molybdenum by making successive extractions on the aqueous solution containing the masked niobium until the molybdenum concentration is reduced below the level of interference.

#### Accuracy

The accuracy and precision of the method were established by analysis of 5 Bureau of Standards standard samples of steel and heat-resisting alloys. The data are given in Table II. As can be seen, the method is as accurate as any of the procedures reported upon by the Bureau of Standards and the precision as found from the standard deviation of the samples is good.

TABLE II  
ANALYSIS OF NBS STANDARD STEEL AND ALLOY SAMPLES

NBS #	%Nb		Difference	Standard deviation	No. of samples	Sample description and % composition
	Reported	Found				
101e	0.013	0.017	+0.004	±0.001	7	Steel: W(0.06), Mo(0.43), Sn(0.02), V(0.04), Mn(1.8), Ni(9.5), Cr(18)
123b	0.75	0.753	+0.003	±0.007	11	Steel: W(0.18), Ta(0.2), Mo(0.2), V(0.05), Ti(0.006)
345	0.231	0.225	-0.006	±0.003	6	Steel: Mo(0.12), Ta(0.002), V(0.04), Mn(0.22), Cu(3.4), Ni(4.2), Cr(16)
167	3.15	3.12	-0.03	±0.01	8	Heat-resisting alloy: Ni(20), Co(43), Cr(20), Mo(3.9), W(4.5), Fe(2.1), Ta(0.08), V(0.03), Cu(0.04)
168	2.95	2.91	-0.04	±0.04	9	Heat-resisting alloy: Mn(1.5), Fe(3.4), Cu(0.04), Ni(20), Co(41), Cr(20), V(0.03), Mo(4.0), W(4.0), Ta(0.95), Ti(0.06), Fe(3.4)

#### SUMMARY

A rapid and accurate spectrophotometric method for niobium is described. Tetraphenylarsonium chloride is used to form an aqueous insoluble ion-pair, tetra-

phenylarsonium thiocyanato-niobate, which upon extraction into 9:2 chloroform-acetone solution has a molar absorptivity of 36,000/M/cm at 390 nm. Niobium is masked with fluoride before a separation step in which the interferences of molybdenum, tungsten, and iron are removed by reduction and extraction. Niobium is subsequently extracted after being demasked with boric acid. The method has been applied successfully to 3 NBS steels and 2 heat-resisting alloys.

#### RÉSUMÉ

On décrit une méthode spectrophotométrique rapide et précise, pour le dosage du niobium. Elle consiste à extraire le thiocyanatoniobate de tétraphénylarsonium dans une solution chloroforme:acétone (9:2); absorption molaire 36,000/M/cm à 390 nm. Molybdène, tungstène et fer sont éliminés au préalable par réduction et extraction, après avoir masqué le niobium avec un fluorure. Le niobium est ensuite extrait après "démasquage" au moyen d'acide borique. La méthode a été appliquée avec succès à 3 aciers NBS et 2 alliages résistants à la température.

#### ZUSAMMENFASSUNG

Es wird eine schnelle und genaue spektralphotometrische Methode zur Bestimmung von Niob beschrieben. Dazu wird das wasserunlösliche Tetraphenylarsonium-thiozyanatoniobat mit Chloroform-Aceton (9:2) extrahiert und die Extinktion (36,000/M/cm) bei 390 nm gemessen. Molybdän, Wolfram und Eisen, welche stören, werden vorher durch Reduktion und Extraktion abgetrennt; dabei wird das Niob mit Fluorid maskiert. Für die folgende Extraktion des Niobs wird Borsäure zur Demaskierung zugegeben. Die Methode wurde erfolgreich bei Stählen und hitzebeständigen Legierungen angewendet.

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## SPECTROPHOTOMETRIC DETERMINATION OF COBALT AND NICKEL WITH PYRIDINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE

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Pyridine-2-aldehyde-2-quinolyldrazone (PAQH), a tridentate chelating agent that forms colored complexes with only a few metals<sup>1</sup>, has been recommended for the spectrophotometric determination of palladium<sup>2</sup>. The cobalt complex of PAQH has a high molecular extinction coefficient and obeys Beer's law from 0.2 to 2 p.p.m.; since the complex is kinetically stable to protons, the reaction can be made very selective for cobalt. The nickel complex has a molecular extinction coefficient of  $51 \cdot 10^3$  and follows Beer's law from 0.1 to 1 p.p.m.; by chloroform extraction of the nickel complex, in the presence of thioglycolic acid, selective determination of nickel can be made.

## EXPERIMENTAL

*Apparatus, reagents, and solutions*

A Bausch and Lomb Spectronic 505 recording spectrophotometer was used to determine the spectra of the complexes and a Beckman DU spectrophotometer was employed for measurements at a particular wavelength.

PAQH was prepared, as previously described<sup>1</sup>, by refluxing equimolar quantities of pyridine-2-aldehyde and 2-hydrazinoquinoline in ethanol in the presence of a drop of acetic acid. The product was recrystallized from ethanol-water (m.p. 197°). Aqueous solutions of the reagent were prepared by dissolving the solid in a minimum amount of hydrochloric acid and diluting to a pH of 3-4; such solutions were stable indefinitely. The yellow colour of 0.05% solutions of PAQH in ethanol faded after 24 h and the decomposition was much faster at high pH (~10); the reagent has maximum absorption at 370 nm but does not absorb light beyond 520 nm (Fig. 1).

Spectrographically pure nickel sponge and iron- and nickel-free cobalt(II) sulphate were used to prepare stock solutions. All other reagents used were of analytical reagent grade quality.

*Effect of pH*

The effect of pH on colour development was studied by adding 5 ml of a 0.05% solution of PAQH in ethanol to the metal solution followed by 5 ml of appropriate buffer; the final volume of solution was 25 ml and was 1:1 in ethanol-water. Measurements were made at 510 nm for cobalt and 480 nm for nickel (Fig. 1). Maximum

colour development was from pH 6.5 to 11.5 for cobalt and from pH 8.5–11.5 for nickel (Fig. 2). In further studies the pH was adjusted to about 10 by the use of an ammonia–ammonium chloride buffer. All measurements were made against a reagent blank.

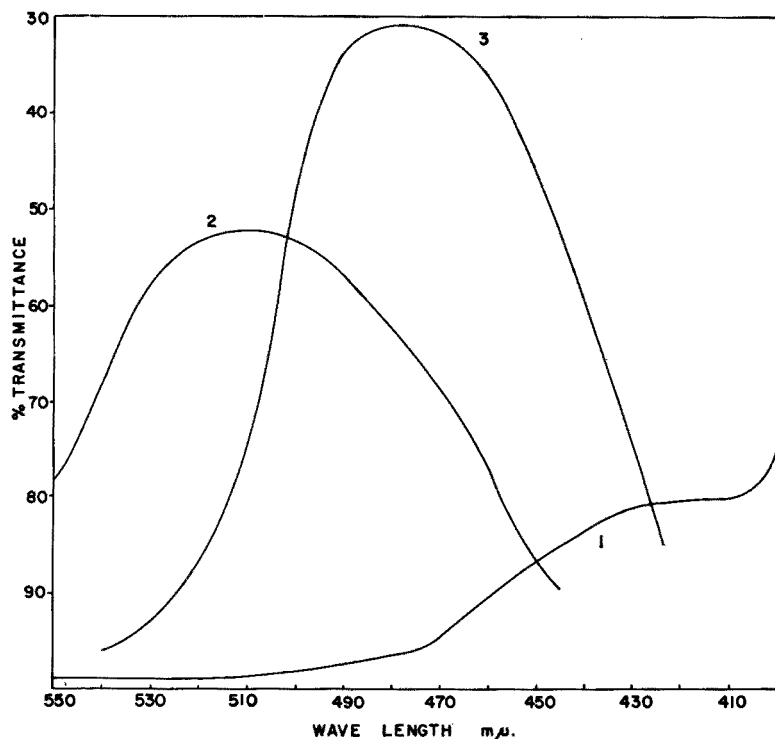


Fig. 1. Absorption spectra. (1)  $2.0 \cdot 10^{-5} M$  PAQH; (2)  $9.5 \cdot 10^{-6} M$  cobalt complex; (3)  $9.9 \cdot 10^{-6} M$  nickel complex.

#### *Effect of alcohol*

For solutions containing 0.6 p.p.m. of metal, turbid solutions were obtained when the alcohol to water ratio was less than 1:3. Solutions containing more than 50% ethanol did not enhance the colour markedly and 1:1 ethanol–water solutions were used in other experiments.

#### *Effect of order of addition*

Addition of ammonia–ammonium chloride buffer before reagent addition gave initially lower absorbances which slowly increased in value on standing. Maximum colour developed in about 1 h but the same intensity was obtained immediately when the order of addition was reversed. Reagent solution, therefore, should be added, followed by addition of buffer to adjust the pH.

#### *General procedure*

To 5 ml of metal solution containing 5–50  $\mu\text{g}$  of cobalt or 2.5–25  $\mu\text{g}$  of nickel,



add 5 ml of a 5% sodium citrate solution (to complex Fe(III), Al(III), etc.), 5 ml of an alcoholic 0.05% solution of PAQH, and 2.5 ml of ammonia-ammonium chloride pH 10 buffer. Dilute to 25 ml with ethanol. Read the absorbance against a reagent blank prepared in the same manner; make readings for cobalt at 510 nm and for nickel at 480 nm.

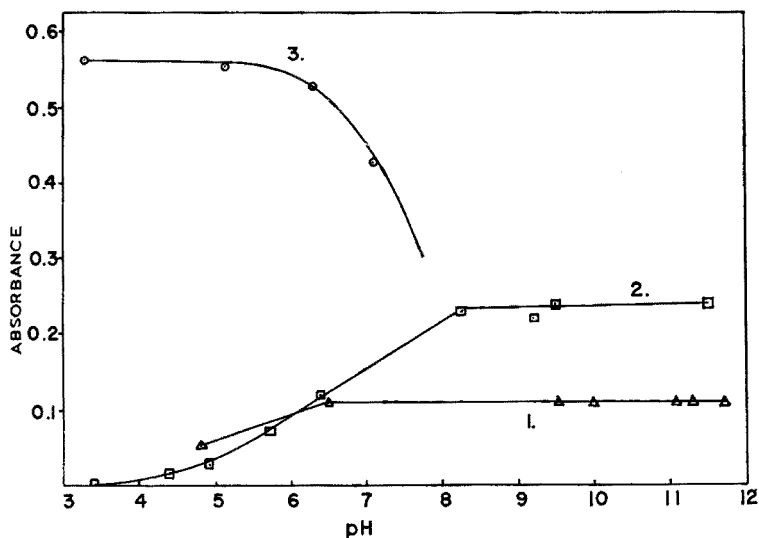


Fig. 2. Effect of pH on colour development. (1)  $4.0 \cdot 10^{-6}$  M cobalt complex; (2)  $4.0 \cdot 10^{-6}$  M nickel complex; (3)  $9.9 \cdot 10^{-6}$  M nickel complex in the presence of thioglycolic acid.

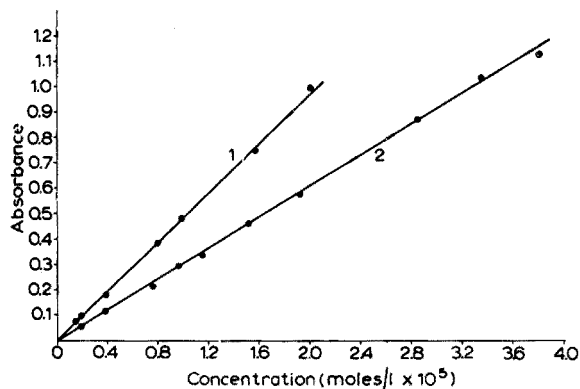


Fig. 3. Beer's law plots. (1) nickel complex at 480 nm; (2) cobalt complex at 510 nm.

Molecular extinction coefficients for cobalt and nickel chelates are  $30 \cdot 10^3$  and  $51 \cdot 10^3$  respectively. Beer's law is obeyed from 0.2 to 2 p.p.m. for cobalt and from 0.1 to 1 p.p.m. for nickel; typical results are shown in Fig. 3.

#### Effect of foreign ions

The reagent reacts with cobalt, copper, iron, zinc, cadmium, lead, nickel,

palladium and manganese<sup>1</sup> to give coloured products. However, when 0.6 p.p.m. of cobalt or nickel were determined in the presence of 100 p.p.m. of manganese or lead, absorbance differences were less than 2% from that of nickel or cobalt alone; 25 p.p.m. of iron(III) also did not interfere. In addition, results were excellent in the presence of 100 p.p.m. of a large number of other metal ions (*e.g.* Al(III), Cr(III), Sb(III), Bi(III), Sn(IV), Sn(II), Ca(II), Mg(II), Na(I), K(I), Mo(VI), W(VI), etc.). Fe(II), Zn(II), Hg(II), Cu(II), Cd(II), and Pd(II) interfere in the general procedure and should be absent.

The following anions (100 p.p.m.), when added as the sodium or potassium salts, did not interfere: fluoride, iodide, bromide, chloride, nitrate, sulphate, per-sulphate, phosphate, borate, thiocyanate, oxalate, tartrate and citrate. Cyanide, ethylenediaminetetraacetic acid, and silicate prevented formation of cobalt and nickel complexes with PAQH.

#### SELECTIVE DETERMINATION OF COBALT

Nickel, iron, zinc, mercury, copper, and cadmium react with PAQH to give coloured complexes that interfere in the general procedure for determining cobalt. However, these complexes are destroyed on the addition of acid whereas the cobalt complex is relatively stable towards protons; by formation of the complexes at pH 10 and then adding dilute hydrochloric acid to lower the pH to 3, cobalt can be determined in the presence of these otherwise interfering metals.

#### Procedure

To 5 ml of solution containing 10–100  $\mu\text{g}$  of cobalt, add 5 ml of a 10% sodium citrate solution (to prevent precipitation of iron(III) etc. at high pH) and adjust the pH to 3–4 with dilute hydrochloric acid. Add 5 ml of aqueous 0.5% solution of PAQH, 10 ml of ethanol, and 2 ml of ammonia–ammonium chloride buffer pH 10. Allow the solution to stand for 10 min. Adjust the pH to 3 with dilute hydrochloric acid, transfer to a 50-ml volumetric flask, and dilute to the mark with a suitable volume of water and alcohol (the final solutions were 50% in ethanol). Measure the absorbance of the solution at 510 nm against a reagent blank carried through the same procedure. Typical results are shown in Table I.

TABLE I

COBALT DETERMINATION IN PRESENCE OF METALS REACTING WITH PAQH

Cobalt taken (p.p.m.)	Cobalt found (p.p.m.)	Metal present (p.p.m.)
0.56	0.59	100 Ni(II)
0.56	0.57	100 Zn(II)
0.56	0.55	100 Fe(III)
0.56	0.59	100 Cd(II)
0.56	0.59	25 Cu(II)
0.56	0.53	20 Hg(II)
0.56	0.53	100 Cu(II) precipitated as CuS
0.56	0.53	100 Hg(II) precipitated as HgS

Copper(II) (>25 p.p.m.) and mercury(II) (>20 p.p.m.) produced a yellow colour and a yellow turbidity respectively. Interference from these metals at higher concentrations was eliminated by precipitation as sulphides, with thioacetamide, from 1 *N* hydrochloric acid solution.

#### SELECTIVE DETERMINATION OF NICKEL

The coloured complexes formed by the few metals that react with PAQH are soluble in chloroform. In the presence of thioglycollic acid, however, only nickel forms a complex that can be extracted by chloroform and an extremely selective determination of nickel is possible. The nickel complex has an absorption maximum at 492 nm in chloroform; the complex obeys Beer's law from 0.1 to 1 p.p.m. and has a molecular extinction coefficient (at 492 nm) of  $50.5 \cdot 10^3$ .

#### Procedure

To the metal solution containing 2.5–25  $\mu\text{g}$  of nickel, add 10 ml of a 10% sodium citrate solution and 1 ml of thioglycollic acid. Adjust the pH to 3–4 and add 5 ml of an aqueous 0.05% solution of PAQH. Add 5 ml of ethanol and 10 ml of pH 10 buffer and allow the solution to stand for 10 min. Extract twice with 10-ml aliquots of chloroform and dilute to 25 ml with ethanol. Measure the absorbance at 492 nm against a reagent blank carried through the same procedure.

Typical results are shown in Table II.

In the absence of alcohol, the nickel complex was incompletely extracted by chloroform and the chloroform extracts were turbid. The pH of the solution containing nickel and thioglycollic acid should not exceed 6.5 before the addition of reagent and buffer (see Fig. 2); nickel is complexed by thioglycollic acid above pH 6.5 and the complex, once formed, is only slowly decomposed by PAQH.

In addition to the results recorded in Table II, experiments showed that 100 p.p.m. of Mn(II), Pb(II), Cr(III), Al(III), Bi(III), Sn(II) and (IV), Mo(VI), W(VI) and V(V) did not interfere in the determination of 0.6 p.p.m. of nickel by the above procedure. Copper catalyzes the decomposition of thioglycollic acid<sup>3</sup> but this difficulty can be avoided by the addition of sodium citrate or ammonia so that the pH does not fall below 3.0 on adding thioglycollic acid. Iron(II and III) reacts with thioglycollic acid and PAQH to give a greenish chloroform-soluble species and interferes in the

TABLE II

NICKEL DETERMINATION IN PRESENCE OF METALS REACTING WITH PAQH

<i>Nickel taken</i> (p.p.m.)	<i>Nickel found</i> (p.p.m.)	<i>Metal present</i> (molar ratio to Ni)
0.59	0.56	170 Zn(II)
0.59	0.56	170 Cu(II)
0.59	0.55	170 Hg(II)
0.59	0.60	50 Cd(II)
0.59	0.60	20 Co(II)
0.59	0.64	30 Co(II)
0.59	0.64	170 Fe(III) <sup>a</sup>

<sup>a</sup> First extracted with isobutyl alcohol in the presence of ammonium thiocyanate.

determination of nickel; iron interference was removed by extracting with isobutyl alcohol in the presence of ammonium thiocyanate<sup>4</sup>.

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#### SUMMARY

Pyridine-2-aldehyde-2-quinolyldrazone (PAQH) is a selective and sensitive reagent for cobalt or nickel. The reagent reacts with only a few metals to give coloured complexes; with the exception of palladium, the cobalt chelate is the only complex relatively stable towards protons and PAQH is a very selective reagent for cobalt. In the presence of thioglycolic acid only nickel reacts with PAQH; the chelate is extracted with chloroform and its absorbance measured at 492 nm. The high molecular extinction coefficients ( $30 \cdot 10^3$  and  $51 \cdot 10^3$ ) permit the determination of 0.2–2 p.p.m. of cobalt and 0.1–1 p.p.m. of nickel.

#### RÉSUMÉ

La pyridine-2-aldéhyde-2-quinolyldrazone (PAQH) est un réactif sélectif et sensible du cobalt ou du nickel. Ce composé ne réagit qu'avec quelques métaux seulement pour donner des complexes colorés. A l'exception du palladium, seul le cobalt est stable en milieu acide. En présence d'acide thioglycolique seul le nickel réagit avec PAQH. Le chélate est extrait dans le chloroforme. Les coefficients d'extinction moléculaire élevés permettent le dosage de 0.2–2 p.p.m. de cobalt et 0.1–1 p.p.m. de nickel.

#### ZUSAMMENFASSUNG

Pyridin-2-aldehyd-2-chinolyldrazon (PAQH) ist ein selektives und empfindliches Reagenz für Kobalt oder Nickel. Das Reagenz reagiert mit nur wenigen Metallen zu gefärbten Komplexen. Mit Ausnahme von Palladium ist das Kobaltchelate der einzige Komplex, der relativ stabil gegen Protonen ist, und damit PAQH ein sehr selektives Reagenz für Kobalt. In Gegenwart von Thioglycolsäure reagiert nur Nickel mit PAQH. Das Chelate wird mit Chloroform extrahiert und seine Absorption bei 492 nm gemessen. Die hohen molaren Extinktionskoeffizienten ( $30 \cdot 10^3$  und  $51 \cdot 10^3$ ) erlauben die Bestimmung von 0.2–2 p.p.m. Co und 0.1–1 p.p.m. Ni.

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## SPECTROPHOTOMETRIC DETERMINATION OF TIN IN STEEL

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The sulfide-iodimetric method<sup>1</sup> is usually used for the determination of tin in steel. However, when the amount of sample available is limited, it is necessary to use a sensitive instrumental method for the analysis<sup>2,3</sup>. Recent work has shown that traces of tin in steel can be determined by the spectrophotometric phenylfluorone method after the tin has been isolated by acid sulfide separation<sup>1</sup> followed by double carbamate-chloroform extraction<sup>4</sup>. It has been found that the specificity of the phenylfluorone method can be improved by developing the color in acid solution containing peroxide plus oxalate as masking agents and that the sensitivity can be markedly increased by extracting the tin-phenylfluorone compound into a small volume of methyl isobutyl ketone (MIBK) for the spectrophotometric analysis. The proposed new method is suitable for the determination of 0.001-0.1% of tin in 0.1-0.01 g samples of low-alloy steel. In order to analyze steel containing tantalum, niobium, more than about 5% of molybdenum or more than traces of tungsten, the method would have to be modified.

## EXPERIMENTAL

*Preparation of calibration graph*

Evaporate 0-, 0.25-, 0.50-, 0.75- and 1.00-ml aliquots of standard tin sulfate solution (20  $\mu\text{g}$  Sn/ml) on a Meker-type flame to expel all of the sulfuric acid<sup>4</sup>. Avoid excessive baking of the bottom of the flask. Cool, and dissolve the tin(IV) sulfate by warming with 1.0 ml of 1:3 hydrochloric acid. Cool, wash down the inside of the flask with 20.0 ml of water and add 1.0 ml of 1% (w/v) ammonium oxalate solution, 1.0 ml of 15% hydrogen peroxide solution and 1 g of sodium chloride. Add 5.0 ml of phenylfluorone solution<sup>4</sup> and swirl to dissolve the sodium chloride. Allow to stand about 9 min. Then pour into a 75-ml separatory funnel and add 10.0 ml of MIBK (b.p. 114° to 116°). Ten minutes after adding the phenylfluorone solution, shake the solution for 15 sec. Drain off and discard the lower layer. Pour most of the MIBK layer through a dry 7-cm coarse-texture paper into a dry 50-ml conical flask. Without delay, measure the solution spectrophotometrically in a 1-cm absorption cell at 530  $\mu\text{m}$  using water as the reference solution. Prepare a calibration graph.

*Analysis of sample*

Dissolve a portion of the sample containing 1-20  $\mu\text{g}$  of tin in 5 ml of freshly prepared 4:1 hydrochloric acid-nitric acid mixture by heating gently. Then destroy

the nitric acid with a small excess of formic acid<sup>5</sup>. Precipitate the tin as sulfide from 100 ml of 1:19 hydrochloric acid solution containing 1 g of tartaric acid plus 1 mg of copper as chloride<sup>1</sup>. Filter, wash, return the paper to the flask and destroy organic matter by digestion with sulfuric, nitric, and perchloric acids. Expel the latter 2 acids and obtain the tin in 50 ml of 1:9 sulfuric acid. Make a double carbamate-chloroform extraction separation<sup>4</sup> except shake for 60 sec in the first extraction and omit the heating to 50° and the addition of potassium iodide-ascorbic acid solution before the reduction of the tin with thioglycolic acid solution. After destruction of the organic matter from the carbamate-chloroform extract and the flaming to remove all acid, dissolve the tin(IV) sulfate in 1 ml of 1:3 hydrochloric acid and proceed as directed in *Preparation of calibration graph*. Correct for a reagent blank carried through the procedure.

#### DISCUSSION

##### *Use of masking agents in the spectrophotometric analysis*

Tests on 100  $\mu\text{g}$  of 56 of the common elements<sup>6</sup> showed that only 12 metals react with phenylfluorone in 1:99 hydrochloric acid solution (Table I). A study of the behavior of various masking agents showed that peroxide and oxalate are useful in

TABLE I

REACTION OF 100  $\mu\text{g}$  OF METALS WITH PHENYLFLUORONE

<i>Metal</i>	<i>HCl (1:99)</i>	<i>HCl (1:99) + H<sub>2</sub>O<sub>2</sub></i>	<i>HCl (1:99) + oxalate</i>	<i>HCl (1:99) + H<sub>2</sub>O<sub>2</sub> + oxalate</i>	<i>10 <math>\mu\text{g}</math> Sn + HCl (1:99) + H<sub>2</sub>O<sub>2</sub> + oxalate <math>\mu\text{g}</math> Sn found</i>
Sn <sup>4+</sup>	S <sup>a</sup>	S	L <sup>b</sup>	S	
Ge <sup>4+</sup>	S	S	S	S	
Sb <sup>3+</sup>	S	S	S	S	
Ta <sup>5+</sup>	S	— <sup>c</sup>	L	—	10.0
Nb <sup>5+</sup>	S	—	—	—	10.0
Zr <sup>4+</sup>	S	L	—	—	8.0
Hf <sup>4+</sup>	S	S	—	—	7.9
Ti <sup>4+</sup>	S	—	L	—	9.9
Mo <sup>6+</sup>	S	—	L	—	10.1
W <sup>6+</sup>	S	—	—	—	10.1
V <sup>5+</sup>	S	—	—	—	10.0
Fe <sup>3+</sup>	S	S	—	—	10.0

<sup>a</sup> S = strong color.

<sup>b</sup> L = light color.

<sup>c</sup> — = little or no color.

the analysis of tin. When aliquots containing 100  $\mu\text{g}$  of the 12 metals mentioned were treated as directed in *Preparation of calibration graph* the results shown in Table I were obtained. It can be seen that, when both oxalate and peroxide are used as masking agents, the only metals that interfere in the tin analysis are germanium and antimony(III); neither of these metals is normally found in steel. By using the 2 masking agents, any interference due to traces of metals that may escape the sulfide and double carbamate separations in the proposed method for the analysis of steel can be com-

pletely eliminated. Since oxalate eliminates the interference of iron, it is not necessary to reduce this metal with iodide-ascorbic acid solution before the second carbamate extraction. The masking with oxalate plus peroxide is so efficient that, in some instances, it may even be possible to omit the double carbamate separation. The combination of the rather high acidity at the time of color development plus the masking action prevents interference from as much as 100  $\mu\text{g}$  of the metals listed in Table I plus antimony(V) and bismuth(III); or from as much as 1 mg of iron(III), gallium(III) or copper(II).

Quantitative tests showed that oxalate reduces the intensity of the tin-phenylfluorone color produced. On the other hand, peroxide increases the intensity of the color. Hence, the 2 effects cancel each other and the color produced in the presence of the 2 masking agents is about the same as that produced in their absence. Zirconium and hafnium cause the color development of tin to be low. Apparently some non-reactive tin compound similar to that formed with copper is produced<sup>7</sup>. When the specificity tests described above for tin were repeated with germanium, the findings were the same except that neither zirconium nor hafnium caused low recoveries for germanium. Hence, it must be concluded that no nonreactive compound of germanium with zirconium or hafnium is formed.

#### *Solvent extraction of the tin-phenylfluorone compound*

In order to make it possible to analyze small samples of steel, it is necessary to obtain high sensitivity in the spectrophotometric phenylfluorone determination of the tin. In the determination of germanium, the sensitivity can be appreciably increased by extracting the reagent plus the germanium-phenylfluorone compound into a small portion of an immiscible organic solvent such as benzyl alcohol<sup>8</sup>; or by extracting germanium chloride into carbon tetrachloride<sup>9</sup> or MIBK<sup>10</sup> and then forming the colored compound directly in the organic solvent by the addition of an alcoholic solution of phenylfluorone. In these methods it is necessary to make the spectrophotometric measurement at a somewhat longer wavelength than normal (*i.e.*, 520 nm) in order to minimize the absorption of the reagent itself. Tests have shown that it is not possible to form colored tin compounds by adding oxine-chloroform solution or methanol solutions of phenylfluorone to MIBK extracts of tin chloride. However, the tin-phenylfluorone compound, formed in dilute acid solution, can be quantitatively extracted with MIBK. The phenylfluorone reagent tends to divide between the aqueous and organic phases. The higher the acidity of the aqueous phase, the higher the percentage of phenylfluorone remaining therein. After extraction, the color of the tin compound tends to fade slowly just as it does in aqueous solution<sup>4</sup>. The rate of fading increases with an increase in acid concentration of the solution being extracted.

The compounds of phenylfluorone with germanium, molybdenum and certain other metals can also be extracted with MIBK. When appreciable amounts of metal are being extracted, traces of a fine red precipitate can be seen in the MIBK extracts. The amount of red precipitate obtained can be reduced by adding sodium chloride to the solution before color development. Under such conditions, the calibration graph for tin is linear and that for germanium is nearly so. Moreover, excellent results can be obtained in the determination of tin in steel and tin or germanium in doped samples of gallium phosphide. In the work on gallium phosphide, the tin or germanium is isolated by an acid sulfide separation using 1 mg of copper as a coprecipitant and then

determined directly by the phenylfluorone method without making a double carbamate separation.

## RESULTS

In order to demonstrate the validity of the proposed new method, 0.1-g portions of 4 low-alloy NBS standard steel samples were analyzed for tin. In the analysis of sample 125 a few drops of hydrofluoric acid were added to help in the dissolution of the sample and an ammonia separation was made to remove the fluoride before making the sulfide separation. The results obtained are shown in Table II.

TABLE II  
ANALYSIS OF NBS SAMPLES OF STEEL

Sample	% Tin	
	Present	Found
36a(Cr2-Mo1)	0.011	0.011, 0.010
101d(Cr18-Ni9)	0.009	0.009, 0.009
125(Si5)	0.007	0.007
170(Ti0.2)	0.018	0.018, 0.018

## SUMMARY

A new spectrophotometric method for the determination of traces of tin in steel is presented. The tin is isolated by an acid sulfide separation and a double carbamate-chloroform extraction and then determined by a phenylfluorone method in which the selectivity is increased by the use of peroxide and oxalate as masking agents and the sensitivity is increased by extracting the colored tin compound into a small volume of MIBK for the spectrophotometric analysis.

## RÉSUMÉ

On propose une nouvelle méthode spectrophotométrique pour le dosage de traces d'étain dans l'acier. L'étain est séparé par précipitation comme sulfure, en milieu acide et extraction double carbamate-chloroforme; il est enfin dosé à l'aide d'une méthode à la phénylfluorone avec augmentation de la sélectivité au moyen de peroxyde et d'oxalate comme agents complexants. La sensibilité est améliorée par extraction du composé d'étain coloré dans un petit volume de méthylisobutylcétone.

## ZUSAMMENFASSUNG

Es wird eine neue spektralphotometrische Methode zur Bestimmung von Spuren Zinn in Stahl angegeben. Das Zinn wird isoliert durch eine saure Sulfidfällung und zweifache Carbamat-Chloroform-Extraktion und anschliessend mit der Phenylfluoron-Methode bestimmt. Hierbei wird die Selektivität durch die Verwendung von Peroxid und Oxalat als Maskierungsmittel erhöht und die Empfindlichkeit der spektralphotometrischen Analyse durch Extraktion der gefärbten Zinn-Verbindung in ein kleines Volumen von Methylisobutylketon gesteigert.



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## SEPARATION OF AMINES BY LIGAND EXCHANGE

## PART IV. LIGAND EXCHANGE WITH CHELATING RESINS AND CELLULOSIC EXCHANGERS

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Previous papers in this series<sup>1-3</sup> have shown the possibilities of ligand exchange for chromatographic separation of mixtures of amines. Columns are used that contain cation-exchanging materials loaded with metal-ammonia complex ions. The columns are washed with aqueous ammonia before use, then a small amount of the amine is placed on the top of the column and displaced downwards by passing aqueous ammonia solutions. Different amines travel at different rates.

A difficulty with the ligand exchange technique is that metal ions are displaced from the column by ordinary ion exchange with the ammonium ions present in aqueous ammonia. This fact has restricted the choice of metal ions. Hitherto, nickel ions have been held the most strongly of those ions which form ammonia complexes, and a sulfonated polystyrene resin loaded with nickel(II) "throws" somewhat more than  $10^{-4}$  M nickel ions into 0.5 M ammonia. The metal leakage from the same resin loaded with copper(II) is much greater.

In attempts to reduce the metal leakage, and so to permit the use of a wider range of metal ions, ligand exchange with chelating resins containing iminodiacetate as the functional group has been investigated. The performance of these resins has been compared with that of sulfonated polystyrene resins. In addition preliminary tests have been made with ion exchangers based on cellulose, with the idea of using this type of exchanger for separating large molecules by ligand exchange. Unfortunately the metal leakage from the cellulosic exchangers was too great to warrant further testing.

This paper reports, not only comparisons between chelating and sulfonic resins, but also new data on selectivity orders in aliphatic amines, and on the chromatography of substituted hydrazines, purine and pyrimidine bases, and ethyleneimine.

## EXPERIMENTAL

*Materials*

Carbon-14 labelled amines were used in certain tests as previously described<sup>3</sup>. Other amines were purified by distillation, except for the purine and pyrimidine bases, hydrazine and ethyleneimine. The propylamines were also purified by recrystallization of the hydrochlorides. Hydrazine was obtained as an aqueous 80% solution from Arapahoe Chemicals, Inc., Boulder, Colorado (now the Arapahoe Division of Syntex, Inc.), ethyleneimine as the pure liquid from the Dow Chemical Co.

The exchangers were obtained from Bio-Rad, Inc., Richmond, California, except that preliminary tests on a chelating resin were made with the early production of "Dowex A-1", obtained directly from the Dow Chemical Co. This material contained functional carboxyl as well as iminodiacetate groups. Current production of this resin, sold as "Chelex-100" by the Bio-Rad Corporation, contains only iminodiacetate as functional groups. The polymer matrix is polystyrene crosslinked with divinylbenzene.

#### *Columns and analytical methods*

The columns had 10–12 mm internal diameter; most were 15 cm long, but some tests were made with longer columns. In some experiments, fractions were collected by a Vanguard fraction collector, Model 1000; in others, the progress of the elution was followed by a Waters Associates flowing differential refractometer and recorder<sup>4</sup>. Random fluctuations in refractive index were reduced by enclosing the column in a styrofoam box, which protected the column from drafts and temperature variations.

The carbon-14 compounds were counted by liquid scintillation; the pyrimidine and purine bases were determined by ultraviolet absorption. Hydrazine, mono-methyl- and dimethylhydrazine were titrated with bromate in acidic bromide solutions. Ethyleneimine was determined by a photometric method depending on its reaction with 1,2-naphthoquinone-4-sulfonate<sup>5</sup>.

The nickel and copper concentrations of the effluents were determined by evaporating 100–500-ml portions to 5–10 ml and titrating with EDTA. Precipitation of nickel by dimethylglyoxime was also used.

#### *Determination of ammonia-metal binding in resins*

To measure the extent of association between metal ions and ammonia in chelating resins, shaking tests were performed. Batches of "Chelex-100" (see above) were saturated with nickel(II) and copper(II) by contact with ammoniacal solutions of nickel and copper salts, then washed and air-dried at 60° to remove the ammonia. The completeness of removal was checked by distilling the resins with sodium hydroxide and passing the vapor into standard acid; no ammonia was detected. The metal contents of samples of the resins were found by extracting with acid and titrating with EDTA. Weighed portions of the resins were placed in flasks with measured volumes of aqueous ammonia solutions of known concentrations, then the flasks were stoppered and shaken for several hours. The ammonia concentrations were then measured by titration. The metal-ion concentrations in the aqueous solutions were so low that no corrections were needed for them, and the ammonia-to-metal ratios in the resins were simply calculated.

## RESULTS AND DISCUSSION

### *Ammonia binding*

The results of the tests described in the preceding section are shown in Fig. 1. The curve for ammonia-nickel association in water<sup>6</sup> is shown for comparison; it is the same as that found in a sulfonic acid resin<sup>7</sup>. Evidently the attachment of the iminodiacetate groups of the chelating resin to the metal ions blocks some of the coordination sites, so that a nickel ion can bind only 3 ammonia molecules instead of 6. It also

weakens the attachment of those ammonia molecules that are bound. This effect was found in carboxylic resins by KAMATA, INOUE AND ISHIBASHI<sup>8</sup> and by LATTELL AND WALTON<sup>2</sup>. The consequence is that the binding of ammonia and their ligands by metal-loaded chelating resins is considerably less than the binding by metal-loaded sulfonic resins. Elution volumes in ligand exchange chromatography are correspondingly smaller.

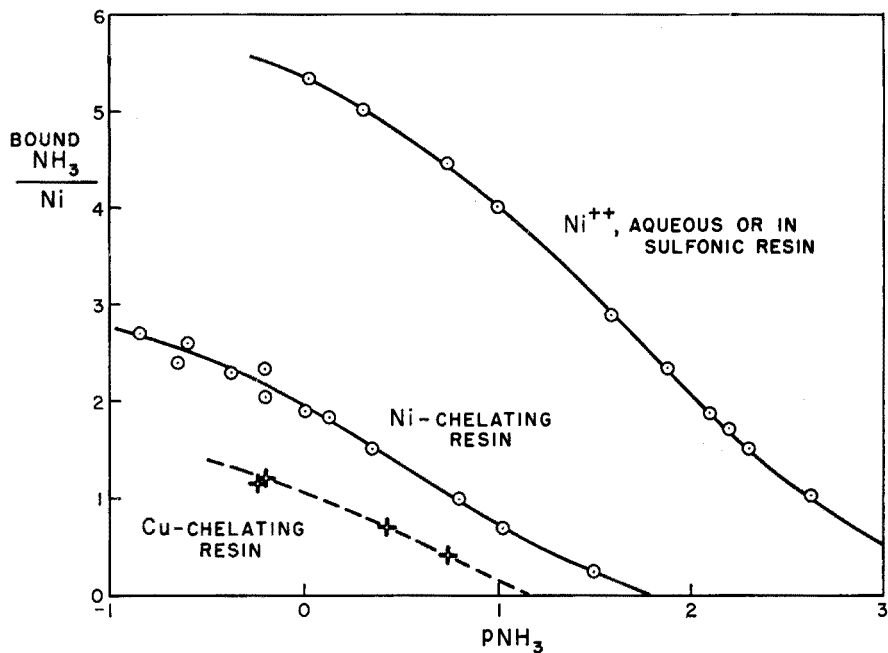


Fig. 1. Ammonia binding with chelating resins.

TABLE I

METAL BINDING AND LEAKAGE WITH DIFFERENT EXCHANGERS

Exchanger type	Sulfonic crosslinking		Carboxylic	Chelating	Cellulose <sup>a</sup>	
	8%	12%			P	CM
Metal capacity (mmol/ml bulk volume)	0.95	1.0	0.65	0.5	0.05	0.06
Ammonia concentration (M)	1.0	1.5		1.4	1.5	1.5
Metal concentration in effluent (M) for: Cu	High	High	$5 \cdot 10^{-4}$	$7 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-3}$
Ni	$2 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	—	$4 \cdot 10^{-5}$	$3 \cdot 10^{-4}$	$4 \cdot 10^{-4}$

<sup>a</sup> Cellulose P has functional phosphonic groups, CM has carboxylic groups.

#### Metal leakage

Table I shows the approximate concentrations of metal ions found in the effluents from columns containing various exchangers. These were obtained with freshly prepared columns through which about a liter of aqueous ammonia had been

passed. On continued use the metal ion concentrations fall to perhaps one-tenth of the values here quoted. The seriousness of the leakage depends on the concentrations of metal in the exchangers. Leakage from the cellulosic exchangers is serious because of the small amounts of metal held by these exchangers; the columns soon become white at the top, because all the metal ions have been stripped off.

The original "Dowex A-1", which contained carboxyl groups, showed somewhat better metal retention than the currently produced resin which only has iminodiacetate groups.

#### *Elution orders of selected amines*

Previously<sup>3</sup> elution volumes were reported for trace amounts of 4 <sup>14</sup>C-labelled amines and 4 benzylamines, and it was noted that the order of elution depended on the chemical nature of the exchanger matrix. The comparison has been extended to chelating resins and phosphorylated cellulose, and the results are summarized in Table II. Of the 16 different sequences possible with 4 amines, 4, and possibly 5 are observed. Diethanolamine, with its strongly hydrophilic character, is eluted first except with zirconium phosphate, where it comes out the last. The chelating resin gives the same elution sequence as the sulfonic resin, presumably because it has the same crosslinked polystyrene matrix.

TABLE II  
ELUTION ORDERS OF SELECTED AMINES

<i>Metal</i>	<i>Nickel</i>				<i>Copper</i>		
	<i>Sulfonic</i>	<i>Carboxylic</i>	<i>Chelating</i>	<i>Zirconium phosphate</i>	<i>Carboxylic</i>	<i>Chelating</i>	<i>Phosphonic cellulose</i>
Diethanol-amine	I	I	I	IV	I	I	I
Ethanol-amine	II	IV	II	III	(II)	II	II
Dimethyl-amine	III	III	III	II	III	III	IV
<i>n</i> -Butyl-amine	IV	II	IV	I	(II)	IV	III

TABLE III  
COMPARISON OF SULFONIC AND CHELATING RESINS  
(Ni-loaded: eluant, 1.5 M NH<sub>3</sub>)

<i>Amine</i>	<i>pK<sub>b</sub></i> <sup>a</sup>	<i>Elution volume, multiple of bulk column volume</i> <sup>b</sup>	
		<i>Sulfonic</i>	<i>Chelating</i>
CH <sub>3</sub> NH <sub>2</sub>	3.45	4.8	2.3
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	3.31	3.5	2.0
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	3.06	6.3	2.1
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3.46	2.5	1.8
<i>n</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	3.36	7.3	3.2

<sup>a</sup> The *pK<sub>b</sub>* values were measured at 0° (ref. 10).

<sup>b</sup> These volumes are uncorrected for the void column volume.

*Aliphatic amines: isomers*

Table III lists peak elution volumes for small amounts of amines on nickel-loaded columns of sulfonic and chelating resins. The volumes are inversely proportional to the ammonia concentrations, provided that allowance is made for the void volume of the column and its connections, and in certain cases where the ammonia concentrations differed from those cited in the Table, the elution volumes were correspondingly adjusted. The differential refractometer was used, and typical recorder traces for mixtures are shown in Figs. 2, 3, 4 and 5. Figures 2 and 3 are for the chelating resin, and Figs. 4 and 5 for the sulfonic. The peaks are identified from runs with individual amines. Because of "noise" and drifting base line the curves can be used for only rough quantitative determinations at present, but it was found that careful control of the temperature of the resin column improved the quality of the refractometer curves.

There is a peak in refractive index which is caused by displacement of ammonia from the resin. The sample containing about 0.5 mmole of amine is added as a small volume, about 0.25 ml of a relatively concentrated aqueous solution. When the amine enters the resin bed it displaces ammonia from the metal ions, and if the concentration of displaced ammonia is greater than that of the ammonia solution used as the eluant (this is *not* the case in Fig. 5, but is so in Figs. 2, 3 and 4), a pulse of higher ammonia

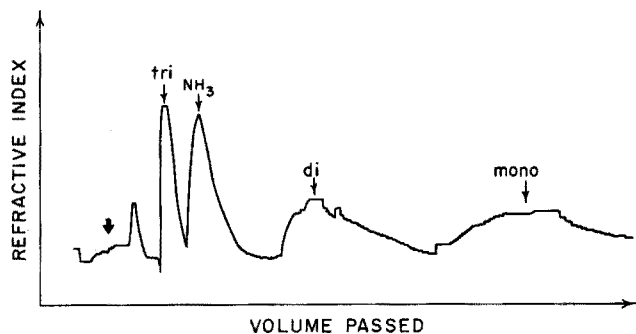


Fig. 2. Elution of methylamines (Chelex 100-Ni; 0.14 *M* NH<sub>3</sub>). Column 1.2 × 30 cm; resin 200–400 mesh; loading 0.5 mmole of each amine; flow 30 ml/h.

concentration travels down the column. If the resin is already saturated with ammonia this pulse travels at the same rate as the flowing solution, but if the resin is *not* saturated, which is true with the chelating resin, the pulse travels more slowly. Its rate of travel depends on the slope of the sorption isotherm<sup>9</sup>, and in Fig. 2 it travels more slowly than the most weakly bound amine.

The elution order of the primary propylamines and butylamines (Table IV) is of interest. There is very little difference in the ionization constants of the isomeric bases<sup>10</sup> and the marked differences in elution volumes cannot be attributed to differences in strengths of metal–amine binding. Indeed, the stability of the metal–amine complexes in solution is very small<sup>3</sup>. The more highly branched the carbon chain, the more easily is the amine eluted from the resin. This effect can be attributed to the greater ease with which the more compact, branched molecule enters the *water* in the external solution. Thus *n*-butylamine exerts a greater structure-breaking effect on the water than does *tert.*-butylamine, and therefore tends to stay in the resin.

This correlation is suggested by the ion-exchange selectivity theory of CHU, WHITNEY AND DIAMOND<sup>11</sup>.

That this is not the only factor, however, is shown by the order of elution of mono-, di- and trimethylamine (Fig. 2) and of the ethylamines (Table III). Here a

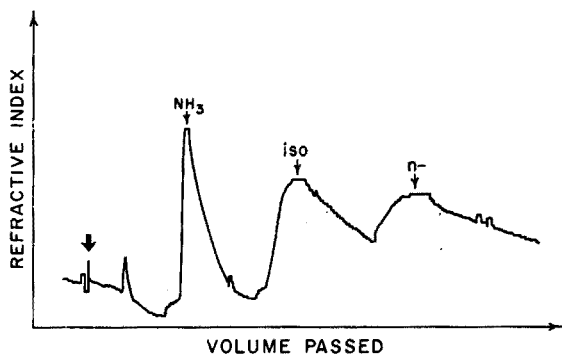


Fig. 3. Elution of propylamines (Chelex 100-Ni; 0.14 M NH<sub>3</sub>).

Loading 20 mg n-propylamine, 10 mg iso-; other conditions as in Fig. 2.

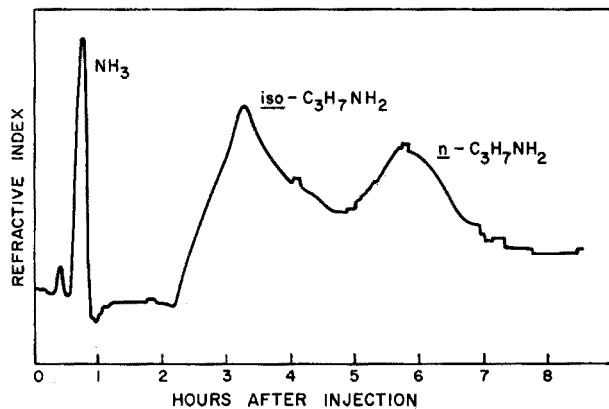


Fig. 4. Elution of propylamines (Ni-sulfonic acid resin).

Column 1.2 × 28 cm; resin 200-400 mesh, 8% cross-linked; loading 36 mg n-propylamine, 30 mg iso-; eluant 1.3 M NH<sub>3</sub>, flow 32 ml/h.

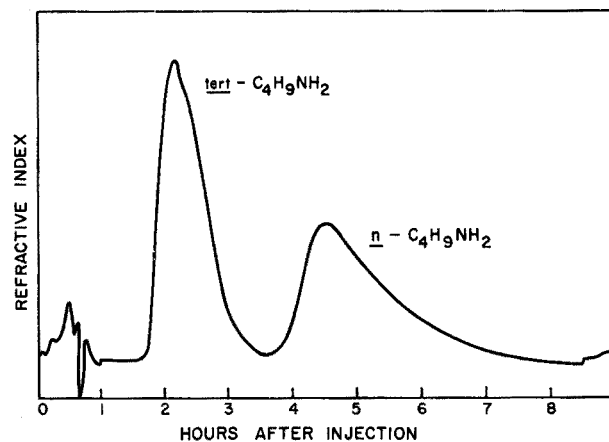


Fig. 5. Elution of butylamines (Ni-sulfonic acid resin).

Loading 0.30 mmole n-butylamine, 0.26 mmole tert-; eluant 3.0 M NH<sub>3</sub>; other conditions as Fig. 4.

TABLE IV

ISOMERIC PRIMARY AMINES: CHELATING RESIN, Ni-LOADED<sup>a</sup>

Amine	$pK_b^b$	Eluant $NH_3$ concn.	Elution volume, multiple of bulk column volume <sup>b</sup>
$n-C_3H_7NH_2$	3.36	0.14	4.1
iso $C_3H_7NH_2$	3.40	0.14	6.4
$n-C_4H_9NH_2$	3.35	1.5	3.2
$(CH_3)_2CHCH_2NH_2$	—	1.5	2.3
$C_2H_5CH(CH_3)NH_2$	—	1.5	2.0
$(CH_3)_3C \cdot NH_2$	3.30	1.5	1.7

<sup>a</sup> For Ni-sulfonic resin see Figs. 4 and 5.<sup>b</sup> See footnotes to Table III.

correlation may exist with the base strengths but it is not clear. The elution order of the ethylamines is the reverse of the order of base strengths, which is understandable, but the  $pK_b$  values for mono-, di- and trimethylamine are 3.45, 3.39 and 4.53, respectively, and these are not in the same sequence as the elution volumes.

#### Hydrazine and methylhydrazines

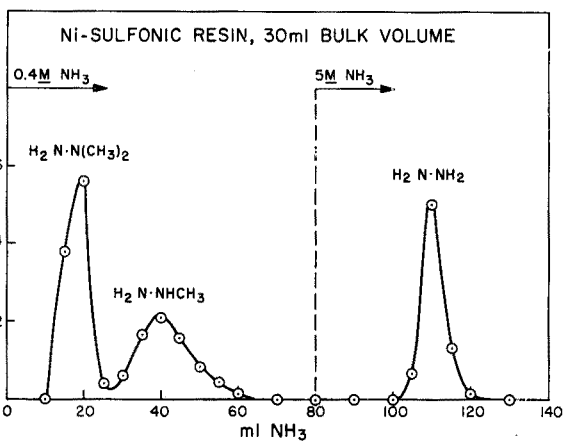
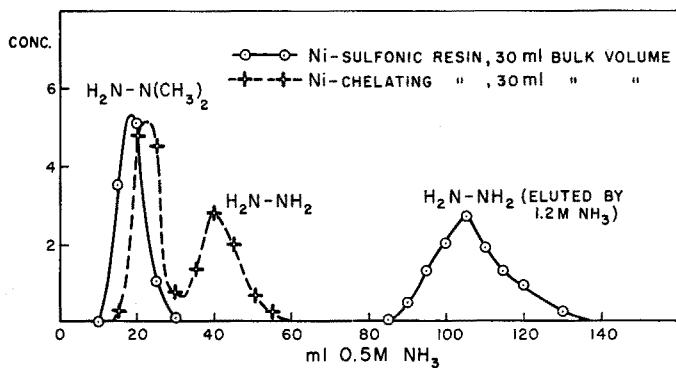
Some time ago<sup>1</sup> it was noted that hydrazine was bound quite strongly by a nickel-loaded sulfonic acid resin, and this fact suggested that hydrazine might be separated from dilute aqueous solutions by ligand exchange. Tests showed that 10 mmoles of hydrazine, or more, could be absorbed into a 15-ml column of nickel and ammonia-loaded resin column, left overnight, and eluted with 5 *M* ammonia with a recovery of 85–90% of the hydrazine originally added. The elution of small amounts of hydrazine, methylhydrazine and 1,1'-dimethylhydrazine was next studied, with the results shown in Figs. 6 and 7. Dimethylhydrazine is not retained at all, methylhydrazine only weakly, and hydrazine relatively strongly, permitting a good chromatographic separation.

Though this point was not studied in detail, it seemed that the elution volume of hydrazine was inversely proportional to the *square*, rather than the first power of the ammonia concentration. A column of nickel-loaded sulfonic resin, bulk volume 14 ml, gave elution volumes of 19 ml with 3.0 *M* ammonia and 58 ml with 1.2 *M* ammonia. These volumes are uncorrected for the void volume and "dead" volume below the column, which together were about 8 ml. The implication is that one hydrazine molecule displaces *two* ammonia molecules; this can happen if hydrazine bridges two nickel ions. A similar effect was found with 1,3-propanediamine, which can form a chelate ring with nickel(II). In this case the elution volume depended on a power of the ammonia concentration between -1 and -2.

#### Ethyleneimine

This compound is hydrolyzed rapidly by dilute acids but is stable in alkaline aqueous solutions. It is thus of interest to know if it can be absorbed and desorbed by ligand exchange. As far as could be told from our analyses, quantities of the order 10–100 mg could be absorbed on nickel-loaded sulfonic and chelating resins and eluted by ammonia with 100% recovery. A typical peak elution volume was 4.0 bulk column





Figs. 6-7. Elution of hydrazines. Loading 1 mmole of each; concn. in arbitrary units.

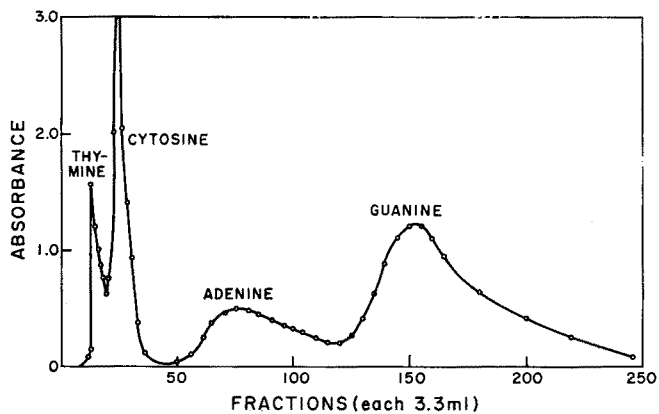


Fig. 8. Elution of purine and pyrimidine bases (Ni-chelating resin; 70 ml bulk volume; eluant 0.5 M NH<sub>3</sub>).

volumes with nickel-loaded sulfonic resin and 1 *M* ammonia as eluant. The elution chromatography of substituted ethyleneimines will be investigated at a later date.

#### *Purine and pyrimidine bases*

Because of their biochemical interest, the chromatography of thymine, cytosine, adenine and guanine by ligand exchange was studied. A curve obtained with the chelating resin in the nickel form is shown in Fig. 8. A nickel-sulfonic resin column showed a poorer separation. With a sulfonic resin in acid solution, the bases being exchanged as their protonated cations in the conventional way, sharper bands were obtained with a shorter column, and the sequence of the 2 purine bases was reversed, that is, guanine was eluted before adenine. Ligand exchange is thus no better than conventional cation exchange for this separation, unless there is a reason for working in ammoniacal rather than acid solution.

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#### SUMMARY

Chelating, sulfonic and cellulosic exchangers were compared in ligand exchange chromatography. Chelating resins retain metal ions the best, but have a low ligand binding capacity. Cellulosic exchangers show excessive metal leakage. Sulfonated polystyrene resins loaded with nickel ions give best results in most cases. Data are presented on ligand exchange chromatography of simple aliphatic amines, hydrazine and substituted hydrazines, purine and pyrimidine bases.

#### RÉSUMÉ

Les auteurs ont examiné les échangeurs chélatants, sulfoniques et cellulose pour la chromatographie d'échange de "ligand". Les résines polystyrène sulfoné, chargées d'ions nickel ont donné les résultats les meilleurs dans la plupart des cas. On donne des résultats pour des amines simples aliphatiques, l'hydrazine, les hydrazines substituées, les bases purine et pyrimidine.

#### ZUSAMMENFASSUNG

Chelatbildende, sulfonische und Zellulose-Austauscher wurden bei der Ligandenaustauscher-Chromatographie verglichen. Chelatbildende Harze halten Metallionen am besten zurück, besitzen aber eine niedrige Liganden-Bindungskapazität. Zellulose-Austauscher zeigen übermässigen Metaldurchlass. Mit Nickelionen beladene sulfonierte Polystyrolharze ergeben in den meisten Fällen die besten Resultate. Es werden Daten angegeben für die Ligandenaustauscher-Chromatographie von einfachen aliphatischen Aminen, Hydrazinen und substituierten Hydrazinen, Purin- und Pyrimidin-Basen.

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## ADSORPTION CHARACTERISTICS OF TRACES OF SILVER ON SELECTED SURFACES

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In an earlier study by WEST, WEST AND IDDINGS<sup>1</sup>, the erratic and serious losses of silver by adsorption to container surfaces from dilute aqueous solutions was solved by the addition of sodium thiosulfate. While the thiosulfate noted in the first study was adequate for prevention of silver losses for a 30-day storage period, the use of any complexing ligand imposes severe limitations in the selection or development of a subsequent analytical procedure.

This second study is a continuation of the evaluation of container materials in an effort to find a material that would satisfactorily contain potable water samples without recourse to the addition of a complexing ligand. However, anomalous behavior associated with some ligands on some container materials suggested the advisability of including further studies of ligands as an adjunct to the primary investigations.

## EXPERIMENTAL

*Apparatus*

The scaler, Geiger-Müller tube, and autoradiographic techniques were previously described<sup>1</sup>. Griffin, low-form, 250–300 ml beakers were selected as test containers. The materials considered in this study were Teflon, Vycor, polypropylene, polystyrene, and coatings of paraffin, acrylic spray, and Tygon paint, applied to polypropylene beakers.

*Reagents*

The radioactive silver (<sup>110</sup>Ag and <sup>111</sup>Ag) was obtained from Oak Ridge National Laboratories in the form of silver nitrate in 3 *N* nitric acid. Portions of these solutions were evaporated to dryness with carrier silver nitrate and then diluted to volume with distilled water to obtain the desired concentrations of silver(I) (0.05 and 1.0 mg/l).

Ligands included in the study were: 0.1 *M* solutions of ammonium hydroxide, disodium salt of ethylenediaminetetraacetic acid (EDTA), and ethylenediamine (en); 0.1 *M* and 1.0 *M* solutions of sodium thiosulfate; and 0.1 *M*, 0.01 *M* and 0.001 *M* solutions of sodium chloride.

*Procedure*

Because of possible discrepancies that might be introduced through used, scratched beakers, new beakers were selected from random cases of stock. The test beakers were carefully cleaned by several immersions in a dilute detergent solution (Dreft), followed by careful rinsing with double-distilled water. The beakers were then drained, air-dried, and individually wrapped in plastic until used.

Background levels of radioactivity were established for all beakers before introduction of the samples. A sufficient volume of radioactive silver was added to each beaker and test solution to provide 100-ml volumes of 0.05 mg/l or 1.0 mg/l silver concentrations. Mixing of the silver tracer with the sample solutions was accomplished by pouring the solutions back and forth 5 times between the test beaker and the holding or receiving beaker. The pH was recorded following mixing and all solutions were held at 22°. Beakers were rinsed, air-dried, and counted at the end of 2, 4, 8, 16, 32, 64, 128 and 248-h intervals. An additional holding period was added in some instances to provide a total of 30 days for solution contact with the selected beakers.

Daily decay corrections for the  $^{111}\text{Ag}$  isotope were made in preference to applying corrections from the theoretical decay curve. Standard practice was followed in checking the scaler and detector before each period of use. Adequate counting intervals were made so as to provide an estimated standard deviation of 100 counts. Calculation of adsorption values was performed by first determining the specific adsorption ( $\mu\text{g}$  of  $\text{Ag}/\text{cm}^2$ ), then multiplying the area of solution contact (area determined for each beaker) by the specific adsorption to yield the percentage total micrograms of silver adsorbed. The total micrograms of silver adsorbed divided by the total micrograms of silver originally present in solution and multiplied by 100 gave the percentage silver adsorbed on the surface of the respective containers.

While the calculations assume uniform adsorption of the silver on all surfaces, this was not the case. Adsorption values in excess of 100% were found in several instances. Autoradiographs also confirmed non-uniform adsorption and when this discontinuity occurred on areas beneath the detector probe, the results represented concentrated activity not present over the entire solution contact area.

The pH values for all solutions used in the study were recorded after addition of the radiotracer, followed by thorough mixing. These values were:

$\text{Na}_2\text{S}_2\text{O}_3$ (0.1 M)	7.7	Distilled water controls	7.0
EDTA (0.1 M)	9.1	$\text{Na}_2\text{S}_2\text{O}_3$ (1.0 M)	8.2
$\text{NH}_4\text{OH}$ (0.1 M)	11.6	NaCl solution (0.01 M)	4.4
Ethylenediamine (0.1 M)	11.9	NaCl solution (0.001 M)	4.5
NaCl (0.1 M)	4.6		

## RESULTS AND DISCUSSION

*Silica glass*

"Vycor", or silica glass is specified<sup>2</sup> for the determination of silver in potable waters. Twenty beakers of this material were studied, as duplicate beakers were used for each ligand series and for the distilled water controls. Figure 1 is a range profile of maximum and minimum adsorption values for the distilled water controls, plotted on

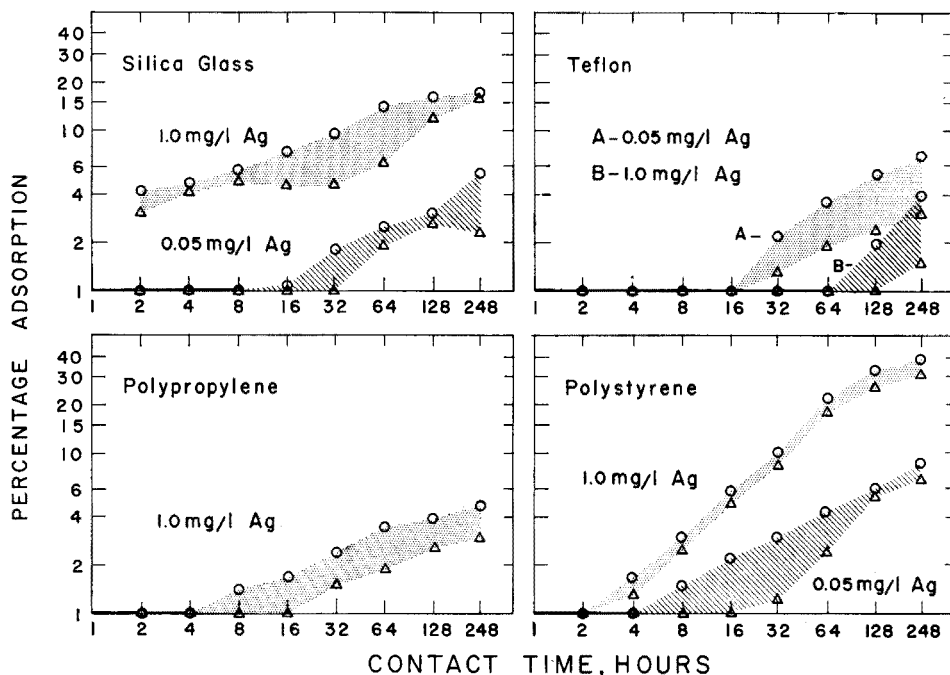


Fig. 1. Adsorption range profiles for silica glass, Teflon, polypropylene, and polystyrene with spiked distilled water at the indicated silver concentrations. Values plotted represent maximum (O) and minimum (Δ) percentage adsorption values.

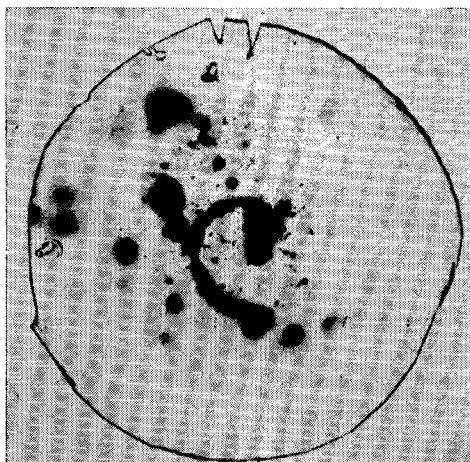


Fig. 2. Autoradiograph for Vycor, spiked distilled water control.

semilog paper as percentage adsorption *versus* contact time. The percentage adsorption values for the 2 silver concentrations studied, 0.05 mg/l and 1.0 mg/l, are shown.

The lower silver concentration was adsorbed at a much slower rate by the beakers. Reference to Fig. 1 indicates the great difference in induction periods for the 2 concentrations of silver. The silver in the solution containing 0.05 mg/l was not adsorbed to any significant degree for the first 32 h of contact with the beakers —

compared to significant adsorption for the 1.0 mg/l silver concentration at the end of 2 h of contact. Significant adsorption, for purposes of this study, is defined as more than 1% for any given contact interval. Reproducibility of adsorption data between beakers, for both silver concentrations, was generally good compared to the data for Pyrex obtained in the earlier study<sup>1</sup>. An autoradiograph of a Vycor beaker (Fig. 2) confirms the uniformity of adsorption obtained with this material.

The serious losses occurring during prolonged storage of water samples for silver analysis are shown in Table I. At the end of 30 days, the Vycor beakers had adsorbed from 58 to 108% of the silver from solution. At this same silver concentration, 0.05 mg/l, only 2–5% adsorption had occurred at the end of 248 h.

Table II presents the data obtained in the evaluation of various ligands. Of the

TABLE I  
30-DAY CONTACT SERIES  
(Percentage Ag adsorbed)

<i>Materials</i>	<i>Distilled water with 0.05 mg/l Ag</i>
Vycor	58–108
Polypropylene	53– 70
Polystyrene	13– 36
Teflon	8– 44

TABLE II  
SILICA GLASS  
(Percentage adsorption from 1.0 mg/l Ag concentration in the presence of ligands)

<i>Contact time (h)</i>	<i>0.1 M NH<sub>4</sub>OH</i>	<i>0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub></i>	<i>0.1 M EDTA</i>	<i>0.1 M en</i>	<i>0.1 M NaCl</i>	<i>0.01 M NaCl</i>
2	— <sup>a</sup>	—	—	—	—	3
	—	—	—	—	—	2
4	—	—	—	—	—	4
	—	—	—	—	—	4
8	—	—	—	1	1	6
	—	—	—	6	2	9
16	—	—	—	7	5	11
	—	—	—	25	6	15
32	—	—	—	10	6	13
	—	—	—	36	7	21
64	—	—	—	26	9	18
	2	—	—	47	10	26
128	1	—	—	52	8	18
	2	—	—	55	9	27
248	1	—	—	69	7	22
	2	—	—	57	8	32

<sup>a</sup> Adsorption values < 1%.

ligands studied, 0.1 *M* thiosulfate most effectively prevented the adsorption of silver from solution by Vycor. It became obvious that small concentrations of sodium chloride in the water samples increased adsorption drastically. As chloride is always present in water supplies, it was necessary to study an additional series. Therefore, 0.001 *M* sodium chloride solutions were spiked with 0.05 mg/l Ag and held for a 30-day period. It was found that a 1.0 *M* thiosulfate concentration was required to hold adsorption losses to less than 1%. The ethylenediamine concentrated silver on surfaces, as did the more dilute sodium chloride solutions.

### Teflon

While possibly prohibitive in cost for general use as sample containers, the well known inertness of Teflon necessitated study of this material. Figure 1 indicates the range of adsorption occurring with the 2 silver concentrations in distilled water during a 248-h contact period. The extended induction period was an interesting characteristic of Teflon. In contrast to the Vycor, the samples with the lower silver concentration produced higher and more rapid rates of adsorption. The 30-day contact period (Table I) shows the delayed but erratic and serious losses of silver from dilute aqueous solutions to the Teflon surfaces.

Table III details the adsorption data for duplicate beakers used for evaluation of the efficiency of the various ligands. The presence of sodium chloride again increased adsorption. While 0.1 *M* thiosulfate effectively held adsorption to 1% for the

TABLE III

## TEFLON

(Percentage adsorption from 1.0 mg/l Ag concentration in the presence of ligands)

Contact time (h)	0.1 <i>M</i> <i>NH</i> <sub>4</sub> <i>OH</i>	0.1 <i>M</i> <i>Na</i> <sub>2</sub> <i>S</i> <sub>2</sub> <i>O</i> <sub>3</sub>	0.1 <i>M</i> <i>EDTA</i>	0.1 <i>M</i> <i>en</i>	0.1 <i>M</i> <i>NaCl</i>	0.01 <i>M</i> <i>NaCl</i>
2	— <sup>a</sup>	—	—	—	13	1
	—	—	—	—	—	2
4	—	—	—	—	14	2
	—	—	—	—	—	2
8	—	—	—	—	17	4
	—	—	—	—	1	4
16	—	—	—	—	20	9
	—	—	—	—	4	7
32	—	—	—	2	22	9
	—	—	—	6	6	8
64	—	—	—	5	25	10
	—	—	—	15	8	10
128	—	—	—	12	22	11
	—	—	—	22	7	10
248	1	1	1	18	23	10
	2	1	—	27	8	12

<sup>a</sup> Adsorption values < 1%.



spiked distilled water samples, it was necessary to increase the concentration to 1.0 M in the presence of traces of chloride. The 1.0 M thiosulfate was successful in holding adsorption to less than 1% for 30 days contact. Ammonia acted as a stabilizing ligand for Teflon, but the data indicated increasing adsorption with increased contact periods and was not further studied. Ethylenediamine, again, acted to concentrate silver on surfaces. This concentrating effect by en, noted in the earlier study<sup>1</sup>, suggests its possible use as a reagent for concentrating silver from large portions of sample. This action is evidenced in Fig. 3, which shows autoradiographs of a distilled water control beaker and of a beaker which contained en solution, both in contact with a 1.0 mg/l solution of <sup>111</sup>Ag for 248 h.

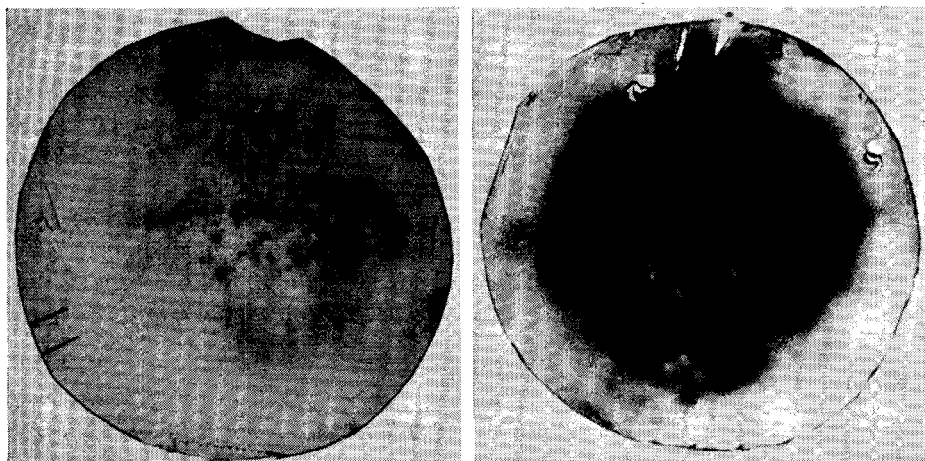


Fig. 3. Autoradiographs for Teflon. Left view: spiked distilled water control; right view: spiked 0.1 M ethylenediamine solution.

### *Polypropylene*

Polypropylene has been used to a limited extent in the fabrication of shipping and storage containers, beakers, pipets, etc. Figure 1 shows the remarkable uniformity of the adsorption occurring on this material for the 1.0 mg/l Ag distilled water series. Adsorption values for the 0.05 mg/l concentration were not plotted as they so nearly paralleled the values obtained for the higher silver concentration. The percentage adsorption found for the 248-h contact interval (6% maximum) would not preclude the use of this material for brief storage of dilute aqueous solutions of silver, but Table I dramatically emphasizes the serious nature of losses occurring upon storage of samples for a 30-day period.

Table IV reflects the previously established trend of increasing adsorption due to the presence of chloride. Increasing the thiosulfate concentration to 1.0 M kept adsorption to well under 1% for a 30-day period. Ethylenediamine, again, followed the established trend by increasing adsorption by concentrating the silver on the container surfaces. The presence of 0.1 M ammonia introduced no unusual behavior compared to the control beakers. In the EDTA series the silver losses were negligible at first but became serious after 128 h of contact.

TABLE IV

## POLYPROPYLENE

(Percentage adsorption from 1.0 mg/l Ag concentration in the presence of ligands)

Contact time (h)	0.1 M NH <sub>4</sub> OH	0.1 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.1 M EDTA	0.1 M en	0.1 M NaCl	0.01 M NaCl
2	— <sup>a</sup>	—	—	—	—	2
	—	—	—	—	—	2
4	—	—	—	—	—	3
	—	—	—	—	—	4
8	—	—	—	—	—	6
	—	—	—	—	—	6
16	—	—	—	17	3	10
	1	—	—	19	2	10
32	1	—	—	32	6	12
	2	—	—	37	4	13
64	2	—	—	46	9	15
	5	—	1	51	8	16
128	4	—	1	56	8	17
	6	—	2	64	7	17
248	5	—	2	61	8	18
	7	—	3	68	7	20

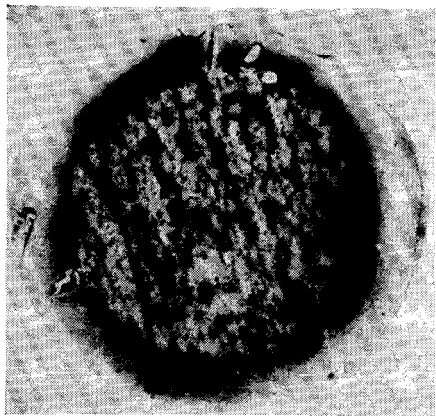
<sup>a</sup> Adsorption values < 1%.

Fig. 4. Autoradiograph for polystyrene, spiked distilled water control.

*Polystyrene*

Polystyrene adsorbs silver from dilute aqueous solution much more rapidly than the other materials studied. Figure 1 shows the narrow range of adsorption values between beakers for both silver concentrations. The 0.05 mg/l Ag samples showed approximately  $\frac{2}{3}$  less percentage adsorption than did the 1.0 mg/l Ag samples.

Samples held for 30 days (Table I) had adsorption values comparable with those for Teflon. The autoradiograph for polystyrene (Fig. 4) emphasizes the random distribution of adsorption.

Because of the certainty that all potable waters and most other systems contain some chloride, studies were made with 0.001 *M* chloride and adsorption was again drastically increased. However, the 1.0 *M* thiosulfate solution effectively held adsorption to less than 1% for the 30-day contact interval. The EDTA solution was not an effective stabilizing agent for extended contact periods, and ammonia solution was only partially effective for this material. The ethylenediamine, again, showed concentrating properties when compared to adsorption values obtained for the controls.

### Coatings

Due to the difficulty of applying coating materials to non-uniformly shaped containers, laboratory glassware, etc., only the 1.0 mg/l Ag concentration was studied. Thirty-day contact intervals were not employed with the coatings, but data obtained for the materials above may be extrapolated in the case of the coatings. Silicone coating, "Desicote", was evaluated in an earlier paper<sup>1</sup>.

Acrylic spray was obtained in aerosol form and thus permitted relatively even application to polypropylene beakers. The beakers containing the distilled water controls adsorbed less than 1% for the first 8 h of contact, with maximum adsorption of 5% and 6% being reached at the end of 248 h. The presence of ammonia reduced

TABLE V

## POLYSTYRENE

(Percentage adsorption from 1.0 mg/l Ag concentration in the presence of ligands)

Contact time (h)	0.1 <i>M</i> <i>NH</i> <sub>4</sub> <i>OH</i>	0.1 <i>M</i> <i>Na</i> <sub>2</sub> <i>S</i> <sub>2</sub> <i>O</i> <sub>3</sub>	0.1 <i>M</i> <i>EDTA</i>	0.1 <i>M</i> <i>en</i>	0.1 <i>M</i> <i>NaCl</i>	0.01 <i>M</i> <i>NaCl</i>
2	— <sup>a</sup>	—	—	—	—	1
	—	—	—	—	—	1
4	—	—	—	—	—	2
	—	—	—	—	—	2
8	—	—	—	—	—	4
	—	—	—	—	—	4
16	2	—	—	1	2	9
	—	—	—	2	4	8
32	3	—	—	28	5	14
	1	—	—	14	9	15
64	6	—	—	59	9	19
	2	—	—	31	12	23
128	9	—	—	65	9	18
	2	—	—	39	12	21
248	13	—	1	70	11	23
	4	—	1	44	13	23

<sup>a</sup> Adsorption values < 1%.

adsorption by 50% for the 248-h interval and delayed any significant adsorption through the 64-h interval. Thiosulfate held adsorption to less than 1% for the full 248 h of contact. EDTA began to break down after 128 h. The en, again, concentrated the silver on the acrylic surface.

A vinyl-based paint, "Tygon", was used as a coating material. There was an 8-h induction period for the distilled water controls, with maximum adsorption values of 8% and 11% at the end of 248 h. Thiosulfate effectively complexed the silver for 248 h so that the maximum adsorption was 1%. EDTA, again, broke down at the end of 64 h. After 4-h contact, the beakers containing ethylenediamine solution began to adsorb silver very rapidly for maximum 248-h values of 102% and 116%.

Paraffin-coated beakers adsorbed the highest percentage of silver in the distilled water control series, compared to the other 3 coating materials. There was a 16-h induction period with final adsorption values of 8% and 11% for the 248-h interval. The ligand solutions continued the trends noted for the other coatings.

The Analytical Reference Service, U. S. Public Health Service, has just completed a broad evaluation<sup>3</sup> of analytical methods for determining metals in water. Twenty member laboratories analyzed a standard sample containing 0.15 mg/l of silver and obtained a mean recovery of 0.07 mg/l. The report concluded that the greatest problem was the loss of silver through adsorption to the walls of sample container and to glassware used in the analytical procedures.

This investigation was supported by United States Public Health Service Research Grant Number WP 00788.

#### SUMMARY

A study of materials used for the storage of dilute aqueous solutions of silver established the adsorption characteristics of Teflon, Vycor, polypropylene, polystyrene and coatings of paraffin, acrylic spray, and Tygon paint. None of these materials or coatings was found satisfactory for prolonged storage of water samples containing trace quantities of silver. As in an earlier study, it was necessary to complex the silver in the sample with sufficient sodium thiosulfate to insure less than 1% adsorption to containers over a 30-day contact period.

#### RÉSUMÉ

Une étude a été effectuée sur les matériaux utilisés pour le stockage de solutions aqueuses diluées d'argent, établissant les caractéristiques d'adsorption du téflon, du tyron, du polypropylène, du polystyrène, etc. Aucune de ces matières ne s'est montrée satisfaisante. Il est nécessaire comme précédemment de complexer l'argent, au moyen de thiosulfate de sodium, en quantité suffisante pour avoir moins de 1% d'adsorption, pendant 30 jours de contact.

#### ZUSAMMENFASSUNG

Es wurden verschiedene Materialien untersucht, um ihre Absorptionseigenschaften im Bezug auf die Lagerung verdünnter wässriger Silberlösungen festzustellen.

Keine dieser Materialien oder Beschichtungen eignete sich zufriedenstellend für eine längere Lagerung von Wasserproben, die Spuren Silber enthalten. Wie bei früheren Untersuchungen war es notwendig, das Silber der Probe mit ausreichendem Natriumthiosulfat in einen Komplex zu überführen, um sicherzustellen, dass innerhalb von 30 Tagen weniger als 1% von den Behältern adsorbiert wurde.

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## A SEMI-QUANTITATIVE METHOD FOR THE DETERMINATION OF MICROGRAM AMOUNTS OF MANGANESE ON MILLIPORE FILTERS

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Recently, in our laboratory, a method was developed for the determination of manganese by precipitation as manganese dioxide and subsequent collection on white Millipore filters<sup>1</sup>. The manganese was then determined by comparison of the intensity of coloration produced on the filters with standards prepared in a similar manner. In that method, the manganese was first oxidized to the heptavalent state with potassium persulfate in neutral solution and then precipitated via the Volhard reaction with addition of excess manganese(II)<sup>2</sup>. Several disadvantages observed included decomposition of the permanganate by impurities, slight iron interference, and recoveries sometimes exceeding 100%.

During the above investigation, it was observed that a precipitate would form in highly basic solutions of manganese(II) that would not dissolve after addition of large amounts of nitric acid. This precipitate was found to be manganese dioxide. Thus, it seemed possible to precipitate and collect the manganese dioxide without going through the time-consuming persulfate oxidation steps. This method would also eliminate losses due to reduction of the permanganate by impurities. Advantages would include rapidity, no instrumentation needed, ease of operation, and no need to minimize volumes.

The present paper concerns the study of the optimum conditions for the precipitation and collection of the manganese dioxide. The possible mechanism by which the manganese dioxide is produced is also discussed. The effects of some common metal ions on the recovery have also been investigated. Methods for increasing the sensitivity, such as decreasing filter size, and washing of the manganese dioxide on the filter with benzidine solution to produce an intense blue color, were also studied.

### EXPERIMENTAL

All chemicals used were reagent grade. Manganese(II) was standardized by titrating with (ethylenedinitrilo)tetraacetic acid<sup>3</sup>.

Millipore filters (type AAWP of 0.45- $\mu$  pore size) 25 mm in diameter were used. A Millipore pyrex microanalysis filter holder was used to support the filter. All manganese(II) solutions used were prefiltered through the filters.

#### *Preparation of standards*

Manganese standards in the range of 1–50  $\mu$ g were prepared on 25-mm filters.

A known amount of manganese(II) was added to a 50-ml beaker and the volume adjusted to 10–15 ml with distilled water, before addition of 3 ml of 10 *M* sodium hydroxide. A small crystal of potassium persulfate was also added (see RESULTS AND DISCUSSION) and the solution swirled. The solution was then cooled in an ice bath to 5°. Cold (*ca.* 5°) concentrated nitric acid was added carefully, so as not to heat the solution. When the solution was acidic, it was diluted with 5 ml of cold distilled water and filtered through the Millipore filters. The precipitate was washed with distilled water followed by 5 ml of 0.1 *M* hydroxide and then again with water.

#### *Preparation of samples*

Manganese samples were treated in a similar manner as for the preparation of standards. The intensity of the coloration of the filters was compared with that of the standards.

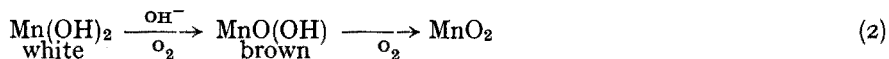
#### RESULTS AND DISCUSSION

This method is based on the fact that when a manganese(II) solution is made strongly basic in the presence of air, manganese dioxide forms through auto-oxidation<sup>4</sup>:



Since manganese dioxide is insoluble in most acids, it will be left as a precipitate when the solution is acidified.

The reaction probably goes through a manganese(III) intermediate as in eqn. (2).



In order to get complete recovery of the manganese, the reaction mixture must stand for about 20 min. Even after that time, recovery is only about 90%. The formation of the manganese(III) is probably the slow step in the reaction; once this is formed it is rapidly oxidized to manganese dioxide. However, if a tiny crystal of potassium persulfate is added to the basic manganese(II) solution, the reaction is complete in less than 5 min and 100% recovery is obtained. The persulfate presumably oxidizes the manganese(II) rapidly to manganese(III) forcing the reaction to go to completion. Thus, a crystal of persulfate is always added to the initial mixture. Table I summarizes the results of the effect of standing and of adding persulfate on the recovery of the manganese.

Typical manganese standards prepared on filters are shown in Fig. 1. Notable differences in color intensity appeared at 1- $\mu\text{g}$  intervals for 0–10  $\mu\text{g}$  of manganese and at 10- $\mu\text{g}$  intervals for 0–50  $\mu\text{g}$ . Larger amounts of manganese were difficult to detect since the colors were too dark. The coloration of these filters was brown and the intensity of the coloration was usually uniform over the entire area of the filter.

The solution should be precipitated in the cold, otherwise an uneven coloration resulted on the filter. If the standards are prepared as described, they are stable for several months if kept refrigerated. The reason for keeping them refrigerated is that the filters will shrivel if exposed to heat. They can be conveniently mounted on a

TABLE I

THE EFFECT OF STANDING ON THE RECOVERY OF MANGANESE

<i>Mn added</i> ( $\mu\text{g}$ )	<i>Time</i> <i>before filtering</i> ( <i>min</i> )	<i>Mn found</i> ( $\mu\text{g}$ )	<i>Mn found</i> <sup>a</sup> ( $\mu\text{g}$ )
5	0.5	2.0	4.0
5	1.0	2.0	4.5
5	3.0	2.5	5.0
5	8.0	4.0	5.1
5	15.0	4.5	5.0

<sup>a</sup> A crystal of potassium persulfate added.

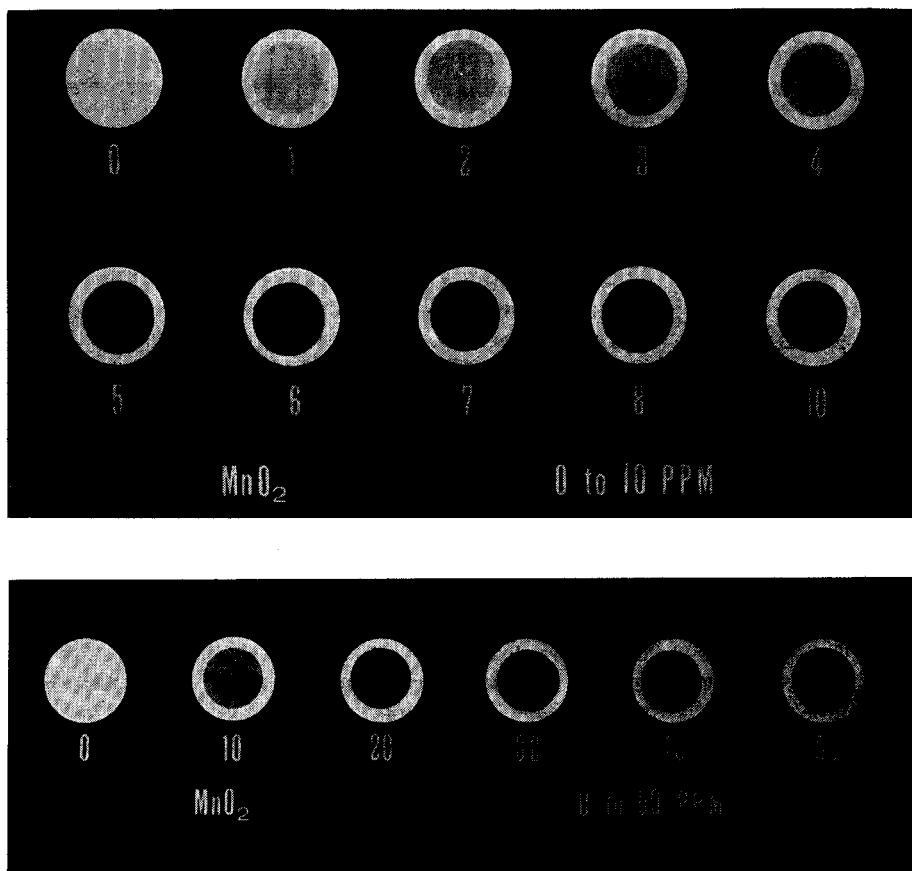


Fig. 1. Manganese standards on filters for the 0-10  $\mu\text{g}$  and 0-50  $\mu\text{g}$  ranges.

5"  $\times$  8" card for storage. Dust particles which are electrostatically attracted to the filters can be removed by gentle brushing with a camel-hair brush.

Care must be taken to use the same type of filters throughout. For example, if type OHWP filters (1.5- $\mu$  pore size) were used to collect precipitates instead of type AAWP, the coloration was an orange brown rather than brown, making comparison



with the standards difficult. Since the OHWP filters have a larger pore size and are less uniform than the AAWP, the difference in coloration was presumably due to trapping of some of the precipitate within these non-uniform pores rather than being retained completely on the surface.

The effect of some common cations on the recovery of the manganese was studied. Since most of the other metallic hydroxides, *e.g.*, iron, cobalt, nickel, etc., are soluble in acid, they will be redissolved when the nitric acid is added and should not interfere with the manganese determination. This is exactly what was observed as summarized in Table II.

Table III shows the results of the determination of the manganese content in some NBS standard steel samples.

TABLE II

THE EFFECT OF SOME COMMON CATIONS ON THE RECOVERIES OF MANGANESE(II)<sup>a</sup>

<i>Mn added</i> ( $\mu\text{g}$ )	<i>Mn found</i> ( $\mu\text{g}$ )	<i>Other ions added</i> ( $\text{mg}$ )
5.0	5.0	—
5.0	5.1	—
5.0	5.0	100, Co(II)
5.0	4.9	200, Co(II)
5.0	4.9	100, Cr(III)
5.0	4.8	300, Cr(III)
5.0	5.1	100, Ni(II)
5.0	5.1	100, Fe(III)
5.0	5.0	200, Fe(III)
5.0	5.0	400, Fe(III)

<sup>a</sup> Compared to standards.

TABLE III

DETERMINATION OF MANGANESE IN STEEL

<i>NBS #</i>	<i>Mn found</i> ( $\mu\text{g}$ )	<i>Mn calculated</i> (%)	<i>Mn actual</i> (%)
8856	7.0	0.94	0.91
SS 0.1	4.5	0.48	0.51
SS 0.1	5.0	0.40	0.41

The sensitivity of the method can be increased by decreasing the size of the filter. A filter holder was constructed to give an exposed area of 28 mm<sup>2</sup> compared to 254 mm<sup>2</sup> for the 25-mm filter. It was, therefore, expected that the limit of detection could be increased tenfold. This was observed; however, the colors on the filter were not uniform when the amount of manganese was less than 0.5  $\mu\text{g}$ .

Another method of increasing the sensitivity was studied. A solution of benzidine was used to produce an intense blue color with the manganese dioxide<sup>4</sup>. This increased the limit of detection to slightly less than 0.1  $\mu\text{g}$ ; however, the coloration was not consistent.

The advantages of this method over standard colorimetric procedures have

previously been discussed<sup>1</sup>. As with other color-comparison methods, this method is semi-quantitative, but its ease and rapidity should make it useful, especially in laboratories with limited instrumentation. This method can also be used for a preliminary separation of manganese for other determinations, *e.g.*, activation analysis.

#### SUMMARY

A method is described in which the intensity of coloration of brown manganese dioxide on white Millipore filters is taken as the measure of the manganese content. A solution of manganese(II) is made strongly basic, whereupon manganese dioxide precipitates via its auto-oxidation. Optimum conditions for the precipitation are studied. Less than 0.5  $\mu\text{g}$  of manganese can be determined.

#### RÉSUMÉ

On décrit une méthode pour le dosage du manganèse par mesure de l'intensité de coloration du dioxyde de manganèse brun sur des filtres blancs "Millipore". La solution de manganèse(II) est alcalinisée fortement; le dioxyde de manganèse précipite par autooxydation. On peut ainsi doser moins de 0.5  $\mu\text{g}$  de manganèse.

#### ZUSAMMENFASSUNG

Es wird eine halbquantitative Methode beschrieben, bei der die Farbintensität des braunen Mangandioxids auf weissen Filtern als Mass für den Mangangehalt genommen wird. Die Fällung des Mangandioxids erfolgt durch Autoxidation aus stark basischen Mangan(II)-Salzlösungen. Die optimalen Bedingungen für diese Fällungen werden untersucht. Weniger als 0.5  $\mu\text{g}$  Mangan können bestimmt werden.

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## ELECTRODE REACTIONS OF TUNGSTATE IONS IN THE PRESENCE OF CARBON MONOXIDE

PAUL STONEHART

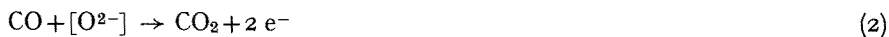
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Tungsten oxides and tungstate ions have been proposed as electrocatalysts for the oxidation of carbon monoxide to carbon dioxide in aqueous<sup>1,2</sup> and molten salt<sup>3</sup> fuel cells. In aqueous systems the mode of operation of the catalyst is not understood, although in acidic solution the overall reaction may be written as



The tungsten oxides have been incorporated into the electrode material as a powder together with platinum black, in tests for synergistic effects and it has been suggested<sup>1</sup> that the tungsten oxides provide sites for water adsorption to facilitate reaction (1). In molten salts<sup>3</sup>, the tungsten oxide-tungstate ions have been used as a redox system with the proposed mechanism *via* a solvated oxide ion  $[\text{O}^{2-}]$ .



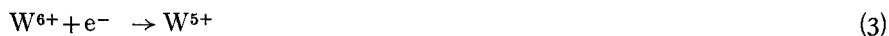
Electrode materials for the molten salt systems were platinum and graphite.

Tungsten compounds<sup>4</sup>, particularly the oxides, sulphides, and heteropoly complexes have been used to a great extent in the petroleum industry as cracking catalysts and reforming catalysts, with and without promoters.

At present, no investigations have been reported for the electrode reactions of carbon monoxide with tungstates in acidic solutions, although the electrochemistry of tungstates and tungsten compounds has been examined at mercury<sup>5-8</sup> electrodes both polarographically<sup>9-20</sup> and using A.C. techniques<sup>21-23</sup>. Due to the insolubility of tungstic oxide ( $\text{WO}_3$ ) in acidic solutions, the electrochemical studies have been carried out on phosphoric<sup>9,12,15,19,22,23</sup>, silicic<sup>9</sup>, hydrochloric<sup>11,17,20</sup>, oxalic<sup>14,16</sup>, and tartaric<sup>10</sup> complexes.

Conflicting views exist for the mechanism of reduction of tungstic oxide ( $\text{WO}_3$ ), as the reduction potential is in the vicinity of hydrogen evolution at an electrode. POLTORAK<sup>7</sup> and KOBOZEV *et al.*<sup>24</sup> indicate that the reduction mechanism depends upon the primary formation of free hydrogen atoms at the electrode surface to promote reduction, while LUKOVITSEV<sup>8</sup> and BAGOTSKII *et al.*<sup>5,6</sup> indicate the electrode mechanism to involve direct electron acceptance. In addition, differing degrees of reversibility have been reported for the oxidation states of tungsten. LINGANE AND SMALL<sup>11</sup> found 2 reduction steps for the chloro complex corresponding to  $\text{W}^{6+} \rightarrow \text{W}^{5+} \rightarrow \text{W}^{3+}$  whereas TAKAHASHI *et al.*<sup>22</sup> resolve 3 steps in phosphoric acid solutions up to 1 M

acid and 4 steps above this acid concentration. These were indicated to be:



and the 2-electron reaction (4) was indicated to be the most reversible. REZNIK<sup>17</sup> examined the tungstate complex in concentrated hydrochloric acid and found a 1-electron reversible reduction of the tungstate ion



or



BREYER AND HACOBIAN<sup>21</sup>, on the other hand, indicate that the reduction of the tungstate ion is irreversible in phosphate-borate-acetate buffers at pH 1.8 and pH 4.0.

KENNEDY<sup>12</sup> examined the various complexes of phosphotungstic acids in sulphuric acid and concluded that in acidic solutions, mixed phosphotungstic acids occurred with tungsten-to-phosphorus ratios of 3:1, 9:1, and 12:1. On acidifying tungstate with phosphoric acid the 12-poly acid is most readily obtained giving 3 distinct reduction waves. Analysis of these waves indicated the reduction to be *irreversible*.

Apart from the controversial measurements of KOBOZEV *et al.*<sup>24</sup>, no examination of the electrode reactions of complexed tungstate ions in acid solution on solid electrodes has been carried out. In addition, there have been no kinetic measurements of the rate of the electrode reaction or examination of the influence of carbon monoxide on the tungstate reaction and *vice versa*.

#### EXPERIMENTAL

Platinum and rhodium electrodes were prepared as wires (0.020 in. dia.; Engelhard) and sealed into glass quills with mercury contacting the wire within the glass seal. The mercury electrode was prepared as a small stationary pool with a submerged platinum wire for electrical contact.

Solutions were prepared from sodium tungstate (Allied Chemical), 70% phosphoric acid (J. T. Baker Company) and diluted with double distilled water.

The cell was a conventional 3-electrode cell with a test compartment, counter electrode compartment and reference probe connected *via* a Teflon capillary to a hydrogen reference electrode<sup>25</sup>. Gas bubblers were sealed into the 2 cell compartments in order to saturate the electrolytes with nitrogen and carbon monoxide.

The electronic apparatus is shown in Fig. 1. The potentiostat and potential scan generator were built using a Tektronix "O" unit having 2 operational amplifier modules with associated variable capacitive and resistive input and feedback circuitry. The Tektronix "O" unit was driven by a Tektronix 536 oscilloscope, with the output of the potentiostat displayed on the oscilloscope screen. A linear voltage scan was produced by integrating a small constant voltage at A, the integral appearing at B from the first operational amplifier. The power boosters at C were transistors coupled

in an emitter-follower mode to supply current in excess of the  $\pm 5$  mA capability of the operational amplifiers *in situ*. The second operational amplifier maintained the potential control of the test electrode with respect to the reference electrode demanded by the potential output at B. The Wagner earth bridge network shown at D compen-

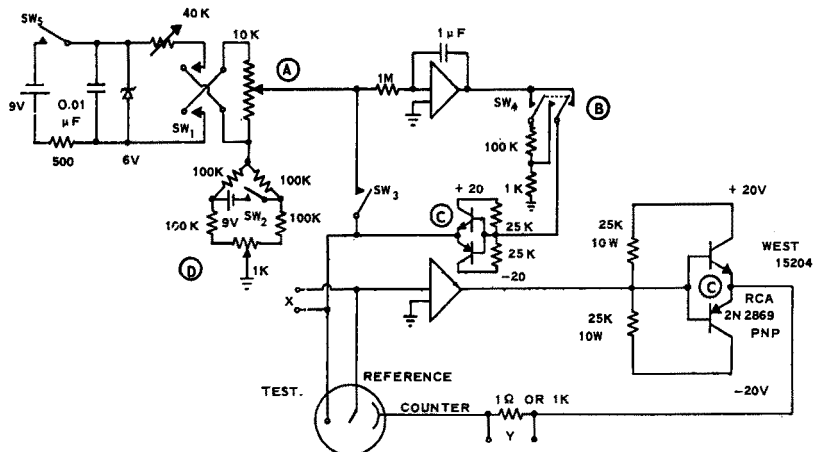


Fig. 1. Potential scanning circuit.

sated for small grid current errors in the differential inputs of the integrating amplifier. The current-voltage curves were recorded on a Tektronix 502 dual-beam oscilloscope in the X-Y mode or on a Moseley 7030 AM X-Y recorder.

## RESULTS AND DISCUSSION

Cyclic voltammetric curves in solutions of sodium tungstate (up to 0.1 *M*) in 1 *M* phosphoric acid were obtained at platinum, rhodium, and mercury electrodes. In all cases, a reversible one-electron reaction was obtained according to eqns. (7) and (3).

Figure 2a shows the current-voltage characteristics of a platinum electrode in

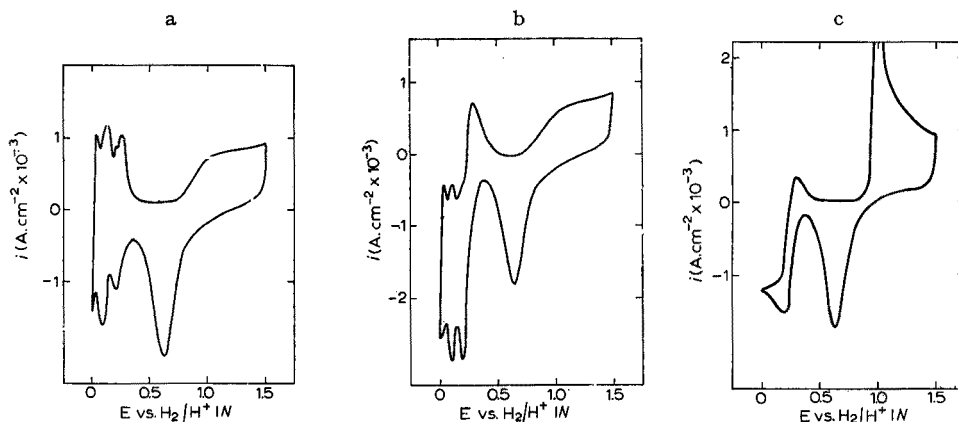


Fig. 2. Cyclic voltammetric curves at a rotating (550 rev./min) platinum electrode. Scan rate 6 V/sec. (a) 1 *M*  $\text{H}_3\text{PO}_4$ ,  $\text{N}_2$  saturated, (b) 1 *M*  $\text{H}_3\text{PO}_4$  + 0.05 *M*  $\text{WO}_4^{2-}$ ,  $\text{N}_2$  saturated, (c) 1 *M*  $\text{H}_3\text{PO}_4$  + 0.05 *M*  $\text{WO}_4^{2-}$ , CO saturated.

1 *M* phosphoric acid saturated with nitrogen, showing the hydrogen adsorption peaks<sup>26</sup> together with oxide formation and reduction. With tungstate added to the solution, the current densities due to hydrogen adsorption on platinum<sup>26</sup> and rhodium<sup>27</sup> were superimposed upon those current densities due to the reduction of phosphotungstate and are shown for platinum in Fig. 2b. In the presence of carbon monoxide, the hydrogen adsorption peaks are not produced, although there is no change in the tungstate reduction (Fig. 2c). The same behavior was noted for rhodium electrodes (Fig. 3). On rotating the wire electrodes at 550 rev./min, well defined diffusion plateaux were obtained with the magnitude of the current densities at the plateaux directly pro-

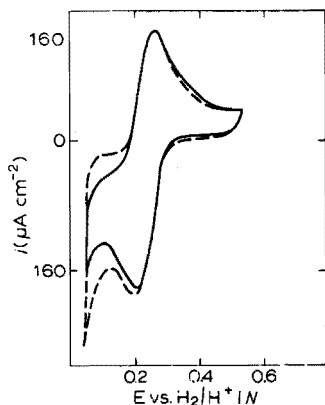


Fig. 3. Cyclic voltammetric curves at a stationary rhodium electrode. 1 *M* H<sub>3</sub>PO<sub>4</sub> + 0.03 *M* WO<sub>4</sub><sup>2-</sup>. Scan rate 0.0475 V/sec. - - - saturated with N<sub>2</sub>; — saturated with CO.

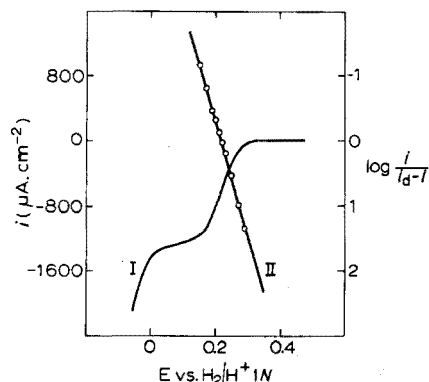


Fig. 4. (I) Voltammetric curve at a rotating (550 rev./min) rhodium electrode. 1 *M* H<sub>3</sub>PO<sub>4</sub> + 0.03 *M* WO<sub>4</sub><sup>2-</sup>. Saturated with CO. Scan rate 0.0475 V/sec. (II) *E* versus  $\log i/(i_d - i)$  for curve I.

portional to the concentration of tungstate ions in solution (Fig. 4). Analysis of the current-voltage curves for the rotating electrodes and plotting  $\log i/(i_d - i)$  versus *E* gave a slope of 59 mV and hence *n* = 1.

$$\text{From } E = E_{\frac{1}{2}} + 2.303 \frac{RT}{nF} \log \frac{i}{i_d - i}, \quad (8)$$

$$E_{\frac{1}{2}} = +0.216 \pm 0.002 \text{ V vs. H}_2/\text{H}^+ \text{ 1 N.}$$

To evaluate the kinetic rate constants for the reversible 1-electron reduction of phosphotungstate, a method of evaluating the anodic and cathodic peak separations as a function of voltage scan rate was used. In this manner, for a perfectly reversible electrochemical reaction in the absence of kinetic limitations, the separation<sup>28</sup> of the anodic and cathodic peaks is 59/*n* mV at 25°. This situation exists in real cases at slow scan rates for reactions with high rate constants. On increasing the scan rate, kinetic limitations produce a separation of the anodic and cathodic peak potentials. Under controlled conditions<sup>29</sup> the separation of the peaks is a function of the voltage scan rate and the kinetic rate constant.

Thus NICHOLSON<sup>29</sup> has shown that for a rapid reversible electrode reaction

$$\psi = \gamma^\alpha \cdot k_s \cdot \left( \pi \cdot \frac{nF}{RT} \cdot D_0 \cdot \frac{dV}{dt} \right)^{-\frac{1}{2}} \quad (9)$$

$$\text{and } \psi = f(\Delta E_p \cdot n) \quad (\text{IO})$$

$$\text{where } \gamma = \left(\frac{D_O}{D_R}\right)^{\frac{1}{2}} \quad (\text{II})$$

$D_O$  and  $D_R$  are the diffusion coefficients of the oxidized and reduced species respectively,  $\alpha$  the transfer coefficient,  $dV/dt$  the potential scan rate,  $\Delta E_p$  the voltage separation of the anodic and cathodic peaks and  $k_s$  the specific rate constant for a first-order reaction involving  $n$  electrons.  $R$ ,  $T$ ,  $n$ , and  $F$  have the usual electrochemical significance. As  $D_O \approx D_R$  and  $\alpha$  is assumed to be 0.5, then  $\gamma \approx 1.0$ . Also  $D_O$  was estimated\* to be  $10^{-6}$  cm<sup>2</sup>/sec. The absolute value is not too important as  $k_s$  varies as  $D_O^{\frac{1}{2}}$ , taking the square root of a small error to be negligible.

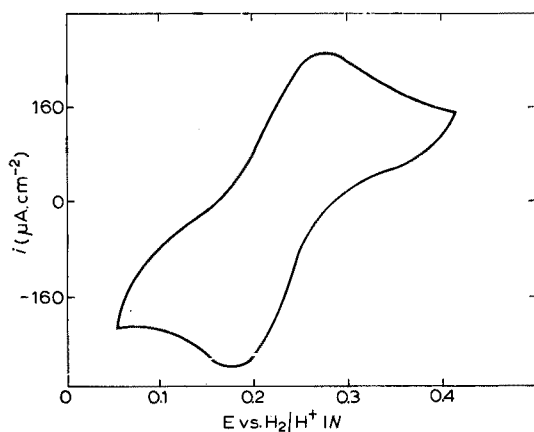


Fig. 5. Cyclic voltammetric curve at a stationary platinum electrode. 1 M H<sub>3</sub>PO<sub>4</sub> + 0.05 M WO<sub>4</sub><sup>2-</sup>, CO saturated. Scan rate 2.16 V/sec.

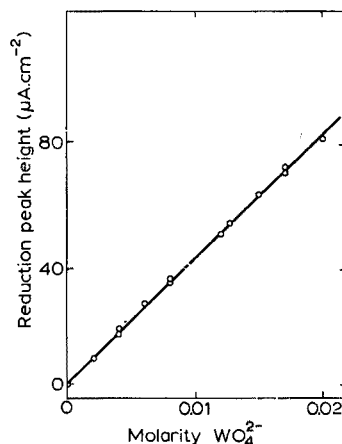


Fig. 6. Reduction peak height as a function of WO<sub>4</sub><sup>2-</sup> concentration. Stationary rhodium electrode. Scan rate 0.07 V/sec. 1 M H<sub>3</sub>PO<sub>4</sub> saturated with CO.

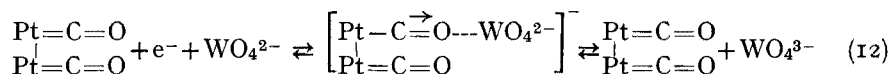
A cyclic voltammetric curve of tungstate reduction obtained at a platinum electrode in 1 M phosphoric acid saturated with carbon monoxide is shown in Fig. 5. The specific rate constants evaluated at platinum, rhodium, and mercury are shown below.

	Pt	Rh	Hg
Specific rate constant			
$k_s$ (cm/sec)	$1.2 \cdot 10^{-2}$	$7.0 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$

In all instances the carbon monoxide did not change the value of  $k_s$  and served only to suppress the evolution of hydrogen at the electrodes. This feature was used for analysis of tungstate solutions in 1 M phosphoric acid. With a constant scan rate and stationary platinum or rhodium electrodes, the cathodic peak height for the reduction of tungstate was measured as a function of the tungstate concentration. A linear dependence was obtained up to tungstate concentrations of 0.02 M (Fig. 6).

\* Measurements of diffusion coefficients to be published.

Also, the phosphotungstate ions in solution did not remove the adsorbed carbon monoxide at the platinum<sup>30-37</sup> and rhodium<sup>37</sup> electrodes. In addition, it was possible to saturate the electrode surface with carbon monoxide ( $p\text{CO} = 1$ ), remove the carbon monoxide from the solution by passing nitrogen, carry out the cyclic voltammetric scan for the tungstate reaction and finally scan the electrode potentials to  $+1.2$  V and obtain quantitative<sup>37</sup> oxidation peaks for oxidation of the adsorbed carbon monoxide. As the surfaces of both platinum and rhodium are completely covered by adsorbed carbon monoxide in carbon monoxide-saturated acid solutions<sup>37</sup>, then the electron transport must be carried out through the adsorbed layer, possibly by conjugation of the carbon monoxide molecule with the metal surface atoms. It is doubtful whether the phosphotungstate adsorbs to any extent on the carbon monoxide surface, *e.g.*



The specific hindrance of the hydrogen evolution reaction by carbon monoxide, yet without effect on the tungstate reduction, indicates that electrons are capable of freely moving through the adsorbed carbon monoxide layer to take part in a reaction within the double layer; whereas a reaction requiring a surface rearrangement, either molecular dissolution or combination, is hindered by the carbon monoxide. It is possible that this phenomenon may be used to evaluate surface mechanisms in more complex hydrocarbon electro-oxidations.

Comparing the results obtained here with those results previously obtained, it is seen that the mode of reduction of tungstates is *via* direct electron transfer<sup>5,6,8</sup> and not by reduction with hydrogen atoms<sup>7,24</sup>. The absence of reversibility noted by KENNEDY<sup>12</sup> may be due to rupture of the phosphotungstate complex on reduction especially in the presence of an excess of sulphuric acid. Indeed, the rate constant obtained on mercury shows that this reaction borders on irreversibility<sup>38</sup>.

#### SUMMARY

Tungstate ions may be reversibly reduced at platinum, rhodium and mercury electrodes in phosphoric acid according to the reaction  $\text{WO}_4^{2-} + e^- \rightleftharpoons \text{WO}_4^{3-}$ . The specific rate constants ( $k_s$ ) on Pt, Rh and Hg are  $1.2 \cdot 10^{-2}$ ,  $7.0 \cdot 10^{-3}$ , and  $6.5 \cdot 10^{-4}$  cm/sec, respectively. In the presence of carbon monoxide, hydrogen evolution at Pt and Rh is blocked while the electron transfer for tungstate reduction is unhindered. This is used as a criterion for a surface dissociation or recombination step in an electrochemical reaction. Two methods may be used with platinum or rhodium electrodes for the determination of tungstate, either rotating the electrode at a constant speed and measuring the diffusion current, or measuring the reduction peak height at a constant potential scan rate.

#### RÉSUMÉ

Les ions tungstates peuvent être réduits réversiblement aux électrodes de platine, rhodium et mercure en milieu acide phosphorique d'après la réaction



$\text{WO}_4^{2-} + e^- \rightleftharpoons \text{WO}_4^{3-}$ . Les constantes  $k_s$  sur Pt, Rh et Hg sont respectivement  $1.2 \cdot 10^{-2}$ ,  $7.0 \cdot 10^{-3}$  et  $6.5 \cdot 10^{-4}$  cm/sec. En présence d'oxyde de carbone, la formation d'hydrogène sur Pt et Rh est bloquée, tandis que le transfert d'électrons pour la réduction du tungstate ne change pas. Deux méthodes peuvent être utilisées, avec électrodes de platine ou de rhodium, pour le dosage des tungstates: soit électrode rotative à vitesse constante et mesure du courant de diffusion, soit mesure de la hauteur du pic de réduction à potentiel constant.

## ZUSAMMENFASSUNG

Wolfram-Ionen können an Platin-, Rhodium- und Quecksilber-Elektroden in phosphorsaurer Lösung gemäss der Gleichung  $\text{WO}_4^{2-} + e^- \rightleftharpoons \text{WO}_4^{3-}$  reversibel reduziert werden. Die spezifischen Geschwindigkeitskonstanten ( $k_s$ ) von Pt, Rh und Hg sind  $1.2 \cdot 10^{-2}$ ,  $7.0 \cdot 10^{-3}$  bzw.  $6.5 \cdot 10^{-4}$  cm/sec. In Gegenwart von Kohlenstoffmonoxid wird die Wasserstoffentwicklung am Pt und Rh blockiert, während der Elektronenübergang für die Wolfram-Reduktion unbehindert ist. Dieses wird als Kriterium für einen Oberflächendissoziations- oder Rekombinationsschritt bei einer elektrochemischen Reaktion benutzt. Für die quantitative Bestimmung von Wolfram können 2 Methoden mit Platin- oder Rhodium-Elektroden verwendet werden, entweder mit konstanter Geschwindigkeit rotierende Elektroden und Messung des Diffusionsstroms oder Messen der Höhe des Reduktionsmaximums bei einem konstanten Potential.

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## SHORT COMMUNICATION

**Spectrophotometric determination of niobium using *o*-dihydroxycoumarins**

The need for more efficient methods for the determination of niobium in ores and alloys has arisen because of the increasing use of this metal in high-temperature alloys and container material for molten salts and metals. Two spectrophotometric methods<sup>1</sup> using ammonium thiocyanate and hydrogen peroxide are commonly employed. Pyrogallol<sup>1</sup> has been used for the spectrophotometric determination of niobium in presence of tantalum and bromopyrogallol red<sup>2</sup> has been found useful for this purpose even in solutions containing EDTA. Bipyridine<sup>3</sup>, oxine<sup>4</sup>, *p*-methoxybenzothiohydroxamic acid in conjunction with ammonium thiocyanate<sup>5</sup>, 1-(2-pyridylazo)-resorcinol<sup>6</sup>, trihydroxyfluorones<sup>7</sup>, gallic acid<sup>8</sup> and tiron<sup>9</sup> are some of the other reagents that have been recently reported for the spectrophotometric determination of niobium. In the present studies, it was found that esculetin (6,7-dihydroxycoumarin) and 4-methylesculetin form orange-red water-soluble complexes with niobium, and these were investigated for its spectrophotometric determination.

*Reagents and apparatus*

Niobium solutions were prepared by dissolving niobium pentachloride (Johnson, Matthey & Co., Ltd.) in dilute hydrochloric acid in presence of tartaric acid, and standardised with oxine gravimetrically. Standard ethanolic solutions of esculetin and 4-methylesculetin prepared by the usual methods<sup>10</sup> were employed. Sodium perchlorate and tartaric acid used were of B.D.H. (L.R.) quality.

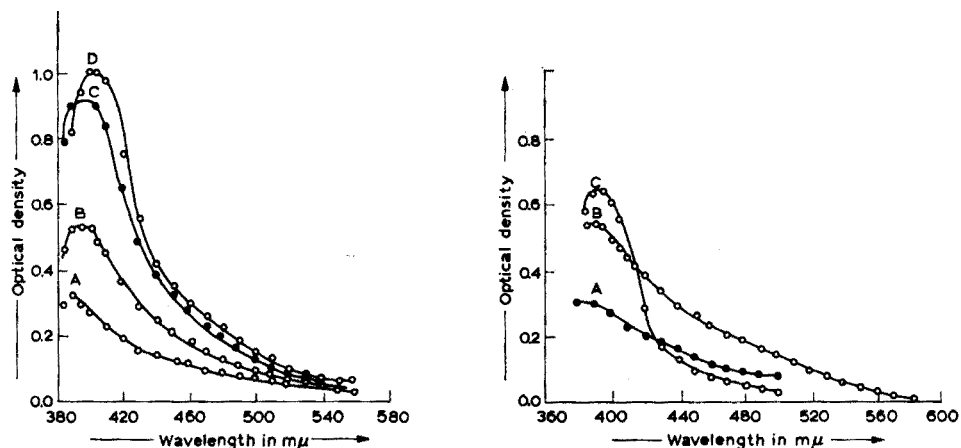


Fig. 1. Absorption spectra of niobium-esculetin complex at pH values: (A) 4.5; (B) 5.5; (C) 6.0; (D) 6.5.

Fig. 2. Absorption spectra of niobium-4-methylesculetin complex at pH values: (A) 4.0; (B) 5.5; (C) 6.5.

A Unicam spectrophotometer, model SP 600 and a Beckman pH meter, model H<sub>2</sub>, were used. The pH was adjusted with ammonia and hydrochloric acid.

#### Absorption studies of niobium complexes

In the pH range 4.0–8.0, the wavelength of maximum absorption of the niobium–esculetin and niobium–4-methylesculetin complexes increased slightly with pH up to 6.5 (Figs. 1 and 2); above this pH, this wavelength increased rather rapidly up to pH 8.0, beyond which there was no complex formation. Further studies were therefore carried out at pH 6.5 and 400–405 nm in each case, as the optical density of the complexes under these conditions was at a maximum while that of the reagent was negligible.

At least a 5-fold excess of the reagent was necessary for full colour development in the case of the niobium–esculetin complex. In the case of the niobium–4-methylesculetin complex, however, a 4-fold excess sufficed for maximum colour development. In the further studies, a 10-fold excess of reagent was always used, since this amount caused no interference under the experimental conditions.

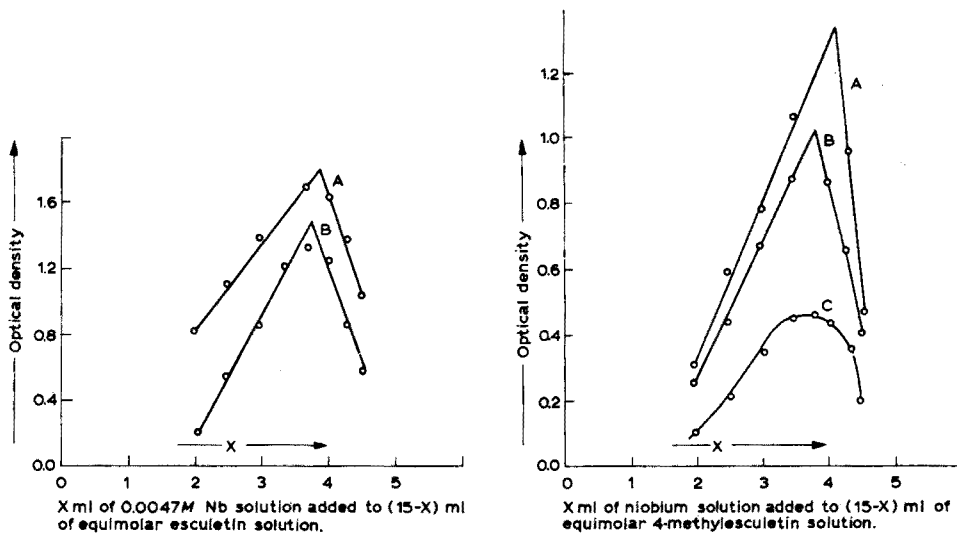


Fig. 3. Molar composition of niobium–esculetin complex at wavelength: (A) 450 nm; (B) 500 nm.

Fig. 4. Molar composition of niobium–4-methylesculetin complex by JOB'S method, at concentrations and wavelengths: (A) 0.0047 *M* at 500 nm; (B) 0.00237 *M* at 450 nm; (C) 0.00237 *M* at 500 nm.

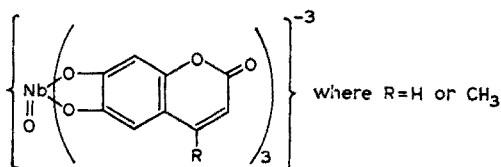
The optical densities of the niobium complexes with esculetin and 4-methylesculetin were found to remain constant for 72 h, but the colour faded on longer standing. The Beer–Lambert law was valid up to niobium concentrations of 1.0 p.p.m. in the case of esculetin, and 5.0 p.p.m. in the case of 4-methylesculetin.

#### Composition of the complexes

The molar composition of the niobium complexes with esculetin and 4-methyl-

esculetin was found by JOB's method of continuous variations to be 1:3 in each case (Figs. 3 and 4).

On treatment with an anion-exchange resin, the complex ions were completely exchanged as shown by the absence of any absorption maxima in the effluent. The optical density of the solution after passing through a cation-exchange resin, remained unchanged, thus showing that the complexes are negatively charged. On the basis of the nature of the electrical charge and the molar composition of the complexes, the following tentative structure for the complex is suggested.



The stability constants of the niobium-esculetin and niobium-4-methylesculetin complexes were determined spectrophotometrically: the mean values of  $\log K$  from several determinations at  $20^\circ$  were found to be 10.43 for the niobium-esculetin complex and 12.07 for the niobium-4-methylesculetin complex.

#### Interferences

$\text{Be}^{2+}$ ,  $\text{WO}_4^{2+}$ ,  $\text{VO}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{ZrO}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Ti}^{4+}$  and  $\text{Ta}^{5+}$  were found to interfere seriously even when present in minute quantities. The limits of certain ions that do not interfere in the determination of 1.0 p.p.m. of niobium are given in Table I.

TABLE I  
INTERFERENCES

Complex	p.p.m. of ion tolerated					
	Acetate	Citrate	$\text{PO}_4^{3-}$	$\text{SCN}^-$	$\text{V}(\text{as } \text{VO}_3^-)$	$\text{Mo}(\text{as } \text{MoO}_4^{2-})$
Nb-esculetin	20	20	50	5	—	60
Nb-4-methylesculetin	50	50	50	20	60	50

#### Recommended procedure

To a solution containing the requisite amount of the metal, add a 10-fold excess of the reagent in ethanol and adjust the pH to 6.5. Measure the optical density at 400–405 nm against the corresponding reagent blank prepared under identical conditions. Prepare corresponding calibration curves in the usual way.

#### Conclusions

The spectrophotometric studies of the 2 complexes of niobium with esculetin and 4-methylesculetin described above, show that 4-methylesculetin is a better reagent for the spectrophotometric determination of niobium, as the resultant complex obtained is more stable and obeys Beer-Lambert's law over a wider range of niobium concentration; the interference of certain cations is also comparatively less.

The authors are grateful to Prof. T. R. SESHADRI, F.R.S., for his keen interest and helpful discussions.

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## BOOK REVIEWS

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K. W. BAGNALL, *The Chemistry of Selenium, Tellurium and Polonium*, Elsevier Publishing Company, Amsterdam, 1965, viii + 200 pp., price Dfl. 35.—.

The chemistry of Group VIb of the Periodic Table is often assumed to refer to the chemistry of oxygen, sulphur, selenium and tellurium, with a mention of the existence of polonium. This book emphasises the place of polonium as a member of the Group, and concentrates attention on the comparative chemistry of the 3 heavier members.

The author has been concerned with a considerable part of the investigation of the chemistry of polonium and he correlates this with the larger volume of information available on selenium and tellurium. The book gives a concise account of the chemistry of the 3 elements, with a section dealing briefly with the extensive work on the principal classes of organo compounds, and should help to further interest in a rather neglected corner of the Periodic Table.

A. J. EDWARDS (Birmingham)

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*Official Methods of Analysis of the Association of Official Agricultural Chemists*, 10th Edn., Edited by WILLIAM HORWITZ, Assoc. of Official Agricultural Chemists, P.O. Box 540, Benjamin Franklin Station, Washington, D.C., 1965, vii + 957 pp., price \$22.50.

The Tenth Edition, again, reflects the combined efforts of hundreds of scientists, referees, and committee members in selecting, developing, evaluating, and standardizing analytical methods for use in the evaluation and regulation of foods, food additives, food products, cosmetics, drugs, disinfectants and fertilizers.

Many methods in this new edition have been updated to utilize such powerful techniques as gas, paper and thin-layer chromatography; emission spectroscopy; atomic absorption spectroscopy and other instrumental techniques. While the new edition has been increased by 125 pages, the publishers have attached information survey cards for users with the request that they report on methods classified as "Surplus", thus possibly eliminating necessity for inclusion in future editions.

This authoritative reference will be required by all analytical laboratories engaged in the analysis of foods and related products.

FOYMAE K. WEST (Baton Rouge)

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FRANK L. SCHNEIDER, *Qualitative Organic Microanalysis*, Monographien aus dem Gebiete der Qualitativen Mikroanalyse, Hrsg. von A. A. BENEDETTI-PICHLER, Band II, Springer-Verlag, Wien, 1965, xi + 535 S., Ganzleinen \$21.40 (in English).

This useful volume dealing with the cognition and recognition of carbon compounds is divided into 4 parts. Part I is concerned with fundamental techniques and preparation of samples (83 pp.). Part II describes the preliminary examination of the sample for elementary composition, physical constants and solubility (65 pp.). Part III deals with the systematic analysis of organic compounds arranged in Orders, Genera, Divisions, etc. (138 pp.). The remaining Part IV comprises tables of physical constants of compounds and their derivatives classified in the manner adopted in Part III; these tables occupy 211 pages and form a valuable part of the book.

On the whole, the methods advocated in this book follow a well-established classical pattern. Emphasis is placed on the classical microchemical techniques associated with the Austrian microchemical schools, although in this respect it is surprising that little or no use is made of the many fine micro-tests which Feigl has developed in the last 15-20 years for qualitative organic purposes. This is, however, a useful contribution to the literature on qualitative organic analysis. The text is somewhat prosaic and the book has an aura of the earlier, more leisurely, days of microchemistry but these factors do not particularly detract from its overall value as a reference volume.

W. I. STEPHEN (Birmingham)

*Anal. Chim. Acta*, 37 (1967) 139

R. KALVODA, *Techniques of Oscillographic Polarography*, 2nd Edn., translated by K. MICKA, Elsevier Publishing Company, Amsterdam, 1965, 214 pp., price Dfl. 30.—.

This book is a completely revised and enlarged edition of the German version entitled *Die Technik der oszillographischen Messungen*.

The introductory chapter is an excellent example of conciseness, providing the theoretical aspects of the method and the construction of the apparatus with selected references to more fundamental papers and monographs. In chapter II, which forms the vigorous heart of the book, the oscillographic behaviour of simple ions and of a number of organic species is described. Procedures for microanalysis and for the determination of metals in alloys and ores are also included. Oscillographic polarography is a relatively simple method, but successful application requires a certain experimental technique. For this reason chapter III contains instructions for carrying out selected exercises and all technically important details are described herein. Following these instructions the chemist will easily become familiar with the experimental technique and the potential applications of the method. Chapter IV deals with maintenance of apparatus and construction of auxiliary electrical circuits.

Oscillographic polarography with alternating current will probably never replace classical polarography, but it appears to be a suitable supplement for it. The present book, which is the first English monograph in this field, contains a great deal of practical experience and it provides a welcome and up-to-date compendium of oscillographic techniques and their applications. It will serve as an introduction to the subject for the general reader and will also prove very useful for the analyst and for research workers engaged in electrode processes.

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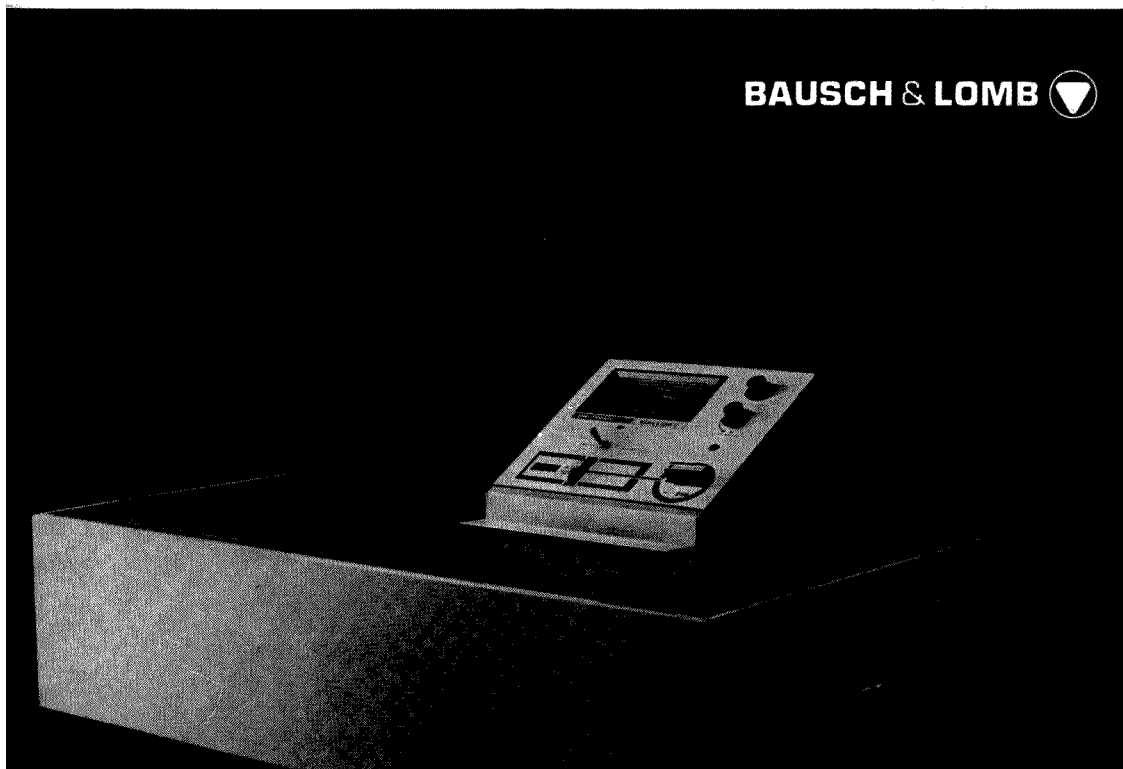
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## ANNOUNCEMENT

concerning the

## JOURNAL OF ELECTROANALYTICAL CHEMISTRY

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Papers for publication should be sent to one of the following addresses:

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Dr. R. H. OTTEWILL, Department of Chemistry, The University, Bristol 8, England;

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Professor C. N. REILLEY, Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27515, U.S.A.

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