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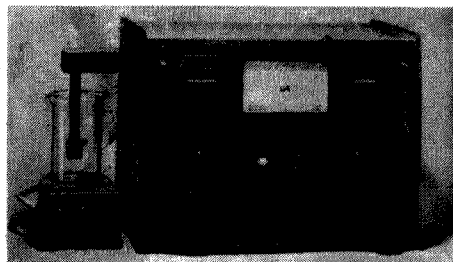


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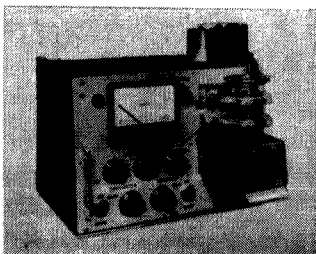
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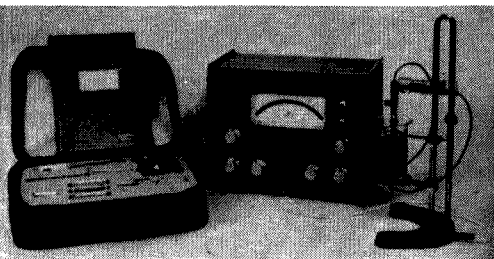
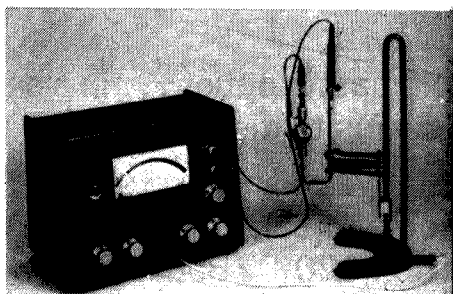
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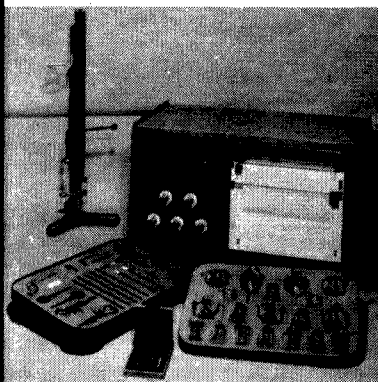
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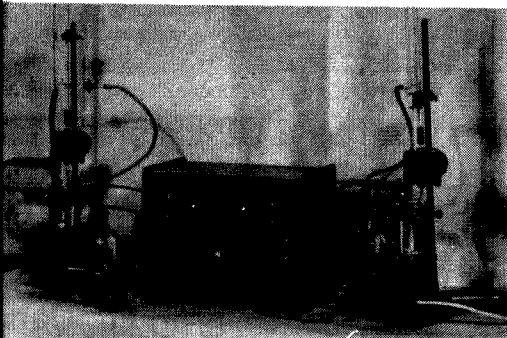
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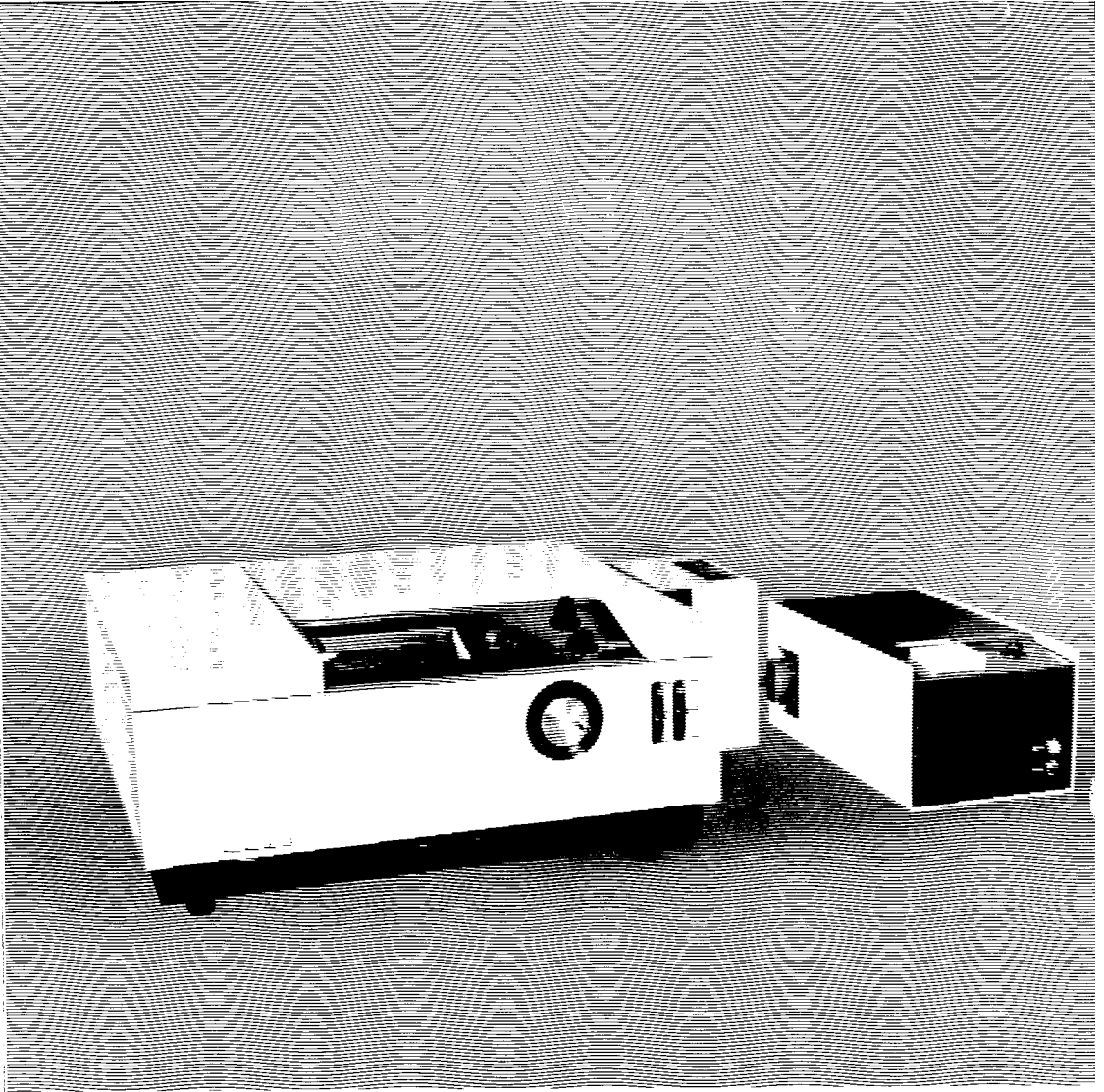
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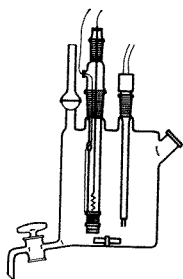
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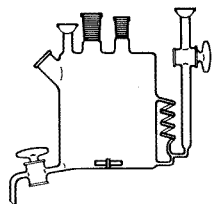
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Ensemble de coulométrie automatique de Jean BIZOT

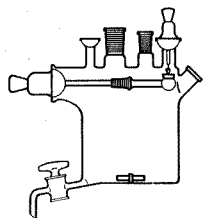
Monsieur BIZOT a présenté à la Société Chimique de France, le 23 avril 1965, une nouvelle méthode de dosage de petites quantités d'eau. Elle est décrite dans la publication suivante:
J. BIZOT - Méthode automatique de dosage coulométrique de petites quantités d'eau.
Bull. Soc. Chim. France janvier 1967, page 151.



Cellule pour liquides avec électrodes et tube à dessécher.



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Cellule pour solides et liquides, sans électrodes.

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Volume 40, No. 2, February 1968

DETERMINATION OF NONMETALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Inorganic anions and organic compounds are determined using conventional atomic absorption apparatus. Several methods are studied in which the desired compound either limits of interferes with the determination or absorption of a metal. A direct relationship is obtained between the absorption by the metal and the amount of substance sought. Substances determined include orthophosphate, sulfate, iodide, sulfide, iodate, glucose, protein, 8-hydroxyquinoline, ethylenediaminetetraacetic acid, and ammonium pyrrolidine dithiocarbamate.

G. D. CHRISTIAN AND F. J. FELDMAN,
Anal. Chim. Acta, 40 (1968) 173-179

AN ULTRASONIC ATOMISER APPLIED TO ATOMIC ABSORPTION SPECTROPHOTOMETRY

An ultrasonic atomiser has been attached to a commercial atomic absorption spectrophotometer and a comparison made between the performance of ultrasonic and pneumatic atomisers in respect of sample consumption, absorbance measurements, stability and droplet size. The principal finding is that, with the ultrasonic atomiser, the same sensitivity as given by a standard pneumatic atomiser can be achieved on a considerably smaller sample volume. Further improvements in the technique should be possible.

H. C. HOARE, R. A. MOSTYN AND B. T. N. NEWLAND,
Anal. Chim. Acta, 40 (1968) 181-186

THE DETERMINATION OF TRACE ELEMENTS IN SULPHIDE MINERALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY WITH ABSORPTION TUBES

A method for the determination of minor and trace elements (Zn, Cd, Pb, Cu and Ag) in sulphide minerals by atomic absorption spectrophotometry is described. For enhancing the sensitivity of the determination, the absorption tube technique is applied. Memory effects and background absorption influences on the measurement with absorption tubes are discussed.

I. RUBEŠKA,
Anal. Chim. Acta, 40 (1968) 187-194

ATOMIC FLUORESCENCE FLAME SPECTROMETRY USING A MERCURY LINE SOURCE

The possibility of exciting the fluorescence of several elements with the "overlapping" lines of other elements and the effectiveness of exciting the fluorescence of Fe, Mn, Ni, Cr, Tl, Cu and Mg with a 90 W mercury discharge lamp, are discussed. A method of increasing the fluorescence radiation by suitable optics, with a simple adaptation of a Jarrell-Ash AA spectrometer, is described. A two-pass system of the incident radiation into the flame is coupled with a mirror, in the optical axis, which reflects the fluorescence radiation emitted at the opposite side to the monochromator slit. This produces an increase of 168% of the signal. Detection limits for 10 elements are reported.

N. OMENETTO AND G. ROSSI,
Anal. Chim. Acta, 40 (1968) 195-200

PRECISION ANALYSES OF MANGANESE IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

A simple and rapid procedure for the determination of manganese in rocks by neutron activation and γ -spectrometry is presented. The precision of the method calculated from analyses of standard rocks is of the order 1.5–2%, and an accuracy of $\pm 2\%$ is attainable. The method is applicable to most types of geological samples, and should be superior to conventional methods used in rock analysis.

O. JOHANSEN AND E. STEINNES,
Anal. Chim. Acta, 40 (1968) 201–205

DETERMINATION OF BARIUM AND STRONTIUM IN SEA WATER

A process based on ion-exchange concentration and separation followed by flame photometry has been developed for the determination of strontium and barium at natural levels in sea water. These elements are stripped from 1-l samples of sea water by means of a cation-exchange resin in the calcium form and selectively eluted with CyDTA and EDTA respectively. Factors influencing the intensity of strontium and barium in hydrogen flames have been studied. The standard deviations of the method are 0.05 p.p.m. for strontium and 0.6 p.p.b. for barium and the accuracy of the method is more than sufficient to demonstrate clearly the variability of Sr/Cl and Ba/Cl ratios with depth and location.

N. R. ANDERSEN AND D. N. HUME,
Anal. Chim. Acta, 40 (1968) 207–220

THE DETERMINATION OF THORIUM, LANTHANUM AND SAMARIUM IN CERIUM(IV) NITRATE BY ACTIVATION ANALYSIS, WITH THE AID OF ELECTROPHORETIC FOCUSING OF IONS

Thorium, lanthanum and cerium were determined in ammonium cerium(IV) nitrate. The chemical separation was carried out by electrophoretic focussing of ions (EFI) in a matter of minutes. The small amount of sample possible in this separation technique is the main limit for the sensitivity of the procedure. With an irradiation time of 2 h at a thermal flux of $4 \cdot 10^{11}$ n/cm²/sec, the lower limits are: Th 0.1 μ g; La $4 \cdot 10^{-2}$ μ g; Sm $5 \cdot 10^{-3}$ μ g.

J. OP DE BEECK,
Anal. Chim. Acta, 40 (1968) 221–228

A NEW METHOD FOR THE CARRIER-FREE PRODUCTION OF ⁹⁰Y FROM ⁹⁰Sr–⁹⁰Y MIXTURE AND ⁸⁹Sr FROM NEUTRON-IRRADIATED Y₂O₃

The extraction of strontium(II) and yttrium(III) ions from aqueous solutions at various pH values into methyl isobutyl ketone containing 1-phenyl-3-methyl-4-caprylpyrazolone-5 is described. Quantitative extraction of Sr and Y at pH 8.6–10 and pH 2.8–5.4 respectively is utilized for the carrier-free production of ⁹⁰Y from ⁹⁰Sr–⁹⁰Y mixtures and ⁸⁹Sr from neutron-irradiated yttrium oxide. A clean separation of these elements from each other and more than 95% calculated activities were recovered.

M. Y. MIRZA,
Anal. Chim. Acta, 40 (1968) 229–234

LIQUID-LIQUID EXTRACTION METHODS FOR THE PRODUCTION OF CARRIER-FREE ^{115}Cd AND $^{89,90}\text{Sr}$ FROM FISSION PRODUCTS

The extraction of fission product elements with 1-phenyl-3-methyl-4-caprylpyrazolone-5 at various pH values has been investigated. The quantitative extraction of cadmium at pH 5.4 and that of strontium at pH 9.0 is utilised in devising procedures for the recovery of ^{115}Cd and $^{89,90}\text{Sr}$ from the fission products. Good decontamination factors and more than 90% ^{115}Cd and 80% $^{89,90}\text{Sr}$ activities were recovered.

M. Y. MIRZA,
Anal. Chim. Acta, 40 (1968) 235-240

CONSTRUCTION OF DEMOUNTABLE HOLLOW-CATHODE LAMPS FOR STIMULATING EMISSION OF ORGANIC COMPOUNDS

A demountable hollow cathode has been constructed which provides emission spectra of organic compounds. The construction and operation of the hollow cathode is described. The emission spectra of organic and inorganic phosphates are illustrated and discussed.

J. W. ROBINSON, H. P. LOFTIN, JR. AND D. TRUITT,
Anal. Chim. Acta, 40 (1968) 241-250

AN ULTRASENSITIVE CATALYTIC METHOD FOR METAL IONS AND CYANIDE-CONTAINING ORGANIC COMPOUNDS

Ultrasensitive methods are described for the detection and determination of cyanide-containing organic compounds and of various metal ions. The methods are based either on the hydrolysis of the organic compounds to give cyanide ion, which then catalyzes the reduction of *o*-dinitrobenzene via formation of the cyanohydrin anion of *p*-nitrobenzaldehyde, or on the inhibition of this catalytic reaction by silver(I), mercury(II), copper(II), cobalt(II), nickel(II), zinc(II) and cadmium(II) which form cyanide complexes. By these methods, tetracyanoethylene, *p*-chlorobenzylidene malononitrile, or benzoyl cyanide (0.1-10 $\mu\text{g/ml}$) may be determined with a deviation of about 2%, and Ag(I), Hg(II) (0.02-0.2 $\mu\text{g/ml}$), Cu(II) (0.003-0.030 $\mu\text{g/ml}$), Co(II) (0.06-0.40 $\mu\text{g/ml}$) and Ni(II), Zn(II) and Cd(II) (1-10 $\mu\text{g/ml}$) can be determined with a deviation of about 3%.

G. G. GUILBAULT AND R. J. McQUEEN,
Anal. Chim. Acta, 40 (1968) 251-258

THERMOMETRIC TITRATIONS IN THE FORMATION OF THE COMPLEX FLUORIDES OF IRON, ALUMINIUM, ANTIMONY, TIN AND LEAD

(in French)

A thermochemical study of the titration of aluminium, iron, copper, lead, tin and antimony salts with sodium fluoride is described. The destruction of fluoride complexes by boric acid has been studied. The measurement apparatus consists of two thermistors and a bridge. Clear breaks were obtained for iron, aluminium, copper and lead but no separation of iron and aluminium was possible. The action of boric acid also gave clear breaks in the curves.

P. DESCHAMPS, A. DEBURCK AND Y. BONNAIRE,
Anal. Chim. Acta, 40 (1968) 259-267

A SIMPLE, SENSITIVE, AND SPECIFIC COLORIMETRIC ASSAY FOR DIHYDROXYUREA

A simple, sensitive and specific colorimetric assay for dihydroxyurea is described. The assay involves only 0.1 M alkali in 70% ethanol, gives a molar extinction coefficient of 6200 for dihydroxyurea, and is insensitive to hydroxamic acids, N-hydroxycarbamates, cyanate, ammonium salts, hydroxyurea, and hydroxylamine. The reaction appears to involve dihydroxyurea itself or some rapidly reversible form of the compound, presumably the dibasic anion. The assay has been used to demonstrate that dihydroxyurea is a substrate for the enzyme urease.

W. N. FISHBEIN,
Anal. Chim. Acta, 40 (1968) 269-275

EFFECTS OF γ -RADIATION ON SPECTROPHOTOMETRIC DETERMINATION OF URANIUM AS THIOCYANATE

The effects of γ -radiation on the spectrophotometric determination of uranium as the thiocyanate complex in water and acetone-water solutions have been studied. When tin(II) chloride is present, the absorbance of uranium thiocyanate in aqueous solution decreases with increasing radiation dose until the appearance of radiolytic elemental sulfur causes an apparent increase. In the absence of tin(II) chloride, the turbidity caused by radiolytic sulfur causes an increase in absorbance over the whole dose range studied. In acetone-water solution, similar but much more severe effects occur. Observations of radiation effects on some of the individual reagents used in the spectrophotometric determinations are included, as well as indications of the errors caused by specific radiation doses.

H. E. ZITTEL AND L. E. SCROGGIE,
Anal. Chim. Acta, 40 (1968) 277-283

THE SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM WITH BISMUTHIOL II AFTER SEPARATION WITH 4,4'-METHYLENEDIANTIPYRENE AND 1,1,2,2-TETRACHLOROETHANE

Tellurium can be isolated from most other elements by the extraction of its complex with 4,4'-methylene-diantipyrine into 1,1,2,2-tetrachloroethane. After isolation tellurium can be determined photometrically as its complex with bismuthiol II in chloroform. The procedure can be applied to copper and copper-based materials in the presence of many elements normally associated with copper, including selenium. The procedure is lengthy but straightforward, precise and subject to few interferences.

E. N. POLLOCK,
Anal. Chim. Acta, 40 (1968) 285-290

GLYOXIMES AS REAGENTS FOR THE GRAVIMETRIC DETERMINATION OF BISMUTH

Several oximes were investigated for possible use as organic precipitating reagents for bismuth. Of the oximes studied, nioxime (1,2-cyclohexanedionioxime) was found to be an excellent gravimetric reagent for 50-500 mg of bismuth. The precipitation of bismuth was carried out in the presence of EDTA at pH 12 in aqueous solution; EDTA was used simultaneously as a masking agent for specificity and to prevent the formation of bismuth hydroxides. Bismuth could be determined in the presence of over 30 cations including Ni and Pd. The determination of lead nioximate was briefly studied.

L. D. WIERSMA AND P. F. LOTT,
Anal. Chim. Acta, 40 (1968) 291-298

1-(*o*-CARBOXYPHENYL)-3-HYDROXY-3-PHENYLTRIAZENE,
A NEW REAGENT FOR THE DIRECT GRAVIMETRIC DETER-
MINATION OF TITANIUM(IV)

A direct gravimetric method for the determination of tita-
nium with a new reagent, 1-(*o*-carboxyphenyl)-3-hydroxy-3-phenyl-
triazene, is proposed. The titanium is precipitated at the pH range
2.0-5.0 and weighed as $\text{TiO}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3)_2$ after drying at 115-120°.
In the presence of EDTA, only niobium and tantalum interfere.

A. K. MAJUMDAR AND S. C. SAHA,
Anal. Chim. Acta, 40 (1968) 299-303

A SPECIFIC METHOD FOR THE SEPARATION OF
MERCURY(II) USING A WEAKLY BASIC CELLULOSE
ION EXCHANGER

A systematic study of the behavior of many metal ions on the
weakly basic cellulose exchanger DEAE in dilute thiocyanate media
showed that few metal ions are adsorbed. The adsorption of mercury-
(II) allows a rapid and highly selective separation from about 40 metal
ions. Quantitative results are quoted for the separation of *ca.* 100 μg
of mercury(II) from milligram amounts of other metal ions; 100 μg to
10 mg of mercury(II) can be quantitatively separated from iron(III)
in proportions of mercury(II):iron(III) = 100:1 to 1:8,000 on a
column containing only 1 g of DEAE.

R. KURODA, T. KIRIYAMA AND K. ISHIDA,
Anal. Chim. Acta, 40 (1968) 305-310

THE NATURE OF LIGHT

PART III. LIGHT AND THE SPECIAL CASE OF RELATIVITY

The Special Case of Relativity is examined. Alternative inter-
pretations are proposed for experiments which have been assumed to
prove that time flow is a variable.

J. W. ROBINSON,
Anal. Chim. Acta, 40 (1968) 311-319

A THERMOMETRIC STUDY OF THE FORMATION OF
LANTHANIDE CITRATE AND TARTRATE COMPLEXES

(in French)

Thermometric measurements make it possible to detect all
citrate and tartrate complexes of lanthanides on only one enthalpo-
gram. A suitable gradient of pH must be chosen in order to allow the
successive formation of the complexes.

J.-P. GALLET AND R. A. PÂRIS,
Anal. Chim. Acta, 40 (1968) 321-327

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF
SILICON IN PURE COPPER AND COPPER ALLOYS

(Short Communication)

P. PAKALNS,
Anal. Chim. Acta, 40 (1968) 328-329

THE DETERMINATION OF BROMINE IN THE PRESENCE OF
FLUORINE AND POSITRON EMITTERS USING FAST
NEUTRON ACTIVATION ANALYSIS

(Short Communication)

G. OLDHAM AND K. G. DARRALL,
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ANALYSIS OF VERY SMALL SAMPLES OF SULFIDE
MINERALS

(Short Communication)

J. C. VAN LOON, C. M. PARISSIS AND P. W. KINGSTON,
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GRAVIMETRIC DETERMINATION OF BISMUTH WITH
N-BENZOYL-N-PHENYLHYDROXYLAMINE

(Short Communication)

B. DAS AND S. C. SHOME,
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THE DETERMINATION OF TRACE AMOUNTS OF TOTAL
NITROGEN IN PETROLEUM DISTILLATES

(Short Communication)

A. J. SMITH, F. F. COOPER, JR., J. O. RICE AND W. C. SHANER, JR.,
Anal. Chim. Acta, 40 (1968) 341-343

GAS-LIQUID CHROMATOGRAPHIC DETERMINATION OF
PYRIDINE BASES WITHOUT TAILING EFFECTS

(Short Communication)

A. A. F. VAN DER MEEREN AND A. L. TH. VERHAAR,
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THE DETERMINATION OF CALCIUM AND MAGNESIUM IN
ACETYLENE FLAMES

(Short Communication)

T. V. RAMAKRISHNA, P. W. WEST AND J. W. ROBINSON,
Anal. Chim. Acta, 40 (1968) 347-350

SPECTROPHOTOMETRIC DETERMINATION OF COPPER

(Short Communication)

FR. C. TRUSELL AND W. F. MCKENZIE,
Anal. Chim. Acta, 40 (1968) 350-351

MICROGRAM DETERMINATION OF IODIDE BY THE USE OF
ISOTOPIC EXCHANGE

(Short Communication)

P. BERONIUS AND A.-B. GABRIELSSON,
Anal. Chim. Acta, 40 (1968) 352-354

DETERMINATION OF CALCIUM AND OXALATE WITH AN
ION-EXCHANGE ELECTRODE

(Short Communication)

A. K. MUKHERJI,
Anal. Chim. Acta, 40 (1968) 354-356

MEASUREMENT OF FLOW RATE AND PRESSURE OF GASES
IN FLAME SPECTROMETRY

(Short Communication)

J. M. MANSFIELD AND J. D. WINEFORDNER,
Anal. Chim. Acta, 40 (1968) 357-359

DETERMINATION OF NONMETALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY*

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The resonance lines for most nonmetals occur in the vacuum ultraviolet region and hence these elements do not lend themselves readily to determination by atomic absorption spectrophotometry. Those most commonly determined by direct methods are boron, silicon, arsenic, selenium, and tellurium. The sputtering technique^{1,2} has been used for the determination of carbon and phosphorus in steel³, but this method has not found wide application. GOLEB *et al.*⁴⁻⁶ have investigated this technique and have reported the near ultraviolet-visible spectra for the noble gases⁷.

Indirect determinations of nonmetals should be readily performed using conventional atomic absorption apparatus. A few such applications have been described based upon direct chemical reaction with an equivalent amount of some metal which is subsequently determined by atomic absorption spectrophotometry. Inorganic phosphate has been determined by either extracting phosphomolybdic acid⁸ or dissolving the phosphomolybdate precipitate⁹ and then determining the molybdenum content. Chloride was precipitated with silver ion, the precipitate was dissolved in ammonia and the silver was determined¹⁰. Sulfur was determined in biological materials by determining the barium in the barium sulfate precipitate¹¹. KUMAMARU *et al.* determined nitrate¹² and phthalic acid¹³ by extracting copper(I) in the presence of neocuproine.

The determination of some nonionic surfactants by complexation and atomic absorption spectrophotometry was recently described¹⁴.

A wide variety of indirect techniques has been considered here; examples of each have been investigated to determine the feasibility of obtaining a direct relationship between the atomic absorption signal and the concentration of the test substance. Both organic compounds and inorganic anions have been determined. Included are orthophosphate, sulfate, iodide, sulfide, iodate, glucose, protein, 8-hydroxyquinoline, ethylenediaminetetraacetic acid, and ammonium pyrrolidine dithiocarbamate. The high sensitivity of atomic absorption spectrophotometry allows the determination of very low concentrations of the substance.

* Presented at the 153rd National Meeting of the American Chemical Society, April 9-14, 1967, Miami Beach, Fla.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used without further purification. Deionized water was used to prepare solutions. Solutions of chelating agents were prepared fresh before use. A stock solution of the sample to be tested was prepared and aliquots of this were taken for analysis. Sulfide solutions were standardized coulometrically¹⁵ by reacting with excess of electrogenerated iodine followed by addition of excess thiosulfate which was back-titrated with electrogenerated iodine.

Apparatus

Atomic absorption measurements were made with a Jarrell-Ash Atomic Absorption Spectrophotometer Model 83-000, unless otherwise specified. Otherwise, a Perkin Elmer Atomic Absorption Spectrophotometer Model 303 was used. Scale expansion was used with both instruments for very dilute solutions. Emission measurements were made with the Jarrell-Ash instrument. The resonance lines used for absorption measurements for different metals were as follows: copper—3248 Å, calcium—4226 Å, cobalt—2406 Å, chromium—3579 Å, iron—2482 Å.

RESULTS AND DISCUSSION

In the methods studied, the test substance either limited or interfered with the amount of absorption by a particular metal in proportion to the concentration of the test substance. Several general methods were investigated and examples of each are listed under the general headings. The concentrations listed in the figures refer to the final concentration of the test substance in the aqueous solution before

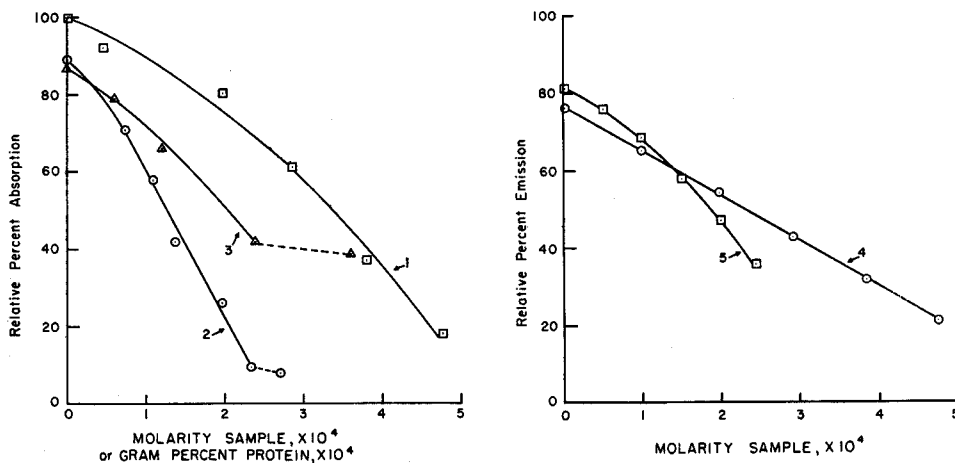


Fig. 1. (1) Effect of sulfate on absorption of calcium. $\text{Ca} = 6.25 \cdot 10^{-4} M$, final volume = 5 ml. (2) Effect of orthophosphate on absorption of calcium. $\text{Ca} = 3.75 \cdot 10^{-4} M$, final volume = 5 ml. (3) Effect of ribonuclease on calcium absorption. $\text{Ca} = 3.75 \cdot 10^{-4} M$, final volume = 5 ml.

Fig. 2. (4) Effect of sulfate on emission of calcium. $\text{Ca} = 6.25 \cdot 10^{-4} M$, final volume = 10 ml. (5) Effect of orthophosphate on emission of calcium. $\text{Ca} = 6.25 \cdot 10^{-4} M$, final volume = 10 ml.

aspiration in the flame or before solvent extraction. The final volume of the aqueous solution was kept constant for each set of analyses.

Direct chemical interference in the flame

In this method, the test substance combines with the metal in the flame and decreases the absorption.

If the substance was present in very small amount, the amount of decrease in absorption was a function of its concentration. Orthophosphate and sulfate anions present at $2.5 \cdot 10^{-4} M$ and $5 \cdot 10^{-4} M$ or less, respectively, and protein (less than $2.5 \cdot 10^{-4} g \%$) when added to $4-6 \cdot 10^{-4} M$ calcium caused a decrease in the relative per cent absorption (Fig. 1). If these concentrations were exceeded, a point was reached at which the absorption decreased to a small and nearly constant value. The limiting concentration of interfering substance could be increased by increasing the concentration of calcium. Proteins studied were glucose oxidase and ribonuclease. Essentially the same effects were found for the flame emission of calcium (Fig. 2). Sulfate caused a linear decrease in emission. The effects on emission were more reproducible. Glucose, in very small concentrations (less $10^{-6} M$) caused a marked decrease in absorption (Fig. 3, Curve 6) or emission of calcium, but as the concentration was increased above $10^{-6} M$, the absorption or emission increased and leveled

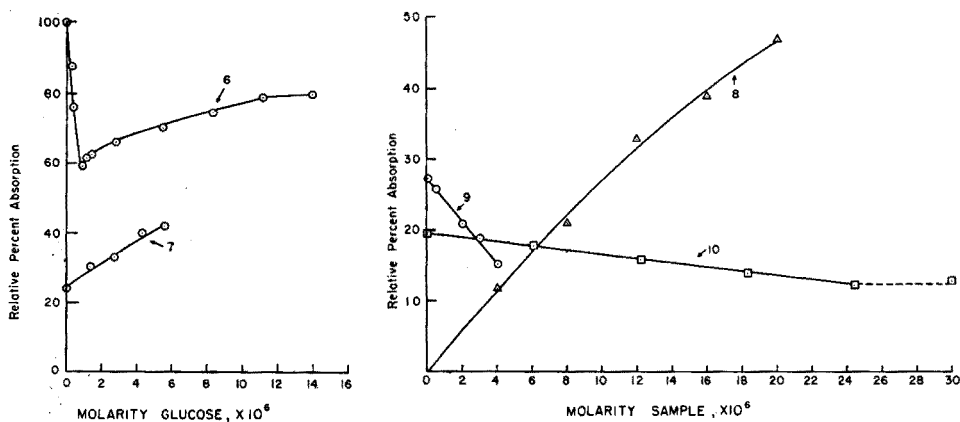


Fig. 3. (6) Effect of glucose on calcium absorption. $Ca = 6.25 \cdot 10^{-4} M$, final volume = 10 ml. (7) Effect of glucose in removing the interference of sulfate on the absorption of calcium. $Ca = 3.75 \cdot 10^{-4} M$, $SO_4^{2-} = 4.0 \cdot 10^{-4} M$, final volume = 10 ml.

Fig. 4. (8) Effect of oxine on the extraction of copper(II). $Cu = 2 \cdot 10^{-5} M$, $NH_4C_2H_3O_2 = 0.1 M$ (pH 6.5), final volume aqueous layer = 5 ml. Extracted into 5 ml MIBK. (9) Effect of EDTA on masking the extraction of copper-oxinate. $Cu = 4 \cdot 10^{-6} M$, oxine = $1 \cdot 10^{-5} M$, $NH_4C_2H_3O_2 = 0.1 M$ (pH 6.5), final volume aqueous layer = 10 ml. Extracted into 5 ml MIBK. (10) Effect of sulfide on masking the extraction of copper-oxinate. $Cu = 2.5 \cdot 10^{-5} M$, oxine = $2.5 \cdot 10^{-5} M$, $NH_4C_2H_3O_2 = 0.1 M$ (pH 6.5), final volume aqueous layer = 12.5 ml. Extracted into 5 ml MIBK.

off at about $10^{-5} M$ glucose. The glucose in the concentrations studied did not exhibit a background emission which would be detected by the d.c. system. These phenomena are not entirely understood. Small amounts of glucose appear to tie up part of the calcium or to add to suppression by some other compound formation such as perhaps with chloride (the salt of calcium used). At higher concentrations, the glucose may alleviate some of this other interference. It was expected that glucose

would eliminate sulfate interference and this was so (see below). Sucrose and EDTA appear to exhibit a physical effect in removal of chemical interference in the flame¹⁶. The observed effects of glucose are perhaps by a similar mechanism.

Small amounts of sodium interfered with both the emission and absorption of calcium, and hence the phosphate and sulfate were added as the acids. The marked effects of small amounts of these substances on calcium absorption were not observed using the Perkin-Elmer instrument with a premix burner as opposed to the Jarrell-Ash instrument with total consumption burners.

Removal of chemical interference in the flame

In this method the test substance complexes with the metal partially to eliminate a chemical interference by another substance which is added at a constant concentration. Glucose, from 10^{-6} to $5 \cdot 10^{-6}$ M, caused a linear increase in calcium absorption in a solution containing $3.75 \cdot 10^{-4}$ M calcium and $4 \cdot 10^{-4}$ M sulfate (Fig. 3, Curve 7). Physiological concentrations of protein (ca. 6 g %) are known to alleviate the interference of the small amounts of phosphate present in serum¹⁶. It was expected the same effect would be seen with the above solution of calcium and sulfate. However, in small amounts ($6 \cdot 10^{-4}$ g % ribonuclease) the protein merely added to the suppressing effect of the sulfate.

Solvent extraction of an equivalent amount of metal

Here, the test substance dissolved in either water or an organic solvent immiscible with water forms an uncharged complex with a metal ion in the aqueous layer which can be extracted into the organic solvent. The amount of metal extracted is limited by the concentration of chelating agent. The organic solvent is then aspirated into the flame and the amount of absorption is proportional to the concentration of the organic chelating agent. This is the reverse technique usually employed in solvent extraction in that an excess of metal ion is added rather than of chelating agent.

Ammonium pyrrolidine dithiocarbamate (APDC) could be determined by extracting an equivalent amount of copper or cobalt into methyl isobutyl ketone (MIBK) at pH 3. The final concentration of APDC in 5 ml of the organic layer ranged up to 10^{-5} M; 1 ml of a 1% solution of the metal ion was added to the aqueous layer. 8-Hydroxyquinoline (oxine) could be similarly determined by extracting copper into MIBK or ethyl acetate from an ammonium acetate buffer at pH 6.5; 1 ml of 10^{-4} M copper was added and the final concentration of oxine in the organic layer was 0 to $2 \cdot 10^{-5}$ M in 5 ml (Fig. 4, Curve 8). The sensitivity of the determinations in organic solvents was enhanced over those determinations performed in aqueous solution.

Masking of solvent extraction of a metal

In this technique, the test substance acts as a masking agent for the extraction of a metal-chelate. The decrease in absorption by the extracted metal is proportional to the test substance present in the aqueous layer.

Ethylenediaminetetraacetic acid (EDTA) forms a charged complex with copper and thereby masks the extraction of the copper-oxinate complex into MIBK at pH 6.5. A 4-ml aliquot of 10^{-5} M copper and 1 ml of 10^{-4} M oxine were added to the aqueous layer to give a solution with a slight excess of oxine. The amount of EDTA

added was 0.2 ml of a $2 \cdot 10^{-5} M$ solution (Fig. 4, Curve 9). At higher concentrations of EDTA, the linear decrease in absorption leveled off.

Sulfide up to $3 \cdot 10^{-4}$ mmole effectively masked the extraction of a proportionate amount of copper-oxinate ($3.1 \cdot 10^{-4}$ mmole copper) (Fig. 4, Curve 10). Direct aspiration of an aqueous solution of copper to which sulfide had been added gave the same absorption as when sulfide was absent. Thus, the copper sulfide precipitate was decomposed in the flame.

In these methods, the test substance must form a more stable compound with the metal than does the extracting agent.

Reduction or oxidation of a metal and solvent extraction of the oxidized or reduced form

Reducing and oxidizing agents can be determined in this manner. The equivalent amount of metal reduced or oxidized in either the organic or aqueous layer can be determined; alternatively, the excess of unreacted metal can be determined.

Iodide was determined by reacting $0.5 \cdot 10^{-3}$ meq with $3 \cdot 10^{-3}$ meq of chromium(VI) in acid solution. The excess chromium(VI) was extracted from 3 M hydrochloric acid into MIBK. The absorption due to chromium(III) in the aqueous layer increased linearly and that due to unreacted chromium(VI) in the MIBK layer decreased linearly with increasing amounts of iodide (Fig. 5, Curves 11 and 12)

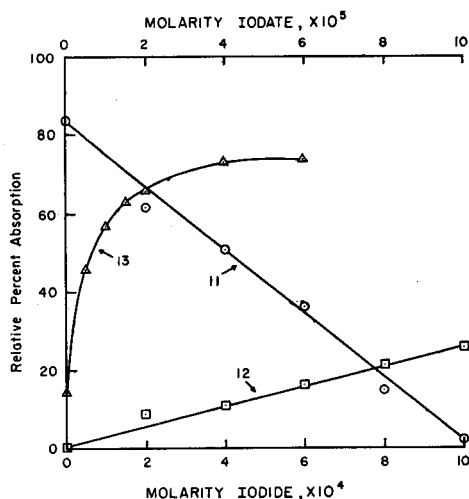


Fig. 5. (11) Effect of iodide on the amount of chromium(VI) extracted into MIBK. Starting $Cr(VI) = 2 \cdot 10^{-4} M$ ($6 \cdot 10^{-4} N$), final volume aqueous layer = 5 ml. Extracted into 5 ml MIBK from 3 M HCl. (12) Effect of iodide on the amount of chromium(III) produced from chromium(VI) and remaining in the aqueous layer after extraction with MIBK. Conditions same as for (11). (13) Effect of iodate on the oxidation of iron(II) with extraction of the iron(III) into diethyl ether. Iron(II) — $2 \cdot 10^{-4} M$, HCl = 9 M, final volume aqueous layer = 10 ml. Extracted into 10 ml ether.

The iodide-chromium(VI) reaction was kinetically slow in these very dilute solutions and did not go to completion.

Iodate ($0.3 \cdot 10^{-3}$ meq) was determined by oxidizing $2 \cdot 10^{-3}$ meq of iron(II) in acid, followed by extraction of the iron(III) from 9 M hydrochloric acid into ether. The per cent absorption of the extracted iron(III) increased logarithmically

with increasing amounts of iodate. It was necessary to deaerate all solutions with nitrogen to prevent air oxidation of iron(II). The marked curvature of the absorption curve is characteristic of iron absorption.

Precipitation of an equivalent amount of metal

The precipitate can be dissolved and the amount of metal determined or the amount of unprecipitated metal in the filtrate can be analyzed.

Reducing agents can be determined by reducing selenium(IV) to the element and filtering the red selenium on Millipore filters. As little as 0.2 μg of selenium can be collected quantitatively on these filters^{17,18}. Iodide, up to 10^{-3} mmole, was reacted with a slight excess of selenium(IV) in acid solution and the decrease in the absorption of the filtrate after filtering was proportional to the amount of iodide taken.

In the determination of chloride¹⁰, sulfur¹¹, and phosphorus⁹, a slightly soluble metal salt was precipitated and the amount of metal in the precipitate was determined.

The present work has demonstrated that direct relationships can be obtained between absorption by a metal and the amount of substance sought by means of several different methods. The principal source of error in these methods is the lack of specificity in the chemical reaction. By selective choice of the chemical reaction, this problem can be reduced or overcome. Very small amounts of nonmetals can be determined using atomic absorption spectrophotometry. The formation of a colored solution is not required.

SUMMARY

Inorganic anions and organic compounds are determined using conventional atomic absorption apparatus. Several methods are studied in which the desired compound either limits or interferes with the determination or absorption of a metal. A direct relationship is obtained between the absorption by the metal and the amount of substance sought. Substances determined include orthophosphate, sulfate, iodide, sulfide, iodate, glucose, protein, 8-hydroxyquinoline, ethylenediaminetetraacetic acid, and ammonium pyrrolidine dithiocarbamate.

RÉSUMÉ

Des anions inorganiques et des composés organiques sont dosés à l'aide d'un appareil conventionnel par absorption atomique. Plusieurs méthodes sont examinées, dans lesquelles la substance à analyser limite ou gêne le dosage ou l'absorption d'un métal. Les composés ainsi dosés comprennent: orthophosphate, sulfate, iodure, sulfure, iodate, glucose, protéine, hydroxy-8-quinoléine, acide éthylènediaminotétracétique et ammonium pyrrolidine dithiocarbamate.

ZUSAMMENFASSUNG

Anorganische Anionen und organische Verbindungen werden mit Hilfe einer konventionellen Flammenabsorptionsapparatur bestimmt. Verschiedene Methoden werden untersucht, bei denen die gewünschten Verbindung entweder begrenzt oder

gestört wird bei der Bestimmung oder Absorption eines Metalls. Eine direkte Beziehung wird zwischen der Absorption des Metalls und dem Gehalt der gesuchten Substanz gefunden. Folgende Substanzen werden bestimmt: Orthophosphat, Sulfat, Jodid, Sulfid, Jodat, Glucose, Protein, 8-Oxychinolin, Äthylendiamintetraessigsäure und Ammoniumpyrrolidindithiocarbamat.

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AN ULTRASONIC ATOMISER APPLIED TO ATOMIC ABSORPTION SPECTROPHOTOMETRY

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The application of ultrasonic atomisers to flame photometry and atomic absorption spectrophotometry has been discussed by several authors¹⁻⁵ in recent years. The advantages to be gained, in terms of increased sensitivity and lower sample consumption, have been experimentally demonstrated for flame emission analysis, in particular, but in the case of flame absorption analysis the advantages have been inferred, rather than illustrated, with the exception of the work of WENDT AND FASSEL⁴, who were also, however, using an induction-coupled plasma source in their equipment.

We have recently investigated the more general case in which the pneumatic atomiser of a standard commercial atomic absorption spectrophotometer is replaced by an ultrasonic atomiser, the remainder of the apparatus being unchanged. The merits of the two systems have been examined in respect of sample consumption and analytical performance generally.

EXPERIMENTAL

Apparatus

The ultrasonic atomiser used in these experiments was basically of the type described originally by WEST AND HUME², later used by WENDT AND FASSEL^{3,4} and more recently re-designed by two of the present authors as a multicell vessel for spectrographic analysis⁶. In the work described here a further modification has been made to the transducer head assembly to reduce power losses. The ultrasonic beam is transmitted from the brass surface through a thin lead sheet (0.003" thickness) and a perspex (polymethylmethacrylate) lens to the water bath and the solution in the sample container. Authors such as ERNST⁷ and CARLIN⁸ have shown that, in ultrasonics technology, the choice and manner of assembly of the transmitting media are vital to the efficiency of the system. Thus, neglecting attenuation and scattering, the energy loss of the original brass-Canada balsam-epoxy resin-water sequence⁶ was 86%, which is the same as for a simple brass-water boundary. For the brass-lead-polymethylmethacrylate-water system, however, the overall loss is reduced to about 70%, *i.e.* the transmitted energy has more than doubled. Air must be excluded, since an air boundary with any of these materials gives essentially total reflection loss. This change in design has given an increase in total solution consumption from 0.2 to 0.4-0.5 ml/min.

The sample mist was introduced to the burner chamber of a standard Perkin-

Elmer Model 303 spectrophotometer, fitted with a 10-cm air-acetylene burner head and modified by replacement of the normal baffle plates by a similar unit made in glass, with a hollow stem for passage of the aerosol. The experimental arrangement is shown diagrammatically in Fig. 1, together with the constant-head cell mentioned later. For convenience, the pneumatic atomiser was left in the atomiser air supply line, to maintain the back-pressure conditions of the normal operating arrangement.

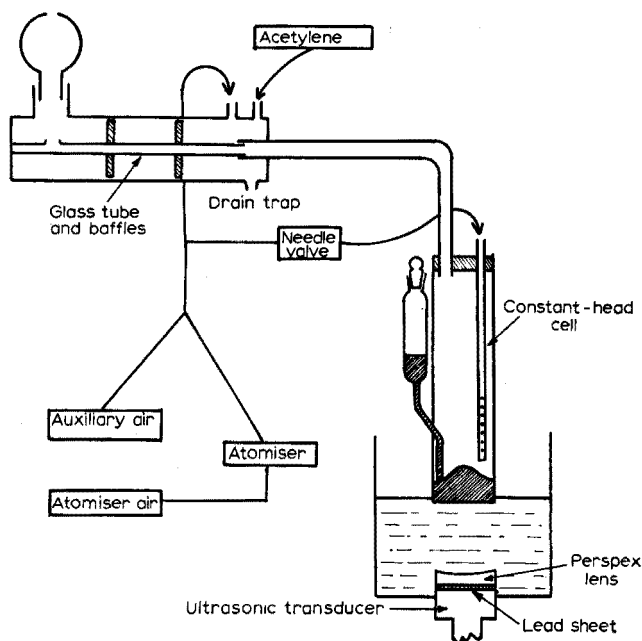


Fig. 1. Experimental arrangement.

TABLE I

COMPARISON OF ULTRASONIC AND PNEUMATIC ATOMISER EFFICIENCIES

	<i>Atomiser</i>	
	<i>Ultrasonic</i>	<i>Pneumatic</i>
Total spraying time (min)	10	10.5
Total volume consumed (ml)	5.5	40
Volume lost (ml)	1.4	34
Volume reaching flame (ml)	4.1	6
Sample used in flame (ml/min)	0.41	0.57
Efficiency (%)	75	15

Sample consumption

For each atomiser, measurements were made to determine the proportion of the sample solution actually reaching the flame. A known volume of solution was atomised for a known time and the volume retained in the burner chamber plus the volume expelled from the drainage tube was carefully measured. The remainder was taken to be the amount consumed in the flame, which was operated at normal gas pressures during the tests. The results (Table I) showed clearly that the efficiency of

the ultrasonic system was much higher than that of the pneumatic system. On the other hand, the quantity of sample solution producing the analytical measurement in the flame was of the same order in the two cases.

Absorbance measurements

To test the performance of the two atomisers in analytical work, comparative absorbance measurements were made on standard solutions of various elements, all other instrument parameters being kept constant during any one comparison, but varied to suit the particular element⁹. Table II summarizes the results of these experiments.

TABLE II

COMPARISON OF ABSORBANCES WITH ULTRASONIC AND PNEUMATIC ATOMISERS

Element	Wavelength (nm)	Concentration (p.p.m.)	Absorbance	
			Ultrasonic atomiser ^a	Pneumatic atomiser ^b
Ba	554	100	0.097	0.110
Ca	423	10	0.197	0.241
Co	241	10	0.131	0.127
Cr	358	4	0.077	0.090
Cu	325	2	0.051	0.054
Fe	248	10	0.125	0.130
Hg	254	100	0.047	0.057
K	766	2	0.089	0.100
Mg	285	0.4	0.127	0.122
Mn	280	2	0.049	0.065
Na	589	0.5	0.078	0.084
Ni	232	10	0.125	0.143
Pb	283	20	0.081	0.093
Sr	461	4	0.097	0.093

^a Sample consumption in flame = 0.41 ml/min.

^b Sample consumption in flame = 0.57 ml/min.

Uniformity of spray production

Consistent operation of the ultrasonic nebulizer depends upon focusing the beam reproducibly on the sample solution. Although the geometry of the system can be arranged quite rigidly, the solution is violently agitated within the cell and tests were made to assess the uniformity of aerosol production during the course of an analytical measurement. It was found that the quantity of mist produced, did in fact, tend to decrease as the level in the sample container fell, but the effect was slow and would not be detectable during a normal absorbance measurement occupying up to say 30 sec. That the effect exists can be demonstrated by means of a constant-head tube, fitted to the sample vessel as shown in Fig. 1. With this modification, the rate of aerosol production, as monitored by the absorbance reading, remains constant over a similar period of operation. The pneumatic atomiser has shown no significant dependence upon the sample solution level.

A more significant difference, analytically, between the two methods of spray production was revealed, however, by these experiments. It was clear that the

pneumatic atomiser gave a more uniform feed to the burner than the ultrasonic atomiser, the latter tending to produce a pulsating stream of mist and hence a more variable read-out. This is essentially a design problem. Figure 2 shows absorption records on a standard manganese solution, to illustrate these effects.

Droplet size

The nature of the aerosols produced by the two atomisers was examined by the technique of collecting a sample on a glass microscope slide coated with a film of

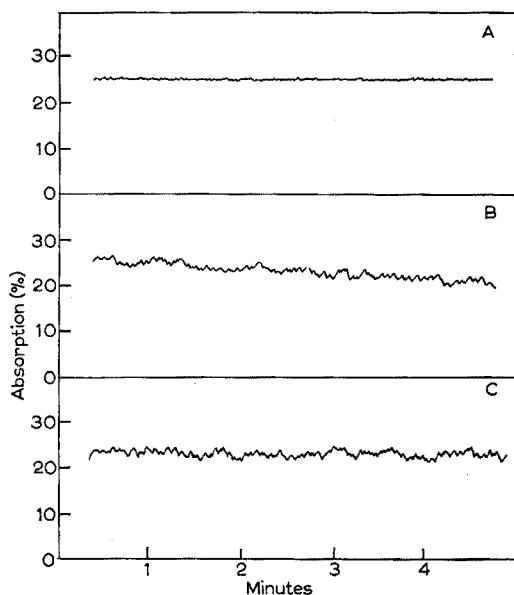


Fig. 2. Absorption records for 4 p.p.m. Mn soln. (A) Pneumatic atomiser; (B) ultrasonic atomiser; (C) ultrasonic atomiser with constant-head cell.

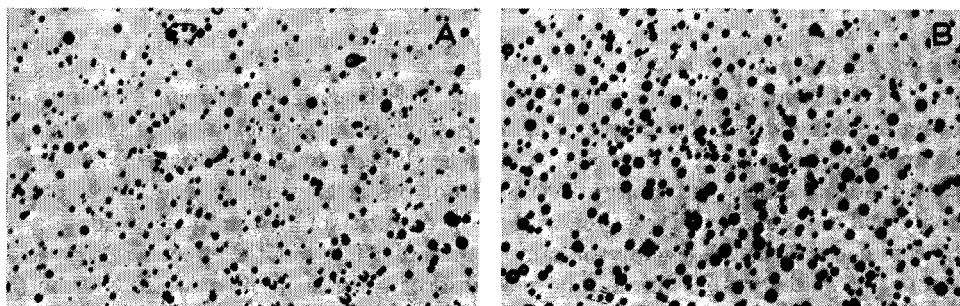


Fig. 3. Photomicrographs of aerosol droplets. Magnification $\times 150$. (A) Pneumatic atomiser; (B) ultrasonic atomiser.

mineral oil^{10,11}. The samples were taken immediately above the central one-inch portion of the burner slot, with the flame and atomiser gas supplies feeding normally but not ignited. The slide was at once covered with a second oil-coated slide and the droplets, so trapped, showed no tendency to evaporate, disperse or coalesce for several

minutes. Thus, time was available for a visual examination of the droplet pattern or for photomicrographs as shown in Fig. 3, to be prepared. Several slides were taken with each atomiser, photographed immediately at $150\times$ magnification, and droplet diameter measurements carried out. The results, summarized in Table III, showed that the average droplet diameter produced at the burner slot was very similar in each case. The difference in the distribution pattern of the droplet sizes was consistent throughout several counts; in all, 250 droplet diameters were measured for each atomiser. It is clear that in the pneumatic system, the larger droplets are very effectively removed by the baffles of the mixing chambers.

TABLE III
COMPARISON OF AEROSOL DROPLET DIAMETERS

Droplet diameter ^a (μ)	Atomiser	
	Pneumatic (%)	Ultrasonic (%)
3 and below	35.4	39.5
4-6	55.4	33.5
7-9	7.4	20.6
10-12	0.9	6.0
13 and above	0.9	0.4

^a Diameters were measured to nearest $1\ \mu$. The respective weighted mean diameters were $4.1\ \mu$ (pneumatic) and $5.0\ \mu$ (ultrasonic).

DISCUSSION

This work has generally confirmed the expectations of other authors. The ultrasonic atomiser is very efficient in the sense that a much greater proportion of the sample can be utilised in the flame and hence the same sensitivity as that given by the standard pneumatic atomiser can be achieved on a smaller sample volume. The system described here enables several readings to be obtained on as little as 2 ml of sample and this could undoubtedly be improved by a design study on an integral atomiser-burner unit.

The absorbance measurements given by the two atomisers on various standard solutions are, in general, in close relation to the respective rates of sample consumption. The droplet size measurements indicate that there is no great difference in the nature of the sprays reaching the flame and, for absorption work, the real merit of the ultrasonic atomiser is that the spray can be fed more directly to the flame. It is realised that there may be inaccuracies in the technique used for measurement of the droplets but the method gives a direct comparison between the two and the mean diameter found for the ultrasonic mist droplets, 5 microns, agrees with the value quoted by WENDT AND FASSEL³.

Considerable scope for improvement of the experimental equipment remains. To obtain a useful gain in sensitivity over existing pneumatic systems it is necessary to increase the sample consumption rate of the ultrasonic atomiser; this requires further study to determine the optimum conditions for the ultrasonic generator frequency, transmission of the ultrasonic energy to the sample, design of sample container and injection of aerosol into the flame.

SUMMARY

An ultrasonic atomiser has been attached to a commercial atomic absorption spectrophotometer and a comparison made between the performance of ultrasonic and pneumatic atomisers in respect of sample consumption, absorbance measurements, stability and droplet size. The principal finding is that, with the ultrasonic atomiser, the same sensitivity as given by a standard pneumatic atomiser can be achieved on a considerably smaller sample volume. Further improvements in the technique should be possible.

RÉSUMÉ

Un atomiseur ultrasonique a été appliqué à un spectrophotomètre par absorption atomique; une comparaison est effectuée avec un atomiseur pneumatique, en ce qui concerne consommation de l'échantillon, mesures d'absorption, stabilité et dimension des gouttelettes. Les sensibilités sont les mêmes, mais l'atomiseur ultrasonique consomme un volume considérablement plus faible de solution à analyser. Des améliorations peuvent encore être réalisées.

ZUSAMMENFASSUNG

Ein Ultraschallzerstäuber wurde mit einem kommerziellen Flammenabsorptionsspektralphotometer verknüpft und Vergleiche mit dem pneumatischen Zerstäuber in Bezug auf den Probenverbrauch, die Absorptionsmessung, die Stabilität und die Tröpfchengröße angestellt. Grundsätzlich ergab sich, dass mit dem Ultraschallzerstäuber dieselbe Empfindlichkeit erreicht werden kann, jedoch bei einem beträchtlich kleineren Probenvolumen. Weitere Verbesserungen dieser Technik sollten möglich sein.

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THE DETERMINATION OF TRACE ELEMENTS IN SULPHIDE MINERALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY WITH ABSORPTION TUBES

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For studies of ore veins determinations of trace elements in different sulphide minerals are needed. Emission spectrographic analysis is often used, but the application of atomic absorption may bring several advantages. Although the analysis is then somewhat more laborious, the precision and accuracy are considerably increased and the analysis of different minerals presents no problem of bias as it often does in spectrochemical emission analysis.

In this laboratory, silver, zinc, cadmium, copper and lead are determined routinely mostly in galena and sphalerite, but also in some other sulphide minerals (tetrahedrite, pyrite, antimonite, sulphantimonate, cinnabarite). In many instances, the content of trace elements is high enough for determination with a 10-cm burner but for very low concentrations the sensitivity is often insufficient. In these cases absorption tubes may be used to enhance the sensitivity of determination.

Absorption tubes have been so far applied for direct determinations of zinc in blood¹, lead in gasoline², tin in peroxide³ and iron in tetraphenyl reactor coolant⁴. These analyses were performed by spraying the samples directly or after appropriate dilution into the flame. Samples with high salt content have been analysed only after separation of the element to be determined, mostly by extraction. Thus ŠTUPAR determined cobalt, iron, copper and lead in drinking water and plant material and copper, cobalt, lead and cadmium in uranium⁵.

The measurements of samples with high salt content are likely to be influenced either by molecular absorption or by light scattering by the unevaporated salt particles^{6,7}. Because of the considerably longer absorption path and the relatively low temperature light scattering is a much greater danger with absorption tubes than with the more usual burners⁸.

Sulphide minerals may be decomposed without the formation of excessive amounts of salts. Moreover all the salts formed, with the exception of iron from pyrite, are volatile and easily dissociated so that the danger of molecular absorption or light scattering is relatively low.

EXPERIMENTAL

Apparatus

A Perkin-Elmer 303 atomic absorption spectrophotometer was used for the measurements in a 10-cm flame. The equipment with absorption tubes consisted of a

Zeiss SPM-1 monochromator with an RCA 1P28 photomultiplier on the exit slit. The anodic current was measured with a galvanometer or a recorder.

The arrangement of the absorption tubes is shown in Fig. 1. Heat-resistant ceramic tubes of 17 mm inner diameter, 45 cm long, were placed in the optical axis and heated in an electric furnace. A total consumption burner supplied with hydrogen and air was used. It was tilted some 30 degrees from the vertical position so that the flame entered the tube, one end of which was cut askew. The monochromator slit was protected by a stream of air.

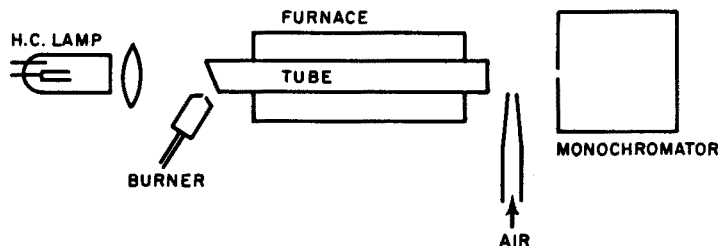


Fig. 1. Schematic arrangement of equipment with absorption tubes.

Hollow-cathode lamps from different manufacturers were used; copper, lead and cadmium lamps were from Hilger and Watts, a zinc lamp from Perkin-Elmer and the silver lamp was laboratory-made.

Reagents

The samples were decomposed simply by dissolution in acids. When silver had to be determined simultaneously, hydrochloric acid could not be used. Sulphuric acid caused a high background absorption below 250 nm, and so was avoided as far as possible. Mostly nitric acid was used with addition of tartaric acid to hinder the precipitation of antimonite and bismuthic acids from samples containing these elements.

All reagents were analytical grade. It is advantageous to use high-purity nitric acid and redistilled water because of possible chloride ion impurities in the analytical-grade specimens. However, these may be blocked by adding mercury(II) nitrate to the solutions⁹.

Standard solutions

Stock solutions of the elements determined were prepared by dissolving 1 g of the particular metals in nitric acid and diluting to 1 l with distilled water. Mercury(II) nitrate was added to the silver stock solution. The standard solutions were prepared by dilution and addition of the same amount of acids as in the samples. Two sets of standard solutions were prepared: one set for the samples decomposed by nitric acid (contained 6 ml of nitric and 1 g of tartaric acid per 100 ml) and the second set contained 4 ml of sulphuric acid and, again, 1 g of tartaric acid. All standard solutions contained 30 mg Hg as mercury(II) nitrate.

Use of absorption tubes

Work with absorption tubes has several special features which should be

briefly mentioned. Approximately 1 hour before the measurements are started, the electric furnace is switched on. A steady state is thus reached shortly after the flame has been lighted. The right fuel pressure must then be set experimentally by measuring the absorption of the particular element. The appropriate dependences for silver, lead and cadmium are shown in Fig. 2. The optimum pressure depends not only on the element determined but also on the tube diameter and the exact burner position¹⁰. The more the burner is tilted, the more atmospheric air is entrained into the tube and the higher the necessary fuel flow.

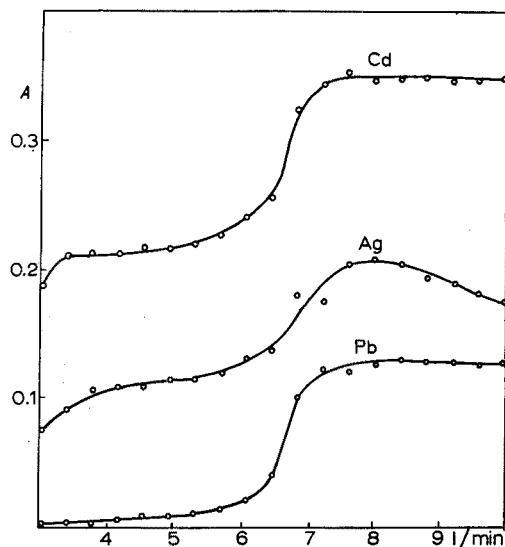


Fig. 2. The effect of hydrogen flow on the absorbance in absorption tubes. Air flow 2.5 l/min.

Another nuisance in working with absorption tubes is their memory effect. After solutions with high concentrations of the required element have been aspirated, the tube must be cleaned by spraying pure solvent, or even dilute acids for some time. This memory effect particularly influences determinations of low concentrations.

The memory effect of the elements determined increases with decreasing vapour pressure of the element, *i.e.* in the order Cd, Pb, Ag. For cadmium, the memory effect is so small that a 100% transmission value is reached almost immediately after the appropriate solution has ceased to be sprayed. For silver and lead, several minutes may be needed. Separate tubes, therefore, had to be used for the analysis of different minerals. For example, lead cannot be determined with a tube which has been used formerly for the analysis of galena.

Background absorption

Background absorption was investigated by scanning the spectrum of a hydrogen lamp in the relevant wavelength region. A considerable background absorption was found for samples decomposed by sulphuric acid (Fig. 3), probably because of the molecular spectrum of sulphur dioxide formed in the flame. This effect

may be corrected for by using standard solutions containing the same amount of sulphuric acid or by subtracting the absorbance due to background absorption measured on some close non-resonance line from the absorbance of the element determined. In the case of lead, sulphuric acid has also a slight depressive effect (Fig. 4).

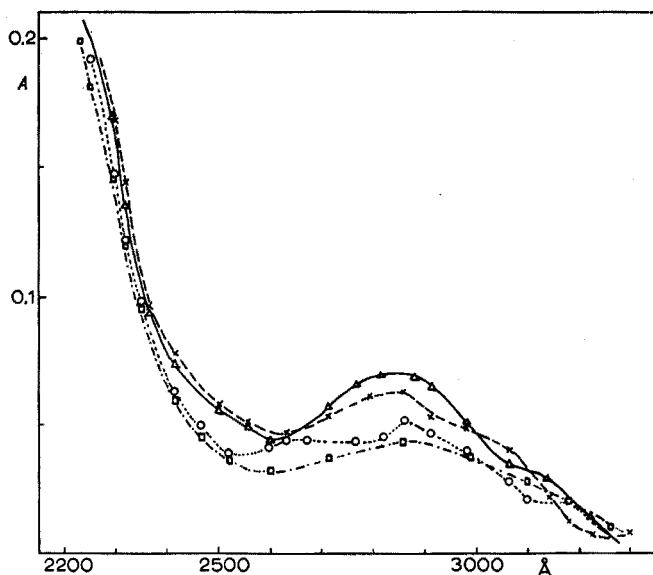


Fig. 3. Background absorption caused by sulphate present in the solution (4 ml $H_2SO_4/100$ ml (Δ)). Part of the sulphate added is lost by precipitation of lead sulphate (tetrahedrite (\square)) or by fuming off during decomposition (cinnabarite (\circ)). (\times) Pyrite.

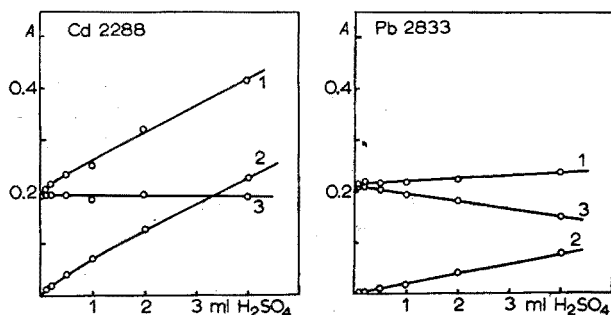


Fig. 4. The effect of sulphuric acid on the absorbance of cadmium and lead. (1) absorbance measured with the analytical line; (2) background absorbance; (3) after correction.

The samples decomposed by nitric acid had no or only a slight background absorption. Antimonite exhibited a background due to Sb_2 molecules whereas pyrite had a monotonous background, probably because of light scattering by unevaporated iron oxide particles.

The analytical lines and the lines used for light scattering corrections are listed in Table I. For cadmium no line other than a resonance line of the cadmium

ion could be found in the proximity of the analytical line—228.8 nm. Because of the very high ionization energy of the cadmium atom, no absorption of the ion line used has been measured, even with the highest cadmium standard solution.

Recommended procedure

Decomposition with nitric and tartaric acids (galena, sphalerite, chalkopyrite, sulphantimonate, pyrite, tetrahedrite). To 0.1–0.3 g of powdered mineral, add 10 ml of 10% tartaric acid solution and 6 ml of concentrated nitric acid, and leave standing

TABLE I

ANALYTICAL LINES AND LINES USED FOR CORRECTION OF BACKGROUND ABSORPTION

<i>Element</i>	<i>Analytical line (Å)</i>	<i>Line for correction (Å)</i>
Cd	2288	CdII 2265
Pb	2833	Pb 2802
Ag	3281	A 3319

at room temperature overnight. Then heat on a steam bath for 2–3 h until the sulphur turns white. Wash the undissolved residue and sulphur formed twice by decantation, filter and wash thoroughly with redistilled water. Collect the filtrate in a 100-ml measuring flask.

If the nitric acid used is not high-purity grade, it may contain chloride impurities and some silver may be adsorbed as silver chloride on the undissolved residue. To avoid this, mercury(II) nitrate should be added¹⁰ after the samples have been warmed on the steam bath for about 1 h. No mercury addition is necessary with tetrahedrites which contain enough mercury themselves.

Decomposition with sulphuric acid (antimonite). Dissolve 0.1–0.3 g of powdered sample in a small Erlenmeyer flask with 4 ml of concentrated sulphuric acid. The mineral dissolves within 10 min on boiling. After cooling, dissolve the salts in 10 ml of the tartaric acid solution and transfer to a 100-ml measuring flask.

Cinnabarite. Boil 0.1–0.3 g of powdered sample with 4 ml of concentrated sulphuric acid, adding several drops of fuming nitric acid from time to time until the sample has completely decomposed. This may be easily recognized because the originally red sample turns yellow-white, which indicates the formation of mercury sulphate. Boil to white fumes of sulphur trioxide, then cool and transfer to a 100-ml measuring flask. Add tartaric acid and fill up with distilled water, whereupon mercury sulphate dissolves.

The samples are then ready for measurement. They may have some undissolved residue, mostly silica. However, it has been verified that its content of the elements determined is negligible. For samples decomposed by nitric or sulphuric acids respectively, the appropriate standard solutions are used.

The concentration intervals measured with the conventional 10-cm burner and with absorption tubes are given in Table II.

The measuring procedure

The furnace should be switched on an hour before starting the measurement.

After the flame has been lighted and the burner position adjusted, the optimal gas flow must be found by measuring the absorption of a standard solution and setting the fuel pressure to secure the highest absorption. The standard solutions and the samples are then measured and the absorbance values corrected for possible background absorption. The calibration curve method is used for evaluation.

TABLE II

ANALYTICAL LINES AND CONCENTRATION INTERVALS MEASURED WITH A 10-CM BURNER AND WITH ABSORPTION TUBES

Element	Line (\AA)	Concentration interval ($\mu\text{g/ml}$)	
		Absorption tube	10-cm burner
Cu	3247	—	0.1–12
Zn	2138	—	0.1–10
Cd	2288	0.002–0.2	0.2–15
Ag	3281	0.005–0.4	0.1–15
Pb	2833	0.05–6	5–100

RESULTS AND DISCUSSION

The sensitivity of the determination and the corresponding lowest concentration in the sample which may be estimated are given in Table III. For silver and cadmium the sensitivity is about 10 times better than the detection limits reported for a 10-cm acetylene air flame. For lead, the enhancement factor is only three. The enhancement compared with the conventional 10-cm burner can be ascribed not only to the increase in the absorption path length but also to elimination of solution losses in the cloud chamber.

TABLE III

SENSITIVITIES ATTAINED WITH ABSORPTION TUBES

Element	Sensitivity	
	in solution (p.p.m./1%)	in sample (%)
Cd	0.001	$3 \cdot 10^{-5}$
Ag	0.003	$1 \cdot 10^{-4}$
Pb	0.05	$1.7 \cdot 10^{-3}$

On the other hand, the precision of the determination with absorption tubes is somewhat poorer than with the conventional flame. The conditions of successive measurements are more liable to deviate from one another and if appropriate care is not taken, the memory effect is likely to influence the determination of extremely low concentrations. Moreover, background absorption which causes a high blank value, decreases the precision of determination at very low concentration levels. Relative deviations of 8% for lead, 7.3% for silver and 6% for cadmium were calculated from 15 replicate measurements.

To test the accuracy, samples with known higher contents were analysed after appropriate dilution. The dilution itself has no influence on the determination

of cadmium and silver, but the lead content found increases, probably owing to traces of sulphates formed during decomposition of the sample (see Table IV). For lead, therefore, a small negative bias (up to 10%) was found in some samples. The atomic absorption analyses of samples with higher Zn, Cu and Cd content were found to be in excellent agreement with polarographic results.

TABLE IV

THE EFFECT OF DILUTING SAMPLE SOLUTIONS ON THE RESULTS WITH ABSORPTION TUBES

<i>mg of sample in 1 ml</i>	<i>Content found (%)^a</i>	
	<i>Ag</i>	<i>Pb</i>
1.5	0.087 ₃	0.070 ₀
0.9	0.090 ₄	0.073 ₃
0.6	0.088 ₆	0.075 ₀
0.45	0.087 ₃	0.077 ₃
0.3	0.085 ₃	0.076 ₆

^a In original sample.

TABLE V

THE RESULTS OF ANALYSES USING DIFFERENT DECOMPOSITION OF THE SAMPLES

<i>Mineral</i>	<i>Acids used</i>	<i>Content found (%)</i>				
		<i>Zn</i>	<i>Cd</i>	<i>Pb</i>	<i>Cu</i>	<i>Ag</i>
Cinnabarite	H ₂ SO ₄	1.33	0.096	0.11	0.074	0.00045
	HNO ₃ + HCl	1.29	0.10	0.11	0.077	—
Pyrite	H ₂ SO ₄	0.45	0.024	0.12	0.40	0.0011
	HNO ₃ + HCl	0.44	0.024	0.14	0.40	—
Antimonite	H ₂ SO ₄	0.14	0.0016	0.22	0.009	0.009
	HNO ₃ + HCl	0.15	0.0012	0.20	0.010	—
Bournonite	HNO ₃	0.18	0.0025	—	—	0.091
	HNO ₃ + HCl	0.17	0.0024	—	—	—
Sphalerite	HNO ₃	—	0.82	0.041	0.066	0.02
	HNO ₃ + HCl	—	0.90	0.042	0.064	—
Sphalerite	HNO ₃	—	0.38	0.095	0.087	0.00063
	HNO ₃ + HCl	—	0.39	0.10	0.090	—

The decomposition of the samples was checked by comparing the contents found after decomposition with the recommended acids and with the generally used nitric and hydrochloric acids. The results are given in Table V. All differences are in the range of the analytical error.

The method described allows a rather easy estimation of trace elements in sulphide and even some other minerals (selenides), after a simple dissolution of the specimen in acids. The use of absorption tubes enhances the sensitivity of the determinations considerably, so that the sample solutions may be sprayed directly into the flame even for the lowest concentrations so far encountered.

SUMMARY

A method for the determination of minor and trace elements (Zn, Cd, Pb, Cu and Ag) in sulphide minerals by atomic absorption spectrophotometry is described. For enhancing the sensitivity of the determination, the absorption tube technique is applied. Memory effects and background absorption influences on the measurement with absorption tubes are discussed.

RÉSUMÉ

On décrit une méthode pour le dosage de traces des éléments: Zn, Cd, Pb, Cu et Ag dans les sulfures, par spectrophotométrie par absorption atomique. On utilise la technique avec tubes d'absorption pour améliorer la sensibilité du dosage.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von kleinen Gehalten und Spuren (Zn, Cd, Pb, Cu und Ag) in sulfidischen Mineralien mittels der Flammenabsorptionsanalyse beschrieben. Zur Steigerung der Empfindlichkeit werden Absorptionslampen verwendet. Memory-Effekte und Untergrundabsorptionseinflüsse auf die Messung mit Absorptionslampen werden diskutiert.

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ATOMIC FLUORESCENCE FLAME SPECTROMETRY USING A MERCURY LINE SOURCE

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The feasibility of atomic fluorescence spectrometry as a means of chemical analysis has been described by WINEFORDNER AND VICKERS¹. Theoretical considerations have been discussed and equations derived relating the fluorescent emission intensity to atomic concentration. The attractive possibilities of using this new technique were fully confirmed by the subsequent works of WINEFORDNER *et al.*²⁻⁴. Extremely low limiting detectable concentrations are reported.

The apparatus used by these authors consists of an intense source of radiation (Osram or Philips discharge lamps and electrodeless discharge tubes) which is focussed with a lens on an air-H₂ or O₂-H₂ flame of a Beckman burner. The fluorescence radiation is analyzed at 90° in respect of the excitation source by a monochromator and measured by a photomultiplier coupled with a high gain d.c. amplifier.

Noticeable improvements were obtained by the proper optimization of the intensity of the source in order to avoid the self-reversal of the exciting line, and by the use of a baffle-box which was effective in excluding stray radiation from the entrance slit of the monochromator. Moreover, in a recent work, VEILLON *et al.*⁵ have extended the field of atomic fluorescence by using a xenon 150 W continuum source and a new type of flame, the argon-H₂-entrained air flame. Much better signal-to-noise ratios were obtained and low limits of detection were reported for 13 elements.

Although many parameters have been investigated, little has been done in order to improve optics. The proper choice of a suitable arrangement of lenses and mirrors would be one of the most important parameters in atomic fluorescence. Thus, the optimization of optics was carefully investigated in this laboratory rather than the choice of sources and flame conditions.

The purpose of this communication is to present a simple adaptation for a Jarrell-Ash atomic absorption spectrometer to the measurement of atomic fluorescence and the first results obtained with this arrangement.

EXPERIMENTAL

Figure 1 shows a block diagram of the apparatus and Table I summarizes its specific components.

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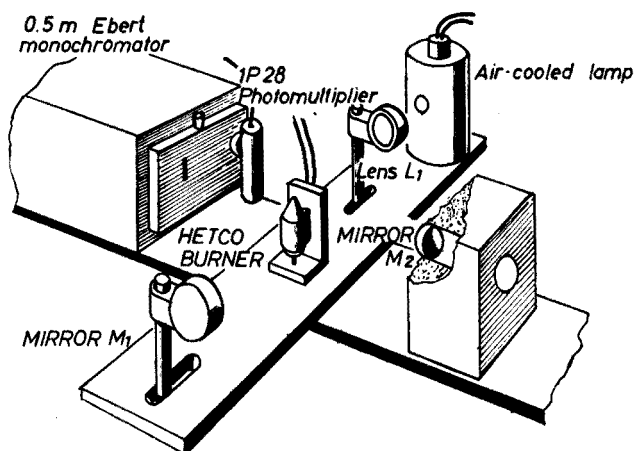


Fig. 1. Block diagram of the apparatus.

TABLE I

Excitation source	Philips metal vapor discharge lamps air-cooled with outer quartz envelope, Cd 25 W, Zn 25 W, Hg 90 W. Hollow cathode lamps—Westinghouse
Optics	Spherical quartz lens 6.5 cm focal length, 10-cm focal length concave quartz mirror.
Monochromator	Jarrell-Ash 0.5-m Ebert grating monochromator equipped with a 1250 lines/mm grating blazed at 3000 Å and variable slits
Detector and associated electronics	RCA 1P28 photomultiplier (2000–5000 Å). Regulated Jarrell-Ash H.V. supply. The d.c. photomultiplier output signal was fed into a Keithley microammeter model 414 and displayed on a 10-mV Dynamaster strip chart Bristol recorder
Flame	Air-H ₂ at a pressure of 20 psig and 20 inch of water respectively
Burner	Total consumption Ditric Corporation HETCO Burner. Beckman medium-bore integral aspirator burner

RESULTS AND DISCUSSION

Optics

In atomic fluorescence, the energy absorbed by the sample (P_{abs}) is proportional to the energy emitted as fluorescent radiation (P_{F})

$$P_{\text{F}} \propto \phi P_{\text{abs}}$$

where ϕ is the quantum efficiency of the process¹. This relation shows that, at constant ϕ , P_{F} will increase according to the increase of P_{abs} . On the other hand P_{abs} is related to the incident radiation power P_0 and the average path length L of the radiation in the flame, by the expression

$$P_{\text{abs}} \propto P_0 (1 - e^{-k_0 L}) \Delta \nu$$

where K_0 is the atomic absorption coefficient at the center of the line, $\Delta\nu$ is the half-width of the absorption line, and the self-reversal is neglected.

An obvious way to increase P_{abs} , when the other parameters are held constant, is to increase L . This can be accomplished either by increasing the absorbing path length (laminar flames extending over 10 cm in length, three burners in series, flame inserted in a suitable tube) or by reflecting several times the emission light through the flame. This was very effective in enhancing the usefulness of atomic absorption and sensitivities for the various elements were greatly lowered⁶⁻⁸. Such a result was indeed to be expected, since the absorption of light by a certain quantity of atoms is measured in the same direction as that of the emitted energy. Thus, increased dispersion of atoms on this axis, *i.e.* increased absorbing cell lengths, will produce a stronger difference in signals to be detected.

On the other hand, in atomic fluorescence, the energy absorbed at a given frequency in one direction is re-emitted at the same or lower frequencies in all directions, *i.e.* isotropically, and measured at 90° . Thus, it would be advisable to have at one's disposal an absorbing cell optically as thin as possible in order that the photo-detector can collect the maximum of the energy emitted as fluorescent radiation. For this reason an increase of P_{abs} can only be accomplished by passing the exciting beam several times through the cell. Moreover, a suitable arrangement of mirrors could be effective in increasing also the solid angle of fluorescent radiation directed on the monochromator slit. In the apparatus depicted in Fig. 1, two concave mirrors are positioned in such a way that M1 reflects the incident radiation into the flame and M2 sends into the monochromator the same energy emitted by the sample in the direction of the entrance slit of the monochromator, but at the opposite side. With this system, the predicted dependence of the fluorescent intensity P_F on a proper choice of optics is clearly borne out. A 31% increase of P_F was obtained by the use of the mirror M1 (further increase could be achieved with a suitable multipass system) and an 100% increase by the use of M2. Hence this resulted in a total increase of 168% of the fluorescent signal.

Excitation source

Preliminary tests were carried out with the Philips metal vapor discharge lamps with their outer quartz envelope, for the elements zinc and cadmium, since for these elements the best fluorescence values are reported in the literature and their high sensitivity would permit a good evaluation of our optical arrangement. The discharge current for these lamps was not varied in order to find the best excitation conditions even if this would be advisable in the case of cadmium whose line at 2288 Å appeared clearly self-reversed in the spectrum.

WINEFORDNER AND VICKERS¹ stated that "it should be possible to excite the fluorescence of a line of one element with a line of a different element as long as there is some overlap between the source line and the absorption line". Some tests were first carried out with the conventional hollow-cathode lamps used for atomic absorption analysis, in order to see if sufficient energy would be available for exciting the fluorescence.

A Microtek cadmium lamp and Westinghouse Zn, Fe, Ni, Cr and Mn tubes, operated at their recommended currents, were used. Although fluorescence was detectable for all the elements investigated, the intensity obtained for cadmium or

zinc was far lower than that emitted by using the Philips discharge lamps as excitation source. In the case of cadmium the fluorescence measured with the metal vapor discharge lamp was 27 times as large as that measured with the hollow cathode, while for zinc the emitted fluorescence showed a 220-fold increase. The low value obtained for cadmium could be attributed to the self-reversal of the 2288 Å line.

These results indicate that the possible coincidences which could be presented by a conventional hollow-cathode lamp would be ineffective owing to the low energy of the emitted lines. Accordingly, a Philips Hg 90 W high-pressure discharge lamp was investigated in order to ascertain if some of the lines emitted could be of analytical use to excite the fluorescence of the possible coincident lines of the other elements. This lamp proved to be effective in exciting the fluorescence of Fe, Mn, Ni, Cr, Tl, Cu and Mg. Whenever the coincidence was good, *e.g.* for Fe (Fe 2483.27, Hg 2482.72), Tl (Tl 3776, Hg 3776.26) and Mg (Mg 2852.13, Hg 2852.42), satisfactory results and low limits of detection were obtained. Table II shows the experimental conditions and the sensitivity data for 10 elements obtained with vapour-discharge lamps. However, even if some overlap of the mercury lines with those of the different ele-

TABLE II
SENSITIVITY DATA AND OPERATING CONDITIONS

Element	Spectral line (Å°)	Source	Slit width (μ)	Limit of detection* (μg/ml)
Zn	2138.56	Philips Zn 25 W	400	0.0005
Cd	2288.018	Philips Cd 25 W	400	0.005
Fe	2483.27	Philips Hg 90 W 2482.72	400	1
Mn	2794.82	Hg lamp continuum	400	0.5
Tl	3775.72	Hg lamp 3776.26	400	0.3
Ni	2320.03	Hg lamp continuum	400	3
Cr	3593.49	Hg lamp 3593.48	400	5
Mg	2852.13	Hg lamp 2852.42	300	0.5
Pd	3404.58	Cd lamp 25 W 3403.65	400	10
Cu	3247.54	Hg lamp continuum	400	0.1

* Values are referred to that concentration which produces a signal due to fluorescence two times as large as the variations in the noise signal.

ments did not exist, the mercury lamp gave sensitivities 4 times better than those given by conventional tubes except in the case of manganese.

On the basis of these results, it seems much more interesting to study the feasibility of a complex high-intensity line source, rather than a continuum, as a general source for exciting the fluorescence of most of the elements.

Flame

All fluorescent studies were carried out using a total consumption aspirator burner (HETCO) and the air-hydrogen flame. Fluorescence signals were measured with the burner at the lowest position. This corresponds to a distance of about 6 cm between the tip of the burner and the center of the entrance slit of the monochromator. In this position, the best signal-to-noise ratio was obtained for all the elements investigated. Scattering of radiation was always present and sometimes in such a degree that it could not be compensated by proper zero suppression. This was mainly due to the relatively large size of the aerosol produced by the burner. The use of a Beckman medium-bore total consumption burner reduced the scattering radiation by about 78%. However, its sensitivity was 60% lower, owing to the decreased aspiration efficiency. Because of the lack of a suitable a.c. system, it was not possible to eliminate the thermal emission for some elements in the flame. Thus, whenever required, an additional reading was taken by shutting the emission source. The thermal radiation was subsequently subtracted from the signal due to the sample.

CONCLUSIONS

In this study a simple adaptation of a conventional atomic absorption-flame emission spectrometer permits rapid conversion for analysis by atomic fluorescence. Limits of detection for zinc and cadmium were very much superior to the best atomic absorption values.

The choice of suitable optics plays a fundamental role in increasing the fluorescent signal. Further improvements could be made with better arrangements of mirrors in order to increase the fraction of excitation absorbed by atoms in the flame. The possibility of using a high-intensity source of an element whose spectrum is very complex in order to excite the fluorescence of the "overlapping" lines of the other elements, seems very attractive.

Tests concerning the different parameters involved in atomic fluorescence (source intensity, flame conditions, scattering radiation, optics and read-out system) are now in progress.

SUMMARY

The possibility of exciting the fluorescence of several elements with the "overlapping" lines of other elements and the effectiveness of exciting the fluorescence of Fe, Mn, Ni, Cr, Tl, Cu and Mg with a 90 W mercury discharge lamp, are discussed. A method of increasing the fluorescence radiation by suitable optics, with a simple adaptation of a Jarrell-Ash AA spectrometer, is described. A two-pass system of the incident radiation into the flame is coupled with a mirror, in the optical axis, which reflects the fluorescence radiation emitted at the opposite side to the monochro-

mator slit. This produces an increase of 168% of the signal. Detection limits for 10 elements are reported.

RÉSUMÉ

On démontre la possibilité d'exciter la fluorescence de plusieurs éléments en utilisant le "chevauchement" de raies d'autres éléments. Une lampe de décharge à vapeurs de mercure, de 90 W, excite la fluorescence des éléments Fe, Mn, Ni, Cr, Tl, Cu et Mg. On met en évidence que l'arrangement d'un système optique convenable joue un rôle important dans l'augmentation du signal de fluorescence. L'emploi de deux miroirs, dont le premier renvoie dans la flamme le faisceau incident et le deuxième, placé derrière la flamme dans l'axe optique réfléchit l'énergie de fluorescence sur la fente du monochromateur, augmente de 168% le signal. On présente une simple adaptation du spectromètre Jarrell-Ash d'absorption atomique pour l'analyse par Fluorescence Atomique ainsi que les limites de détection pour 10 éléments.

ZUSAMMENFASSUNG

Es wird die Möglichkeit aufgezeigt, einige Elemente mit den überlappenden linien anderer Elemente zur Fluoreszenz anzuregen. Mit einer 90 W Quecksilberdampfampe kann die Fluoreszenz von Fe, Mn, Ni, Cr, Tl, Cu und Mg angeregt werden. Besondere Betonung wird auf die Rolle einer geeigneten Optik zur Verstärkung des Fluoreszenzsignals gelegt. Die anregende Strahlung fällt auf die Flamme, hinter der sich in der optischen Achse ein Spiegel befindet, der die in dieser Richtung emittierte Strahlung in die Flamme reflektiert. Auf diese Weise wird eine Erhöhung des Fluoreszenzsignals um 168% erreicht. Eine einfache Modifizierung eines kommerziellen Jarrell-Ash atomic absorption Spektrometers für Fluoreszenzanalyse wird beschrieben. Gleichzeitig werden Nachweisgrenzen für 10 Elemente angegeben.

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PRECISION ANALYSES OF MANGANESE IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

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Determinations of manganese in geological materials are most frequently carried out either by chemical methods based on oxidation to permanganate and subsequent titration, or by emission spectrographic techniques. Interlaboratory comparisons have shown, however, that the agreement obtained by different workers using these techniques may be rather poor. Results obtained for the standard rocks granite G-1 and diabase W-1 by standard chemical methods showed a mean relative deviation of 33.6% and 32.3% respectively¹, and the corresponding figures for spectrographic analyses are 33.1% and 10.9%. More recent analyses of the same two rocks^{2,3} have shown a similar scattering. On the basis of this experience it seemed desirable to develop more precise and accurate methods for the determination of manganese in rocks.

Neutron activation combined with γ -spectrometry has recently come into use for manganese determination in geological materials. SCHMITT *et al.*⁴ and FISCHER AND CURRIE⁵ have reported applications on meteoritic matter, and BRUNFELT AND STEINNES⁶ have analysed some standard rocks, using sodium iodide detectors, while LAMB *et al.*⁷ and COBB⁸ have employed lithium drifted germanium detectors. None of these authors has studied in detail the precision obtainable at different manganese levels, but from the data of BRUNFELT AND STEINNES⁶ a single value relative standard deviation of the order $\pm 4\%$ is indicated. It was assumed that a still better precision might be attained, and a study was therefore initiated in order to investigate the precision at different manganese concentrations.

EXPERIMENTAL

Previous experience has shown that the γ -spectra of irradiated rock specimens are usually composed almost entirely of 2.58-h ⁵⁶Mn and 15.0-h ²⁴Na if the irradiation time is short and when short-lived activities of ¹⁶N, ²⁸Al and ²⁷Mg have decayed to a negligible level. The precision of manganese determinations is therefore assumed to depend upon the ratio Mn/Na in the sample. In the present work 3 standard rocks from the U.S. Geological Survey, *i.e.* diabase W-1, andesite AGV-1 and granite G-2, were selected for analysis. The Mn/Na ratios of these rocks are 0.082, 0.023 and 0.0085 respectively⁶. The γ -spectra of the rocks after irradiation for 5 min and a decay time of 1.5 h are shown in Fig. 1.

The spread of parallel determinations in neutron activation work is in many cases mainly due to flux gradients in the irradiation position. This source of error can be reduced either by using a rotating rack as described by SCHMITT *et al.*⁴ or by reducing the sample size. In this work the second alternative was chosen, as a rotation rack was not available.

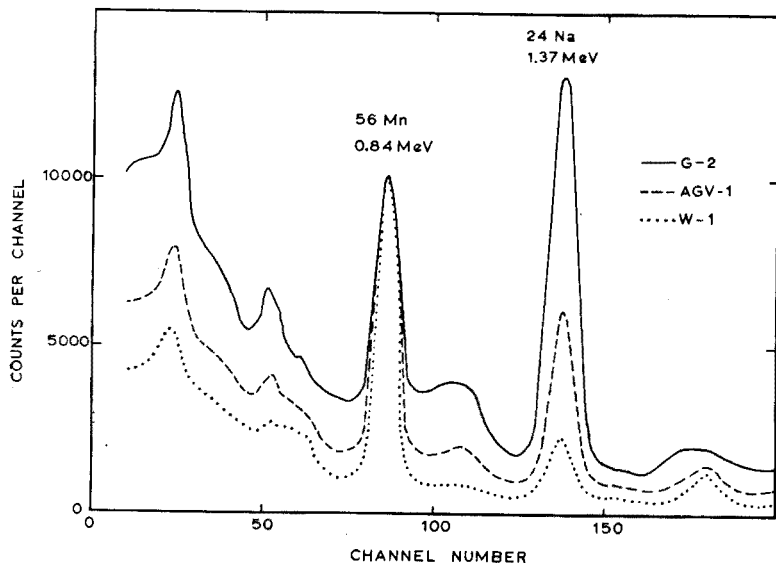


Fig. 1. γ -Spectra of 3 standard rocks, recorded 1.5 h after the end of the irradiation.

Preparation of samples and standards

Samples of about 20 mg were weighed into small polyethylene envelopes which were heat-sealed.

Standards were prepared by pipetting aliquots of 250 μ l of a manganese standard solution onto 2 cm \times 2 cm polyethylene sheets, evaporating carefully to dryness with a heating lamp and heat-sealing. The amount of manganese in the standard was about 10 μ g. The standard solution was prepared by dissolving an appropriate amount of manganese metal (Johnson and Matthey Ltd., spec. pure grade) in a few ml of strong hydrochloric acid and diluting to 250 ml with water.

Irradiation

20 samples and 10 standards were packed closely together and irradiated for 5 min in the reactor JEEP I (Kjeller, Norway) at a thermal neutron flux of $2.7 \cdot 10^{12}$ n/cm²/sec. The volume including all samples and standards was of the order of 1 cm³.

Activity measurements

After a period of 1.5 h to allow the decay of short-lived activities, the γ -activity of samples and standards was recorded with a 400-channel γ -spectrometer with a 3 \times 3" NaI (Tl) detector. The distance between active source and detector was 10 cm. To reduce geometry errors to a minimum, the samples were fixed to a glass plate with Scotch tape before the measurement. The counting period for each sample

was usually 1–2 min, and the area under the 0.84-MeV photopeak was evaluated as described by COVELL⁹. The integrated counts were always above 40000, corresponding to a standard counting error of ± 0.5 – 1.0% ⁹. The disintegration rate was checked by repeated measurements at intervals of 2 h.

Irradiations within a cadmium cover to enhance epithermal activation relatively to thermal activation were also attempted. Due to the high resonance integral of ⁵⁵Mn, this will yield a higher Mn/Na ratio. The precision thus obtained, however, was not as good as in the ordinary irradiations.

RESULTS AND DISCUSSION

Six series of standard rocks (A–F), each consisting of 10 samples, were analysed by the present method; two series of G-2 (A–B), one series of AGV-1 (C) and three series of W-1 (D–F) were included. The analyses of series C and A were repeated once and twice respectively. The results are listed in Table I together with the mean value and the relative standard deviation of a single determination for each run.

From Table I the relative standard deviation for the determination of manganese in G-2 is about $\pm 2\%$. For AGV-1 and W-1 the corresponding figure is $\pm 1.5\%$. The manganese standards showed a standard deviation of the order $\pm 1\%$, mainly because of pipetting errors and counting statistics. Errors due to flux inhomogeneity were reduced to an almost negligible level. For the rock samples, weighing errors and errors due to inhomogeneous distribution of manganese in the crushed rock

TABLE I

MANGANESE CONTENT OF STANDARD ROCKS (p.p.m.)

	<i>Granite G-2</i>				<i>Andesite AGV-1</i>		<i>Diabase W-1</i>		
	<i>A</i>	<i>A</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
1	294*	290*	289*	257	732	713	1348	1298	1376
2	260	251	263	258	730	729	1323	1348	1338
3	252	244	249	258	718	726	1332	1296	1364
4	253	248	256	257	716	726	1338	1330	1330
5	251	252	253	250	723	717	1321	1359	1335
6	240	238	242	247	722	718	1322	1344	1318
7	261	253	257	251	716	715	1263	1296	1328
8	252	253	257	257	715	729	1325	1315	1335
9	252	254	256	260	726	741	1327	1328	1315
10	246	254	252	258	725	735	1354	1315	1315
Mean value (p.p.m.)	252	250	254	255	722	724	1325	1323	1335
Relative standard deviation of single value (%)	2.3	2.1	2.2	1.7	0.8	1.4	1.8	1.6	1.6
Overall mean (p.p.m.)		253			723			1328	

* Not included in calculation of mean value and standard deviation.

material also contribute to the observed statistical error. The precision data presented here should be representative for most common rock types.

There are several sources of error which might affect the accuracy of the method.

(1) Interference from threshold reactions. The most significant interfering reaction is $^{56}\text{Fe} (n,p) ^{56}\text{Mn}$. The contribution to the ^{56}Mn activity from this source has been calculated to be less than 0.1%. Interference from the $^{59}\text{Co}(n,\alpha)^{56}\text{Mn}$ reaction is still less significant, owing to the low abundance of cobalt.

(2) Interference from other radionuclides with γ -energies similar to ^{56}Mn . The most probable interfering nuclides are 9.5-min ^{27}Mg and 14.2-h ^{72}Ga . Interference from ^{27}Mg is less than 0.1% if the measurements are postponed to 1.5 h after the end of the irradiation. From the gallium data available for the actual rocks¹⁰, the most serious interference, *i.e.* in the case of G-2, is calculated to be about 0.4%. The spectrum of ^{24}Na has no peak in the actual energy region used.

(3) Weighing and standardization errors. The microbalance used was regularly checked, and was found to be stable within $\pm 5 \mu\text{g}$ in the range 0–30 mg. The standard solution was found to be accurate to $\pm 0.5\%$.

(4) The manganese content in the polyethylene envelopes was shown to be $< 0.005 \mu\text{g}$, and hence negligible.

(5) The counting geometry was the same for samples and standards.

(6) Absorption of the 0.84 MeV γ -rays in the rock samples was estimated to be less than 0.2%.

(7) Thermal neutron shielding effects were estimated to be less than 0.1%. As the neutron flux in the irradiation position was fairly well thermalized, serious errors due to resonance neutron shielding would not be expected to occur.

From the above considerations, which should include all significant sources of error, it seems reasonable that the present mean values, and results from manganese analyses carried out in a similar way, are accurate to $\pm 2\%$. The agreement between the present mean value 1328 p.p.m. for W-1 and the "recommended value" 1320 p.p.m.² fortifies this assumption. The fact that the mean values found in the present work are 3–5% higher than the previous neutron activation results from this laboratory⁶ is probably due to systematic errors inherent in the analyses carried out before the recent development of the technique. A further check on the accuracy of the analyses is difficult because of the lack of suitable standard materials with compositions similar to rocks and with exactly known manganese contents. No "recommended values" seem to be available for rocks G-2 and AGV-1.

The present procedure is simple and rapid, and should be well suited for routine application without any particular loss in precision and accuracy. One person can analyse a great number of samples a day, especially if a computer is used for the evaluation of data. Owing to its relative simplicity and its high precision and accuracy, the method should be superior to the wet chemical and emission spectrographic techniques commonly used in routine assay of manganese in rocks.

SUMMARY

A simple and rapid procedure for the determination of manganese in rocks by neutron activation and γ -spectrometry is presented. The precision of the method

calculated from analyses of standard rocks is of the order 1.5–2%, and an accuracy of $\pm 2\%$ is attainable. The method is applicable to most types of geological samples, and should be superior to conventional methods used in rock analysis.

RÉSUMÉ

On propose une méthode simple et rapide pour le dosage du manganèse dans les roches par activation au moyen de neutrons et spectrométrie- γ . La précision de la méthode, calculée à partir d'analyses de roches étalons est de l'ordre de 1.5–2%; une exactitude de $\pm 2\%$ est possible. Ce procédé est applicable à la plupart des types d'échantillons géologiques et semble meilleur que les méthodes conventionnelles utilisées pour l'analyse des roches.

ZUSAMMENFASSUNG

Ein einfaches und schnelles Verfahren zur Bestimmung von Mangan in Gesteinen mittels der Neutronenaktivierung und der γ -Spektrometrie wird angegeben. Die Reproduzierbarkeit der Methode, berechnet aus der Analyse von Standardgesteinen, liegt in der Grössenordnung von 1.5–2%, eine Genauigkeit von $\pm 2\%$ ist erreichbar. Die Methode ist für die meisten Typen geologischer Proben anwendbar und sollte den konventionellen Methoden überlegen sein.

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DETERMINATION OF BARIUM AND STRONTIUM IN SEA WATER*

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Few precise determinations of the barium content of sea water have been reported. Early analyses gave either upper limits or very approximate values, and more recent determinations¹⁻⁴ have not established a clear pattern of concentration as a function of depth or geographical location. Although the analytical techniques of activation analysis^{1,3,4} and mass spectrometry² have been demonstrated to be applicable to the problem, it appeared that an alternative procedure utilizing less sophisticated instrumentation and having higher precision than that obtained by activation analysis (*ca.* 18%)⁴ would be desirable for an extensive study. Ideally, such an alternative procedure should also be applicable to the determination of strontium and radium in the sample, with only minor modification.

Of the many methods which have been used for the determination of natural strontium in sea water only direct flame photometry^{5,6} and atomic absorption spectroscopy⁷ appear to have the precision and accuracy necessary for studies of strontium distribution as a function of depth. None of these procedures is applicable to the determination of the very small amounts (*ca.* 0.05 p.p.m.)⁸ of barium which occur naturally. The present investigation has led to the development of a procedure for the quantitative concentration and separation of strontium and barium from sea water by ion-exchange, followed by flame photometric determination of these elements.

The direct flame photometric determination of strontium and particularly of barium at natural levels in sea water is made difficult by the high concentrations of other constituents. Not only is there specific interference by other elements but high salt concentrations cause instability and sea water sprayed into a flame is highly corrosive. A separation from the bulk of the salts, particularly calcium which gives spectral interference, and concentration of the barium, the flame emissivity of which is weak, was therefore felt to be necessary. Of the various possibilities considered, the use of ion-exchange proved to be the most satisfactory. The resulting method is sensitive, accurate, convenient and economical. The only prior application of ion-exchange separation to the flame photometric determination of strontium in sea

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water is the very recent procedure of GREENHALGH, RILEY AND TONGUDAI⁹ which is considerably less direct and does not provide for the determination of barium.

EXPERIMENTAL

Apparatus and materials

Flame emission was measured with a Zeiss PMQ II spectrophotometer with flame attachment (Lundegårdh-type single jet burner). Radioactivity was measured in solution with a well-type scintillation detector coupled to a conventional single-channel analyzer, amplifier, discriminator, power supply and seven-decade scaler.

Radioactive ⁸⁵Sr, ⁴⁷Ca and ¹³³Ba were obtained as the chlorides in 1 M hydrochloric acid from Iso-Serve, Cambridge, Mass. with a specific activity of not less than 100 mC per gram of element. "Specpure" barium chloride dihydrate (< 1.0 p.p.m. strontium) and strontium carbonate (1.0 p.p.m. barium) from Johnson, Matthey and Co. Ltd. were used for calibration standards. Other reagents were of the highest purity available (usually analytical-reagent grade) and redistilled water was used at all times.

Preparation of eluents

CyDTA. A stock solution of cyclohexane-1,2-dinitrilotetracetic acid (CyDTA) was made by dissolving 34.5 g in approximately 0.5 l of water with a minimum amount of ammonia, and diluting to 1.0 l. The pH 5.1, 0.02 M eluent was then obtained by mixing 2 volumes of the stock solution with 4 volumes of acetate buffer (60 g of glacial acetic acid neutralized to pH 5.1 with ammonia, per liter) and 4 volumes of water. The pH 6.5, 0.02 M CyDTA, 1 M in ammonium ion eluent was prepared directly by dissolving 6.93 g of the chelating agent in 600 ml of water and 67.5 ml of concentrated ammonia, adjusting the pH to 6.5 with glacial acetic acid and diluting to 1 l.

EDTA. A pH 10.0, 0.01 M solution was prepared from 2.34 g of EDTA (as the acid), 0.43 g of ammonium chloride and 10 ml of concentrated ammonia dissolved in about 600 ml of water. After adjustment of the pH to 10.0 with ammonia, the mixture was diluted to 1 l.

The selectivity coefficients for the alkaline earths on conventional organic ion-exchange resins are known to increase with increasing ionic radius. Consequently, it would be expected that the use of a conventional cation-exchange resin in the calcium form should permit the retention of strontium and barium while allowing the comparatively large amounts of magnesium and calcium present in sea water to pass through in the effluent. Studies were therefore made with Dowex 50-X12 resin (200-400 mesh) converted to the calcium form by treatment with concentrated calcium chloride solution. Sea water, which had been adjusted to pH 3.0 with hydrochloric acid before storage and filtered through Millipore filter paper Type HA prior to use, was spiked with barium-133 or strontium-85 for tracer studies on barium and strontium uptake and elution.

Breakthrough curves were run on strontium in sea water at various pH values with the resin in the hydrogen, ammonium or calcium forms. The results, obtained on small columns containing only 2 g of resin, illustrated that sea water adjusted to pH 3 and a calcium-form resin gave a relatively high effective capacity for strontium

(Fig. 1). The apparent increase in capacity was very small when sea water diluted 1:1 and adjusted to pH 3 was used, and it was concluded that a significant increase would be obtained only at inconveniently large dilutions. Increasing the temperature was found to lower the effective capacity without causing a substantial change in the shape of the breakthrough curve. The 50% breakthrough volume of 98 ml for strontium at room temperature was reduced to 74 ml at 80°.

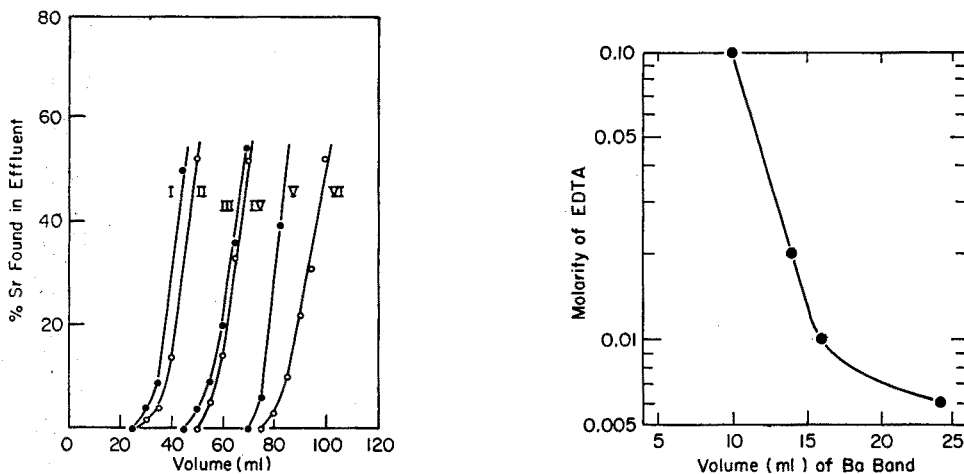


Fig. 1. Breakthrough curves for strontium in sea water. Column 2 g Dowex 50-X12 (200-400 mesh) resin. (I) 0.7 *M* in hydrochloric acid; hydrogen-form resin. (II) 0.7 *M* in hydrochloric acid; ammonium-form resin. (III) pH 0.4; ammonium-form resin. (IV) pH 0.4; calcium-form resin. (V) pH 5.0; calcium-form resin. (VI) pH 3.0; calcium-form resin.

Fig. 2. Variation of barium band volume as a function of EDTA concentration at pH 10.0.

The ion-exchange procedure of WADE AND SEIM¹⁰, in which calcium was removed with EDTA and strontium eluted with 3 *M* hydrochloric acid before its determination by flame photometry, was examined to see if it could be extended to the separation of strontium and barium. Although it was verified that strontium was easily removed with 3-4 *M* hydrochloric acid, barium was not as readily recovered. Hydrochloric acid (5 *M*) at 60° eluted barium in a broad (110-120 ml) band; higher concentrations did not improve the sharpness and, in fact, at 9 *M* the separation was not as good. As a result, the separation by elution of calcium, barium and strontium with organic complexing agents was studied.

Of the various organic chelating agents available, CyDTA was suggested as being the most promising from the standpoint of the published values of the stability constants of the complexes with calcium, strontium and barium¹¹. The logarithms of the stability constants, 12.3, 10.0 and 8.0, respectively¹², suggest that the calcium-strontium separation should be as good as that using EDTA, for example, and the strontium-barium separation should be distinctly better. Unpublished experiments by NOSHKIN AND MOTT¹³ had already indicated that the method should be applicable.

After exploratory experiments, the removal of calcium from barium and strontium was investigated on a full scale column containing 25 g of resin. A liter of filtered sea water at pH 3.0, containing either barium-133 or strontium-85, could be

passed through the column without breakthrough of radioactivity. The calcium was selectively removed with the 0.02 *M* CyDTA reagent at pH 5.1. No radioactivity was found in the eluent. Approximately 500 ml of the reagent was found necessary for removal of the calcium, and twice that amount could be passed through without a breakthrough of strontium or barium.

From values of their selectivity coefficients on cation-exchange resins and stability constants with aminopolycarboxylate chelating agents, one would expect many of the di- and trivalent trace metals in sea water to be concentrated on the resin and then removed by CyDTA with the calcium fraction. No evidence of contamination of the barium and strontium fractions with other elements in sea water has been observed in this work, and a specific check using radioactive zinc as a model element showed all the radioactivity to be in the calcium fraction.

Experimentation with radioactive tracers showed that an adequate separation of strontium and barium could be achieved by selectively eluting the former with 0.02 *M* CyDTA at pH 6.5 and the latter with 0.02 *M* CyDTA buffered at pH 10. The strontium band was rather broad, however, and it was found advantageous to increase the concentration of ammonium ions in the buffer to approximately 1 *M*. This not only reduced the volume of eluent containing the strontium band by about 40%, but also improved the subsequent barium band similarly.

Once strontium has been removed, there is no need to use as selective a reagent as the expensive CyDTA simply to recover the barium from the column. The elution characteristics of barium with EDTA were therefore examined under various conditions. With 0.1 *M* EDTA in ammonium acetate buffers, barium was not eluted at a significant rate below pH 7, although traces might be lost during long elutions with EDTA or CyDTA at pH 6 or 6.5. In view of the low concentrations of barium found in ocean water, the smallest practicable elution volume is desirable, and it was found that a pH 10 EDTA eluent gave the sharpest band. No appreciable difference in the elution behavior of EDTA and CyDTA was found under these conditions.

Because of the flame emission characteristics of barium, which are discussed below, the barium should be eluted from the column with as low a concentration of complexing agent as possible. The width of the barium band was found to increase with decreasing EDTA concentration at pH 10, as shown in Fig. 2. Below 0.008 *M*, however, recovery was not dependably complete and therefore 0.01 *M* was selected for use and the ammonium ion concentration was held constant (0.06 *M*).

For a good analysis, it is necessary to know accurately the location and extent of the bands of the two fractions being taken. In three typical samples, all the strontium activity had come through in the first 35, 31 and 43 ml, respectively. When the eluent was changed for barium elution, 15, 15 and 18 ml passed through before barium activity appeared in the effluent, and the volumes of the barium bands were 15, 13 and 18 ml, respectively. On the basis of this experience, it was felt that to collect the first 60 ml of effluent during the strontium stripping, change to pH 10 reagent and discard the first 10 ml before collecting 35 ml would collect the strontium and barium quantitatively in high purity with an ample margin of safety. Flame photometric tests on fractions isolated from sea water samples showed less than 1 part in 70 of calcium in the strontium, whereas a 1:1 ratio is tolerable in flame photometry. As shown below, one part of calcium to four of barium, and one part of strontium to one of barium causes serious interference in the flame method.

Neither strontium nor calcium could be detected by flame emission in the barium fractions obtained as above. Traces of sodium from impurities in the reagents were evident in the flame, but in amounts too low to offer any interference. Typical blanks using 1-1 samples of deionized water showed no detectable strontium or barium from the reagents. The details of the separation method are summarized in the operating procedure below.

Recommended ion-exchange separation procedure

Samples taken at sea by standard techniques¹⁴ are added to polypropylene or Teflon storage bottles containing sufficient distilled hydrochloric acid to make the final pH 3.0. Before analysis, the stored samples are filtered through Millipore filter paper Type HA (0.45 μ).

A 1-1 analytical sample is passed through a 35 \times 1.3 cm borosilicate glass ion-exchange column containing 25 g of Dowex 50-X12 (200-400 mesh) cation exchange resin in the calcium form. The flow rate through the column is kept at 1 ml per min at room temperature (*i.e.*, 20-22°) for all solutions.

The sample is followed through with approximately 20 ml of 0.01 *M*, pH 5.0 ammonium acetate buffer and the calcium is eluted with 500-600 ml of 0.02 *M* CyDTA in pH 5.0 buffer. The calcium fraction is discarded and the strontium eluted with 0.02 *M* CyDTA in pH 6.5 buffer; the first 60 ml collected contain all the strontium. This solution is diluted to 500.0 ml with redistilled water and aspirated into the air-hydrogen flame for the strontium determination. A blank in which a strontium fraction is collected and treated in the same manner as the sample is used for flame background determinations.

The eluent is then changed to 0.01 *M* EDTA in a pH 10.0 ammonia-ammonium chloride buffer and the first 10 ml coming through are discarded. The following 35 ml are taken as the barium fraction. A 35-ml blank, composed of the same concentration of eluent and treated in exactly the same manner as the effluent from the ion-exchange column is used for background determination. The solution is evaporated under a heating lamp to approximately 6 ml in a Teflon beaker, and when diluted to 10.00 ml, is ready for aspiration into the flame. It was found necessary to use Teflon to avoid the problem of adsorption of barium on the walls of the container.

The column is regenerated by passing through about 100 ml of a saturated calcium chloride solution which has previously been stripped of strontium and barium by ion-exchange. The total time required for analyses is approximately 2 days for 12 samples being analyzed simultaneously.

Flame photometric studies of strontium and barium

A number of investigators have studied the emission characteristics of strontium and barium in high-temperature flames¹⁵⁻¹⁷. The striking concavity of the calibration curve of barium at 553.7 nm in the oxy-hydrogen flame due to ionization diminishes its analytical usefulness. That an improvement can be obtained by using a cooler flame was indicated by DEAN *et al.*¹⁶ and HERRMANN AND ALKEMADE¹⁷ and is found experimentally. A study of the emission characteristics of strontium and barium in an air-hydrogen flame was therefore undertaken.

Because of the strength of the strontium resonance line, the full sensitivity of the instrument was not needed for the determination of this element. However, in

view of the low concentrations of barium found in sea water and the relative weakness of its resonance line, it was found desirable to increase the sensitivity of the instrument as much as possible. This was accomplished by replacing a 200 k Ω load resistor in the PMQ II with a 2 M Ω resistor which increased the amplification by a factor of 4. The slit was also set at 0.10 mm to admit as much light as possible without increasing the background excessively.

A steady reading on the instrument occurred *ca.* 5–10 sec after aspiration of the sample into the flame had begun. No effect on the emission intensity owing to a fall in the depth at sample in the cup could be detected until after about one third of the sample had been consumed.

Barium

Experiments using the oxy-hydrogen and the air-hydrogen flames showed the anticipated greater intensity of barium emission in the latter. Figure 3 illustrates the dependence of the barium emission in hydrogen-rich air-hydrogen flames at the

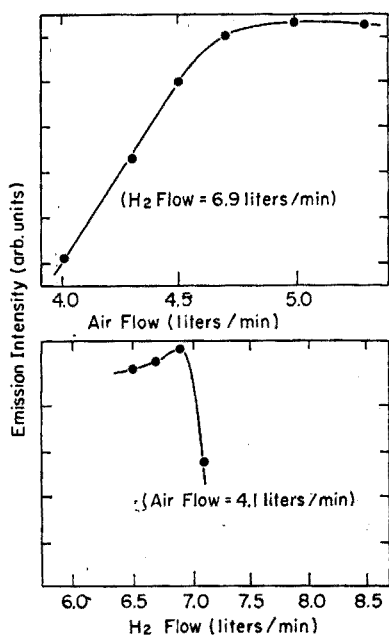


Fig. 3. Barium emission intensity at 553.7 nm as a function of air and hydrogen flow.

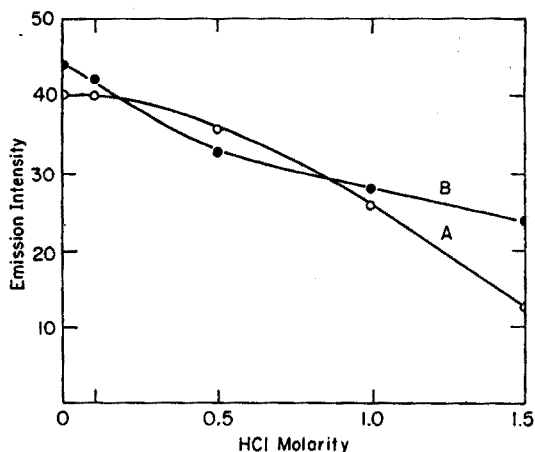


Fig. 4. Barium emission intensity at 553.7 nm *versus* hydrochloric acid concentration. (A) Oxy-hydrogen flame. (B) Air-hydrogen flame.

wavelength of the 553.7 nm resonance line. The optimum flame composition for the burner used in this work was found to be given by a flow rate of 6.9 l per min for hydrogen and 5.0 l per min for air. A more detailed study of the emission characteristics of barium and strontium as a function of flame composition has been described¹⁸.

In view of the composition of the barium eluate in the separation procedure, the effects of pH and EDTA concentration on the emission characteristics of the

neutral barium atom in the air-hydrogen flame were examined. It was found that at pH 6, significant depression occurred at EDTA concentrations above about 0.03 *M*, amounting to as much as 35% at 0.1 *M*. At pH 10, the effect was much greater, being about 50% with as little as 0.01 *M* EDTA and increasing to 60% at 0.1 *M*. At constant EDTA concentration, *e.g.*, 0.02 *M*, the effect of pH was very striking with no change in emission intensity between pH 6.0 and 8.3 and a sharp drop-off between pH 8.3 and 9.1 after which the intensity became constant again at a value about 50% that observed below pH 8. Barium is known to be titratable (and therefore complexed) by EDTA at pH 9 and above. A flame hotter than air-hydrogen is evidently needed for the efficient volatilization and excitation of the complexed barium¹⁸. This poses no problem in the present analysis, however, because the pH of the barium fraction is decreased to approximately 6 during the evaporation step.

Because ammonium ions are present in the solution, their effect on the emission intensity of barium was studied. DEAN *et al.*¹⁶, using an oxy-hydrogen flame, reported no diverse ion effect on barium emission up to an ammonium/barium ratio of ten. No effect was observed in the air-hydrogen flame at ammonium ion concentrations below 1 *M*. However, at this concentration of ammonium ion the flame is noisy, and there is a resulting decrease in the precision of the determination.

Figure 4 shows the effect of hydrochloric acid on the intensity of barium emission both in oxy-hydrogen and in air-hydrogen flames. These data agree with the results obtained by DEAN *et al.* In the cooler air-hydrogen flame, the depressive effect of hydrochloric acid appears at a lower concentration, in harmony with the general trend observed by DEAN when going from oxy-acetylene flame to a cooler oxy-hydrogen flame. The absence of interference by ammonium chloride suggests that the depression is not due simply to the formation of barium chloride in the flame.

Strontium causes a slight decrease in the intensity of the barium atomic line

TABLE I
EFFECT OF STRONTIUM ON BARIUM EMISSION

<i>Sr/Ba</i>	Relative intensity	<i>Sr/Ba</i>	Relative intensity
0	43	1.14	41
0.089	42	2.2	41
0.88	41	10.3	39

TABLE II
ORGANIC SOLVENT EFFECT ON BARIUM EMISSION

Acetone concentration (v/v) (%)	Enhancement factor (air-H ₂)	Enhancement factor (O ₂ -H ₂)
10	1.5	1.7 ^a
20	1.6	2.1
30	1.7	2.4 ^a
40	1.7	3.2
50	1.8	3.9 ^a

^aReference 11.

in air-hydrogen flames as shown in Table I. This is in contrast with the enhancement of the atomic and depression of the ionic lines of barium by strontium which would be predicted in the hotter oxy-hydrogen flame and which was demonstrated by DEAN. A calcium/barium ratio as small as 0.25 was found to be intolerable in barium analyses because of direct spectral interference by the calcium (CaOH band at 554 nm).

Solutions of 11.40 p.p.m. barium at pH 6 were prepared with varying concentrations of acetone in order to observe the effects caused by an added organic solvent and to compare the results with those in an oxy-hydrogen flame. Table II shows that the enhancement of the barium emission by acetone in an air-hydrogen flame is less than that in an oxy-hydrogen flame. Results using isopropanol were similar. It should be noted, however, that on addition of an organic solvent to the solution, a complex series of bands is produced and background is increased in the vicinity of the barium line (Fig. 5). Solutions containing EDTA and ammonium salts, such as would be obtained from the barium isolation procedure, were found to give noisy flames with high backgrounds when organic solvents were added.

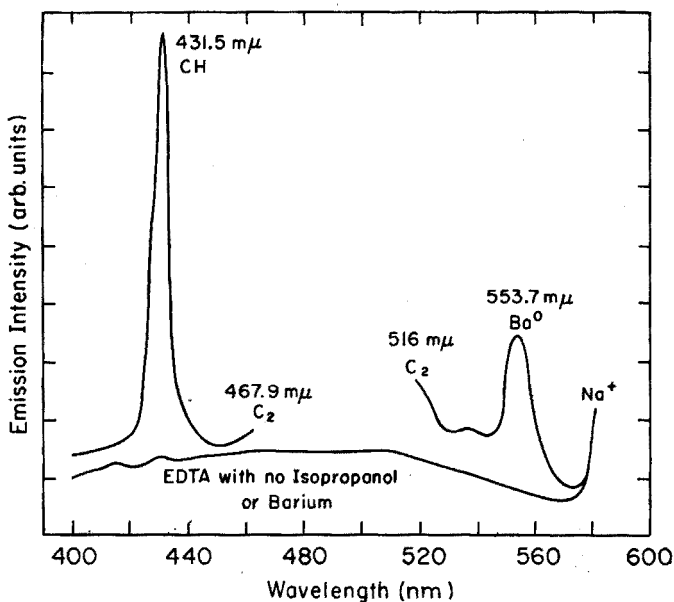


Fig. 5. Flame spectrum of a barium-0.02 M EDTA 20% (v/v) isopropanol solution at pH 6.

Calibration curves for atomic barium emission were linear at least up to 20 p.p.m. in the atomized solution, the highest concentration tested. A slit width of 0.10 mm, air flow of 5.0 l per min and hydrogen flow of 6.9 l per min permitted detection of 0.01 p.p.m. barium in water solutions. This is an improvement of over an order of magnitude compared with results reported for the Beckman D. U. Flame Photometer¹⁹. The minimum concentration which can be detected is about 0.04 p.p.m. when the solution is of the same composition as that of the final solution in the barium separation procedure because of increased flame noise and background. The values so far reported for barium concentrations in sea water are in the range of 0.012

to 0.063 p.p.m. By concentrating the barium of one liter of sea water to 10.0 ml under the conditions of the procedure devised, one should obtain barium concentrations between 1.2 and 6.3 p.p.m., a range for which this procedure is well suited.

Strontium

Strontium emission in our instrument was found to have about the same sensitivity in the air-hydrogen as in the oxy-hydrogen flame. Significant enhancement could be obtained by aspirating mixtures containing around 50% oxygen¹⁸, but the relatively high concentrations of strontium obtained from the sea water samples made increased sensitivity unnecessary. As a matter of convenience, strontium was determined in an air-hydrogen flame. The emission characteristics of strontium as a function of hydrogen and air flow are shown in Fig. 6 for 6 p.p.m. strontium chloride solutions at the 460.7 nm resonance line. Optimum conditions were taken to be 4.8 l per min for air and 6.9 l per min for hydrogen.

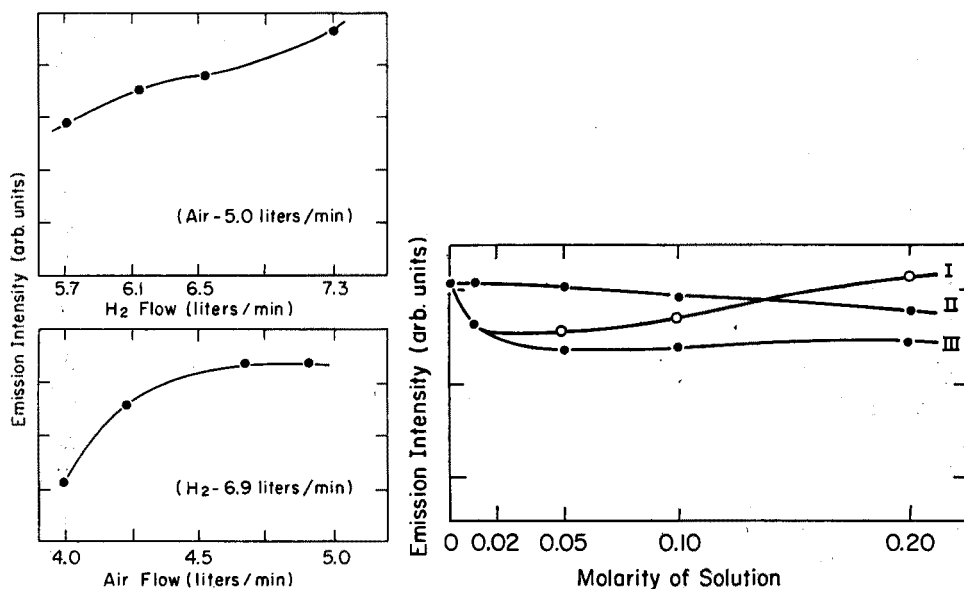


Fig. 6. Strontium emission intensity as a function of air and hydrogen flow at 460.7 nm.

Fig. 7. Strontium emission intensity at 460.7 nm versus acetic acid, ammonium chloride and ammonium acetate concentrations. (I) Acetic acid. (II) Ammonium chloride. (III) Ammonium acetate.

Figure 7 shows the effects of ammonium and acetate ions and acetic acid on the strontium emission. The initial decrease in intensity on addition of acetic acid is in contrast with previous reports of a slight enhancement in the oxy-hydrogen flame observed by DEAN *et al.*¹⁵ and confirmed in the present study. CyDTA was found to be without effect in the presence of the buffer.

The effect of calcium on the emission of the strontium resonance line is much less severe than in the case of barium. It was found that a calcium to strontium ratio of

3:1 resulted in only a 5% decrease in strontium emission intensity and a ratio of unity produced no significant depression.

The first 60 ml of the pH 6.5 CyDTA effluent contain the entire strontium fraction and are collected and diluted to 500.0 ml. Because the strontium content of sea water is in the range of approximately 6–10 p.p.m., the final solution aspirated into the flame will contain 12–20 p.p.m. strontium, a range of concentration well adapted to determination with good precision and accuracy. The calibration curve was linear over this range.

Sampling and storage

The sea water samples were collected simultaneously with samples to be used for fission-product analysis of sea water²⁰. The sampler and its operation have been described¹⁴.

Many elements tend to be adsorbed on surfaces such as the walls of a container or suspended solids. There was, therefore, a need to ascertain whether strontium or barium would be lost during extended storage of the samples. Freshly taken samples of sea water were added to polyethylene, polypropylene and Teflon bottles containing measured amounts of barium-133 or strontium-85 tracers. Aliquots were removed periodically and counted to estimate losses by adsorption. Storage was either at the natural pH of sea water (*ca.* 8.5) or at a pH of 3.0 obtained by addition of concentrated hydrochloric acid. Both filtered and unfiltered sea water were tested.

The results indicated that in solutions at pH 3.0, no adsorption occurred, with or without filtration irrespective of the material of the container. For solutions at the natural pH of sea water, significant adsorption occurred in polyethylene and polypropylene containers. This adsorption amounted to an average of 7% at the end of 23 days, with an additional 2% being adsorbed during the period up to 8 months. No adsorption was observed on Teflon under any of the above conditions. It was assumed that if no adsorption of activity had occurred by this time, there would not be a significant loss of strontium or barium due to adsorption in a normal storage period of up to perhaps one year. Polypropylene containers were used for all sea water samples due to the high cost of Teflon and the opinion of the authors that polypropylene containers would withstand the rigors of shipboard storage better than polyethylene.

Barium-133 and strontium-85 were added to one liter of pH 3.0 sea water, stirred thoroughly and filtered through Millipore filter paper, Type HA, to ascertain if strontium or barium were lost from the sample of sea water by adsorption on the filter paper during filtration. Counting of the filter paper indicated no significant retention of activity.

ANALYSIS OF SEA WATER SAMPLES

Standard analyses

Any procedure devised for the quantitative determination of a constituent in a complex medium, particularly one which requires extensive chemical manipulation, must have its precision and accuracy established if the results obtained by it are to be meaningful. For a measure of the precision of the method, 6 replicates of 1.0-l sea water samples were analyzed for strontium and barium following the recommended

procedure. The mean strontium value obtained was 6.57 p.p.m. with a standard deviation of 0.03 p.p.m. (Table III). The mean value for barium was 11.3 p.p.b. with a standard deviation of 0.5 p.p.b. (Table IV).

The accuracy of the method with respect to strontium was measured by adding 6.495 mg of strontium as "Specpure" strontium carbonate to nine 1.0-l samples of the same sea water used for replication. The mean recovery of the strontium was 6.51 p.p.m. with a standard deviation of 0.05 p.p.m. The accuracy of the method with

TABLE III
STANDARD ANALYSES OF STRONTIUM

<i>Sea water replicates (p.p.m.)</i>	<i>Analyses of sea water of known strontium content</i>	
	<i>Sr added (p.p.m.)</i>	<i>Sr recovered (p.p.m.)</i>
1. 6.55	6.50	6.48
2. 6.62	6.50	6.57
3. 6.58	6.50	6.46
4. 6.57	6.50	6.46
5. 6.55	6.50	6.56
6. 6.56	6.50	6.57
Mean: 6.57	6.50	6.48
Standard deviation: ± 0.03	6.50	6.56
	6.50	6.46
	Mean: 6.51	
	Standard deviation: ± 0.05	

TABLE IV
STANDARD ANALYSES OF BARIUM

<i>Sea water replicates (p.p.b.)</i>	<i>Analyses of sea water of known barium content</i>	
	<i>Ba added (p.p.b.)</i>	<i>Ba recovered (p.p.b.)</i>
1. 11.2	46.4	46.4
2. 11.7	46.4	47.1
3. 10.7	46.4	47.7
4. 10.9	46.4	46.0
5. 11.4	46.4	46.6
6. 11.9	46.4	47.1
Mean: 11.3	Mean: 46.8	
Standard deviation: ± 0.5	Standard deviation: ± 0.6	

respect to barium was measured by adding 46.4 μg of barium as "Specpure" barium carbonate to 1.0-l samples of sea water which showed no detectable levels of barium when analyzed by this method (combined sea water samples collected 20-IX-64 from depths of 683, 994 and 1579 meters from 41°33'N; 29°43'W; Atlantis II; Cruise 13; Station 430). The mean recovery of the barium was 46.8 p.p.b. with a standard deviation of 0.6 p.p.b.

The absolute error realized for the 9 strontium standard analyses was +0.15%, and for the 6 barium standard analyses +0.86%. The accuracy and precision of these determinations compare favorably with those of conventional flame photometry on simple samples not requiring concentration or separations. This in part can be attributed to the extremely clean separation of the elements obtained with CyDTA and

EDTA procedure, and in part to the excellent reproducibility and stability of the Zeiss flame photometer.

In order to compare the present method with the procedure of CHOW AND THOMPSON⁵ in which sea water is atomized directly into a hydrogen-oxygen flame, 14 filtered samples of water taken from an equatorial Atlantic station at depths ranging from the surface to 4400 meters, were run by both methods. The range of values expressed as $Sr/Cl \cdot 10^{-3}$ in mg-atoms/kg/0/00 was from 3.99 to 4.86. The average difference observed between the two methods was +0.02, the range being from -0.21 to +0.43. The average absolute difference was 0.14 and the standard deviation of the distribution of differences 0.18. CHOW AND THOMPSON gave ± 0.2 as the reproducibility of their method, from which it is seen that the two methods are in agreement within the stated reproducibility of their method. As a spot check, a single sample was analyzed before and after filtration by both methods. Direct aspiration gave results 3.2% higher, the column method 3.9% higher on the unfiltered samples, suggesting that the presence and composition of suspended matter is a variable which may be of considerable importance.

RESULTS AND DISCUSSION

Table V includes the data from a typical ocean station in the North Atlantic. The major feature to be observed is that the strontium/chlorinity ratio is not constant with depth as has previously been accepted^{5,7}. The results indicate that there is a

TABLE V

BARIUM AND STRONTIUM ANALYSIS OF SEA WATER

(Taken IX/17/64 at 46°17'N, 35°32'W)

Depth (m)	Temp. (°C)	Chlorinity (‰)	Sr (p.p.m.)	$Sr/Cl \cdot 10^{-3}$ ($\frac{mg-at/kg}{‰}$)	Ba (p.p.b.)	$Ba/Cl \cdot 10^{-6}$ ($\frac{mg-at/kg}{‰}$)
1	16.7	19.643	6.22	3.61	2.6	1.0
57	15.08	19.775	5.77	3.33	0.2	0.1
108	13.13	19.757	6.02	3.48	82.9	30.5
302	10.95	19.594	6.21	3.62	3.1	1.2
496	9.20	19.473	6.13	3.59	6.1	2.3
751	6.25	19.397	6.00	3.52	1.3	0.5
826	5.38	19.371	5.90	3.48	3.3	1.2
1971	3.61	19.340	6.13	3.62	6.5	2.4

considerable variation in the strontium/chlorinity ratio, particularly in the uppermost 200 meters of water. These variations are well outside the statistical variability of the analytical method. The results from this ocean station are, however, the lowest values reported to date for the strontium content of sea water. In view of the results obtained in the studies concerning accuracy and precision, container adsorption, and agreement of the results of the analysis of subsequent stations by two methods, it must be concluded that the low strontium concentrations obtained in these analyses are real and that these conditions did exist at the location indicated at the time of collection.

Particular note should be taken that these are filtered samples and that unfiltered samples tend to run higher. The barium/chlorinity ratio exhibits even greater variability. The oceanographic interpretations of these and other results are being presented in another communication²¹.

The authors wish to express their gratitude to Dr. V. T. BOWEN of the Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, for his continued interest in this work and his valuable suggestions and to Dr. VICTOR T. NOSHKIN of the Woods Hole Oceanographic Institution, for pointing out the desirable qualities of CyDTA as a complexing agent and his research efforts in this area. Also thanks are due to the officers and crew of the R.V. Atlantis II for their assistance in sample collection.

SUMMARY

A process based on ion-exchange concentration and separation followed by flame photometry has been developed for the determination of strontium and barium at natural levels in sea water. These elements are stripped from 1-l samples of sea water by means of a cation-exchange resin in the calcium form and selectively eluted with CyDTA and EDTA respectively. Factors influencing the intensity of strontium and barium in hydrogen flames have been studied. The standard deviations of the method are 0.05 p.p.m. for strontium and 0.6 p.p.b. for barium and the accuracy of the method is more than sufficient to demonstrate clearly the variability of Sr/Cl and Ba/Cl ratios with depth and location.

RÉSUMÉ

Un procédé est proposé pour le dosage du strontium et du baryum dans l'eau de mer. On procède à un traitement sur résine échangeuse de cations, (sous forme calcium) et élution sélective avec CyDTA et EDTA respectivement.

On a examiné les facteurs influençant l'intensité du strontium et du baryum dans la flamme hydrogène. Les écarts standard sont de 0.05 p.p.m., pour le strontium et 0.6 p.p.b., pour le baryum; l'exactitude de la méthode est plus que suffisante pour démontrer clairement la variabilité des rapports Sr:Cl et Ba:Cl, avec la profondeur et le lieu.

ZUSAMMENFASSUNG

Zur Bestimmung natürlicher Gehalte von Strontium und Barium in Seewasser wurde ein Verfahren entwickelt, bei dem die Elemente mit Hilfe des Ionenaustauschers aus 1 Liter Seewasser abgetrennt und selektiv mit CyDTE bzw. AeDTE eluiert werden. Faktoren, die die Intensität des Strontiums und Bariums bei der anschließenden flammenphotometrischen Bestimmung mit der Wasserstofflamme beeinflussen, wurden untersucht. Die Standardabweichung der Methode beträgt 0.05 p.p.m. für Strontium und 0.6 p.p.b. für Barium. Die Genauigkeit der Methode ist mehr als ausreichend, um die eindeutigen Schwankungen der Sr:Cl- und Ba:Cl-Verhältnisse in Abhängigkeit von der Tiefe und vom Ort zu zeigen.

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THE DETERMINATION OF THORIUM, LANTHANUM AND SAMARIUM IN CERIUM(IV) NITRATE BY ACTIVATION ANALYSIS, WITH THE AID OF ELECTROPHORETIC FOCUSING OF IONS

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The separation technique based on the electrophoretic focussing of ions (EFI) has been mainly developed by SCHUMACHER *et al.*¹⁻⁴. These authors fully established the possibilities and limitations of the method. From their publications it is obvious that the maximum amount of sample for a separation by the non-continuous EFI procedure, should not exceed a few micrograms, in order to obtain neat and sharp focussing. This situation is not very promising for application to the determination of trace impurities by activation analysis, where samples up to several gram in weight may be necessary. However if one restricts oneself to the determination of minor constituents in the range of roughly 1 to 0.01%, the procedure is applicable.

The electrophoretic focussing of ions has been applied to the separation of fission products⁵⁻⁸, natural radioactivities⁹ and rare earth mixtures^{4,7,10}. The technique has also been applied to the activation analysis of inorganic minor elements in plants and soils¹¹.

EXPERIMENTAL

EFI separation

A schematic representation of the apparatus used in this work is shown in Fig. 1.

In the middle of a paper strip (22 cm by 2 cm), 100 μ l of the solution containing

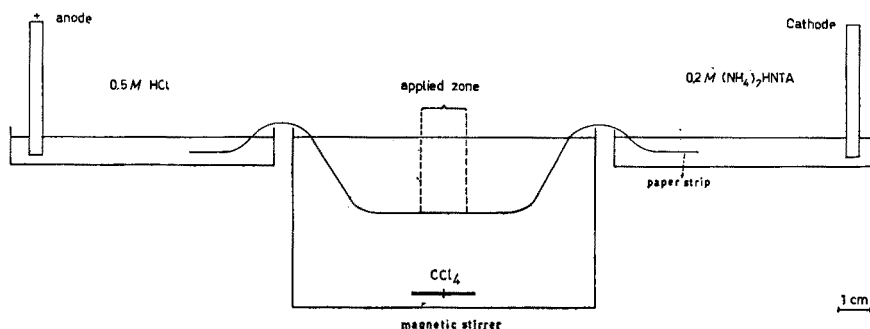


Fig. 1. EFI apparatus.

the metal ions to be separated, is spotted. The ends of the strip dip respectively into the catholyte (0.2 M (NH₄)₂(NTA)) and the anolyte (0.5 N HCl). The middle part of the paper strip, dips into a bath with carbon tetrachloride which acts as a cooling medium. Stirring with a magnetic stirrer improves the cooling action.

The anolyte and catholyte meet and diffuse into each other in the middle of the strip where the solution with the ions to be separated, was originally spotted. In the diffusion area a pH gradient builds up, following the pattern of the titration curve of the diammonium salt of nitrilotriacetic acid with hydrochloric acid.

When a potential of *ca.* 500 V is applied to the apparatus, free chloride and ammonium ions are quickly removed from the diffusion zone. The conductivity is then determined by the dissociation of the NTA acid, and is much lower than in the rest of the paper strip. This results in a decrease of the current through the strip from *ca.* 25 mA in the beginning to *ca.* 10 mA at the end of the separation over a time period of *ca.* 10 min.

As a consequence the greater part of the applied potential builds up a strong potential gradient over the diffusion zone. In this gradient, the ion metals to be separated, present as cations or complex anions, quickly move in the direction of the anode or the cathode. In doing this, they also move along the pH gradient until they reach the pH value where the average charge of the ions is zero and they are no longer influenced by the electric field.

In a matter of minutes all the ions accumulate in a very narrow zone, the width of which is determined by the steepness of the potential as well as the pH gradient. Ions with different stability constants will accumulate at different pH values and as a result they can be quantitatively separated if these stability constants are sufficiently different. A detailed treatment of the focussing procedure has been given by SCHUMACHER¹.

Activation analysis of Th, Sm and La in ammonium cerium(IV) nitrate

The relevant nuclear data and reactions are collected in Table I. It is obvious that irradiation of cerium with thermal neutrons induces a large activity, hence a chemical separation of the impurities present is unavoidable. On the other hand, the small sampling involved in the EFI technique rules out any danger which might arise from the handling of large quantities of irradiated cerium.

Thorium can best be determined by its radioactive protactinium daughter ²³³Pa, because the half-life of the ²³³Th isotope induced by a (n,γ) reaction is in-

TABLE I
NUCLEAR DATA

Stable isotopes	Abundance (%)	Reaction	Cross-section (barn)	Radio-isotope	Half-life
¹⁴⁰ Ce	88.48	(n,γ)	0.3	¹⁴¹ Ce	33 d
¹⁴² Ce	11.07	(n,γ)	1	¹⁴³ Ce	33 d
²³² Th	100	(n,γ)	7.7	²³³ Th	23.3 m
		(n,γ)β ⁻	—	²³³ Pa	27.4 d
¹⁵² Sm	26.63	(n,γ)	150	¹⁵³ Sm	47 h
¹³⁹ La	99.91	(n,γ)	8.4	¹⁴⁰ La	40.2 h

conveniently short. The danger arising from losses by adsorption on the walls of the containers, which occurs in solutions of carrier-free isotopes, can be avoided in the case of protactinium (see below).

All the elements connected with this work have absorption cross-sections large enough to induce serious neutron shadowing effects. For samarium and lanthanum, these effects were avoided by irradiating the standards of these elements in aqueous solution. For cerium and thorium the shadowing effects proved to be negligible with the aid of the straight line test (Fig. 2). Increasing amounts of thorium, as finely

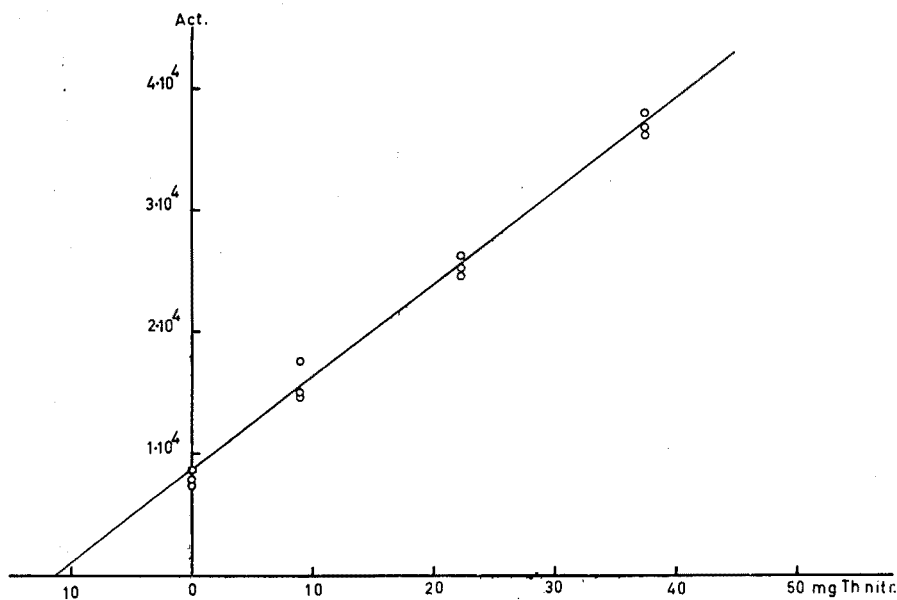


Fig. 2. Straight line test, showing the absence of neutron shadowing effects.

powdered $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ were homogeneously mixed with a constant amount (390 mg) of the powdered $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ matrix. After irradiation and chemical separation the activity of protactinium was measured and plotted against the amount of thorium added. With the least squares procedure, a straight line was plotted through the experimental points. The intercept of this line with the abscissa gives the amount of thorium impurity present in the cerium-matrix. The slope of this line corresponded, within the experimental error, to the specific activity induced in an independent but simultaneously irradiated thorium standard, consisting of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ crystals (10 mg), thus proving the absence of shadowing effects.

All irradiations were carried out in BR-1 at a flux of $4 \cdot 10^{11}$ n/cm²/sec and an irradiation time of 2 h. The method was applied to 9 different cerium samples. One of these was the original pure ammonium cerium(IV) nitrate. Four of the remaining samples were the crops of four successive recrystallizations of the original salt seeded with 1.65% thorium nitrate. The other four were the salts recovered from the filtrate.

Samples of ca. 400 mg of cerium salt and standards of 10 mg of thorium nitrate were packed in sealed silica tubes for irradiation. Standards of lanthanum

and samarium consisted of solutions containing $0.2 \mu\text{g}$ of the metal in $40 \mu\text{l}$, also sealed in silica tubes.

Chemical procedure

The cerium salts were ground to a fine powder and homogeneously mixed in a porcelain mortar. The powders were dried at 110° for 4 h to remove any adsorbed water, and were finally stored in a desiccator. In order to increase the sensitivity of the method, it was necessary to determine experimentally the largest amount of cerium which could be submitted to the EFI procedure. Under favourable conditions it appeared that up to $250 \mu\text{g}$ of cerium showed satisfactory focussing.

To avoid procedural and counting errors, samples and standards were taken through the same chemical and counting manipulations. The irradiated salts were dissolved in 4 ml of water and 1 drop of 6 N hydrochloric acid was added. Cerium(IV) was reduced to cerium(III) with sulfur dioxide gas until the initially formed white precipitate redissolved. Immediately 40 mg of $(\text{NH}_4)_2(\text{NTA})$ was added and the mixture was gently heated on a hot plate until the solution was completely clear. (The addition of an excess of NTA eliminated the adsorption of protactinium on the walls of the container. From a solution of ^{233}Pa in excess of NTA, samples were taken weekly during a period of two months and no decrease in activity could be detected that could not be accounted for by radioactive decay. After cooling, the solutions were diluted to a standard volume of 10 ml from which $25 \mu\text{l}$ was pipetted for the EFI procedure.

For this procedure, the anode solution was 0.5 N in hydrochloric acid, and the cathode liquid 0.2 M in $(\text{NH}_4)_2(\text{NTA})$ and 0.15 M in sodium acetate. The sep-

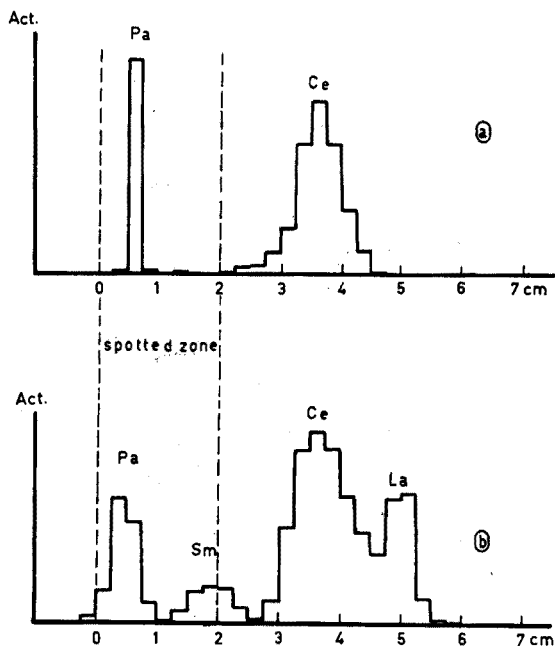


Fig. 3. Focus lines obtained with EFI procedure. (a) synthetic Th-Ce mixture; (b) Ce sample with Th, Sm and La impurity.

aration was accomplished within 12 min with a potential of *ca.* 500 V over the entire paper strip, and a current varying from 25 mA initially to 10 mA at the end.

Finally, after removal of the high voltage, the paper strip was immediately removed from the liquid and dried quickly in a jet of hot air in order to avoid focus broadening by diffusion.

The central part of the paper strip was cut into narrow strips parallel to the obtained focus lines. The strips were collected one by one in 5-ml counting vials and counted individually with a gross γ -counter. A plot of the activities as a function of the succession of the strips results in a stepwise diagram (Fig. 3), which represents the width and separation of the focus lines.

The strips contributing to a single focus line are collected in one counting vial and the corresponding γ -spectrum is recorded with a $3 \times 3''$ NaI (Tl) scintillation detector coupled to a 400-channel analyser.

Quantitative results are obtained by digital integration of the activity under the photopeaks. The following peaks were chosen for the respective elements: Pa 95–100 keV (U–X rays); Sm 103 keV; La 159 keV.

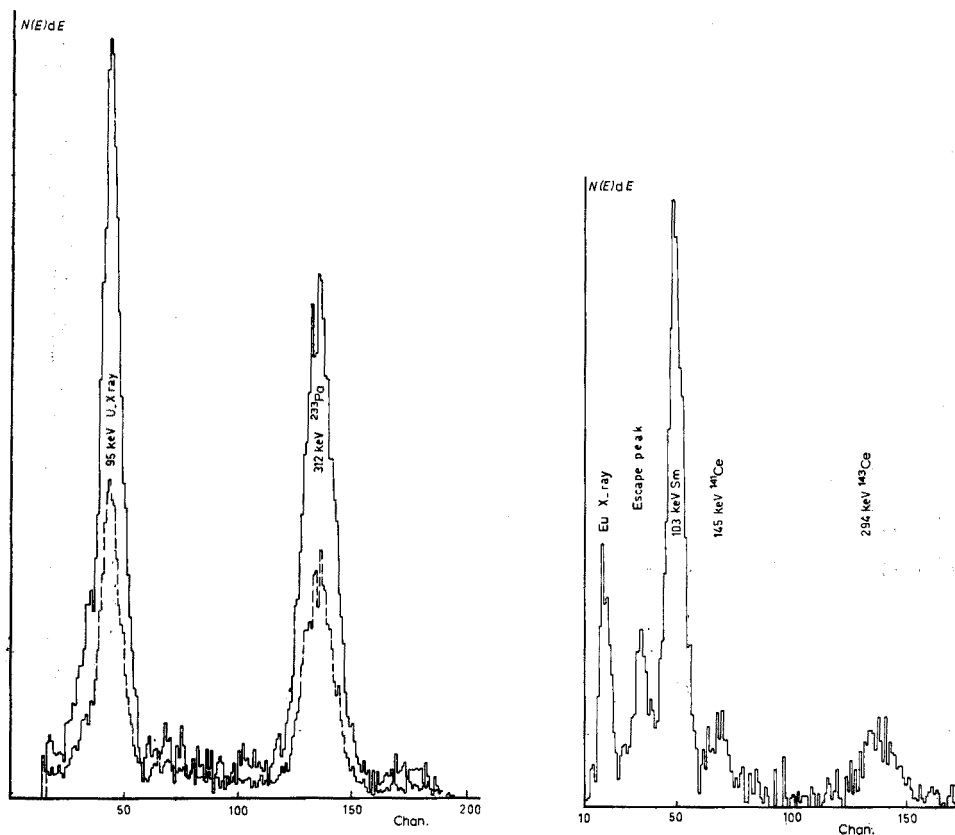


Fig. 4. γ -Spectrum of Pa focus compared with Pa standard. (—) Separated from sample; (--) pure ^{231}Pa standard.

Fig. 5. γ -Spectrum of Sm focus showing Ce contamination.

RESULTS

Typical spectra for respectively the Pa, Sm, Ce and La lines are shown in Figs. 4-7.

The radiochemical purity of the separation can be judged from Fig. 4, where the spectra of ^{233}Pa from a pure thorium standard and one separated from a cerium(IV) sample are compared.

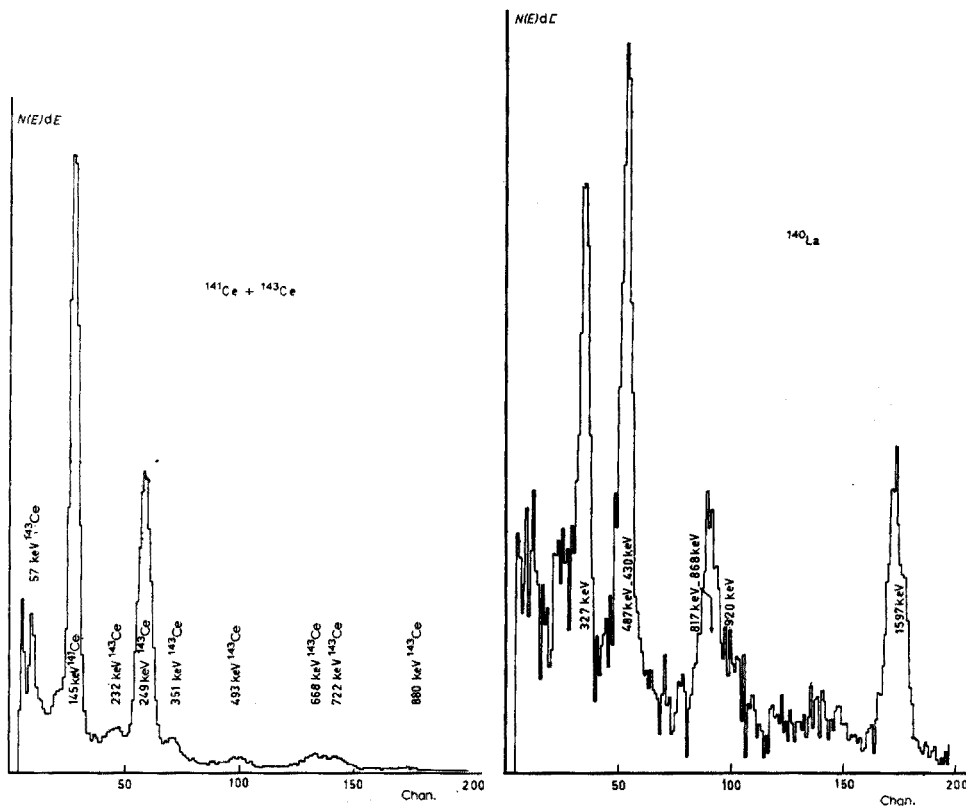


Fig. 6. Mixed γ -spectrum of ^{143}Ce and ^{141}Ce in Ce focus.

Fig. 7. γ -Spectrum of La focus.

The spectrum of the samarium line, however, shows a marked contamination by cerium activity (Fig. 5). Since this might be the case for the protactinium spectra also, the Pa and Sm spectra obtained from the cerium samples were considered as compound spectra of protactinium or samarium with cerium. The pure ^{233}Pa and ^{153}Sm activities under the appropriate photopeaks were subsequently determined with the aid of the matrix equation method previously published¹². Measurement of the cerium activity was done by means of the 145 keV peak of ^{141}Ce (Fig. 6).

The foci of cerium and lanthanum partly overlap, and in order to collect all of the lanthanum activity, part of the cerium focus has to be added. However, because of the high energy of the photopeak chosen for the determination of lanthanum, the cerium activity present does not interfere.

The results are summarized in Table II; the listed concentrations are the average of 3-12 determinations. Concentrations are expressed as p.p.m. impurity element based upon the full weight of $Ce(NH_4)_2(NO_3)_6$. The listed errors are standard deviations.

TABLE II
RESULTS FOR RECRYSTALLIZED SALT AND FILTRATE

Recrystal. sample	Th concn. (p.p.m.)	Sm concn. (p.p.m.)	La concn. (p.p.m.)	Filtrate recovered salts	Th concn. (p.p.m.)	Sm concn. (p.p.m.)	La concn. (p.p.m.)
Original	125 ± 36	14.2 ± 1.5	440 ± 25	—	—	—	—
1st crop	1490 ± 92	< 5	< 50	1st filtr.	10020 ± 150	56 ± 1	935 ± 48
2nd crop	506 ± 26	< 5	< 50	2nd filtr.	3640 ± 290	< 5	< 50
3rd crop	226 ± 27	< 5	< 50	3rd filtr.	1140 ± 190	< 5	< 50
4th crop	129 ± 41	< 5	< 50	4th filtr.	453 ± 27	< 5	< 50

The concentrations for the successive recrystallized salts and the salts recovered from the filtrate show the expected decrease. Because of the difference in oxidation state, one crystallization seems to be sufficient to reduce the samarium and lanthanum concentration below the detection limit of the method.

The following detection limits were established, based on the specific activity of the standards and the background effect of the counting apparatus: Th 0.1 μ g; Sm $5 \cdot 10^{-3}$ μ g; La $4 \cdot 10^{-2}$ μ g. These limits are valid for an irradiation time of 2 h at a thermal neutron flux of $4 \cdot 10^{11}$ n/cm²/sec, and could consequently easily be improved by a factor of more than 100.

Acknowledgments are due to Prof. Dr. J. HOSTE for the interest taken in this investigation, and to Prof. G. FREDERICK SMITH for providing the cerium samples.

SUMMARY

Thorium, lanthanum and cerium were determined in ammonium cerium(IV) nitrate. The chemical separation was carried out by electrophoretic focussing of ions (EFI) in a matter of minutes. The small amount of sample possible in this separation technique is the main limit for the sensitivity of the procedure. With an irradiation time of 2 h at a thermal flux of $4 \cdot 10^{11}$ n/cm²/sec, the lower limits are: Th 0.1 μ g; La $4 \cdot 10^{-2}$ μ g; Sm $5 \cdot 10^{-3}$ μ g.

RÉSUMÉ

Une méthode par activation est proposée pour le dosage du thorium, du lanthane, et du samarium dans le nitrate de cérium(IV). La séparation chimique est effectuée par électrophorèse ("electrophoretic focussing of ions"). La faible quantité d'échantillon utilisable dans cette technique est la principale limite pour la sensibilité du procédé. Avec un temps d'irradiation de 2 h, et un flux thermique de $4 \cdot 10^{11}$ n/cm²/sec, les limites inférieures sont: Th 0.1 μ g; La $4 \cdot 10^{-2}$ μ g; Sm $5 \cdot 10^{-3}$ μ g.

ZUSAMMENFASSUNG

Thorium, Lanthan und Cer wurden in Ammonium-Cer(IV)-nitrat bestimmt. Die chemische Trennung geschah durch elektrophoretische Fokussierung der Ionen. Die geringe Probenmenge, welche bei dieser Trennungstechnik verwendet werden kann, ist die Hauptgrenze für die Empfindlichkeit des Verfahrens. Mit einer Bestrahlungszeit von 2 h und einem thermischen Fluss von 4×10^{11} n/cm²/sec lag die untere Grenze bei 0.1 μg Th, 4×10^{-2} μg La, 5×10^{-3} μg Sm.

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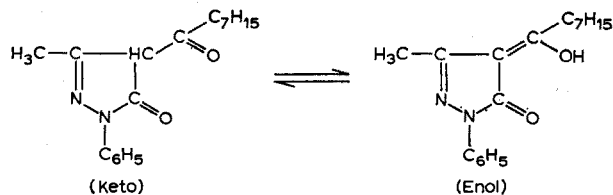
A NEW METHOD FOR THE CARRIER-FREE PRODUCTION OF ^{90}Y FROM ^{90}Sr - ^{90}Y MIXTURE AND ^{89}Sr FROM NEUTRON-IRRADIATED Y_2O_3

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^{90}Y is extensively used as a tracer particularly in biological investigations and as a means of providing intense local radiations to various parts of the internal body. It is also required as a standard β^- source in nuclear spectroscopy. Various procedures for its separation from ^{90}Sr have been reported (*e.g.* Refs. 1-9). ^{89}Sr is also required as a tracer in plant and animal nutrition studies. Neutron irradiation of natural strontium gives ^{89}Sr with low specific activity owing to a low neutron cross section. Carrier-free ^{89}Sr is more suitably produced by the (n,p) reaction on natural yttrium. Various procedures for the separation of strontium activities have been reported¹⁰. The present investigation was undertaken to study the liquid-liquid extraction behaviour of 1-phenyl-3-methyl-4-caprylpyrazolone-5 (PMCyP) in order to devise carrier-free procedures for ^{90}Y and ^{89}Sr . The method of synthesis and the study of physico-chemical constants of 4-acyl derivatives of 1-phenyl-3-methylpyrazolone-5 (excluding 4-capryl derivatives) as chelating agents have been reported by JENSEN^{11,12}.



PMCyP is a β -diketone and exists in both the keto and enol forms. The yellow coloured enol form is obtained by recrystallisation from chloroform while the colourless keto form is obtained by recrystallisation from aqueous ethanol. Both forms were found to behave similarly. In the present work, the keto form was isolated for liquid-liquid extraction study.

EXPERIMENTAL

Reagents

All the reagents obtained were of AnalaR grade and were used without further purification. 1-Phenyl-3-methyl-4-caprylpyrazolone-5 was prepared at Risø and used

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as a 1% solution in methyl isobutyl ketone (MIBK). The radionuclides ^{89}Sr , ^{85}Sr , ^{90}Y , ^{90}Sr - ^{90}Y and ^{86}Rb used as tracers were also prepared at Risø.

Buffers

Standard buffers of KCl + HCl, HCl + potassium hydrogen phthalate, NaOH + potassium hydrogen phthalate, NaOH + boric acid were used to cover pH 1–10. pH measurements were made with a Radiometer pH meter type PHM 22.

Radioassay

The characteristic radiations were measured in an end-window G.M. counter. A β - γ ionization chamber (VIBRON ELECTROMETER Model 33 C) was used for measuring the final yield. A 512-channel analyser coupled with a $3 \times 3''$ NaI(Tl) crystal and a single-channel analyser coupled with an anthracene crystal were used to assay the radiochemical purity.

Preparation of 1-phenyl-3-methyl-4-caprylpyrazolone-5

1-Phenyl-3-methylpyrazolone-5 (17.4 g) was placed in a flask equipped with a stirrer, separatory funnel and a reflux condenser and dissolved in 50 ml of dioxane with gentle heating. Calcium hydroxide (10 g) was added and 10 ml of capryl chloride (prepared at Risø) were added dropwise during 1 min. The mixture was stirred and refluxed for 30 min with infrared lamps till the yellow calcium complex was formed. The complex was decomposed by adding 100 ml of 3 M hydrochloric acid which caused cream coloured crystals to separate. The crystals were recrystallised with ethanol-water containing a few ml of dilute hydrochloric acid to destroy any undecomposed calcium complex (yield 83%; m.p. 76°).

Extraction procedure

To 2 ml of a solution adjusted to a definite pH, a tracer solution (0.1–0.2 ml, activity 10,000–15,000 counts/min and an ion concentration of 5–10 $\mu\text{g}/100$ –200 μl) were added. A portion (2 ml) of 1% PMCyP in MIBK was then added. The phases were shaken for 1 min, centrifuged, separated and counted. The activity of the organic phase was measured before and after equilibration. The activities in the aqueous phase were also measured for material balance.

Target preparation

Yttrium oxide (99.6%; 25.39 mg) was sealed in a standard aluminium isotope can and irradiated in the core of DR 3 for 50 days in two periods with a pile factor of 350 for fast neutrons and 1500 for thermal neutrons. During the irradiation, 712.9 mC ^{90}Y , 169 μC ^{89}Sr and 0.18 μC ^{86}Rb were calculated to grow.

Extraction curves

The extraction curves of the elements with PMCyP in MIBK are reproduced in Fig. 1 while the values of percentage extraction (E) at different pH values are reproduced in Table I. The activities in the aqueous phase indicate the ionic concentration of the elements in the respective phases. The results shown are the mean of 3 experiments and refer to the concentration in the organic phase. Viscous emulsions were obtained above pH 6 which became clear on centrifugation.

From Fig. 1, it is evident that yttrium is extracted almost quantitatively at pH 2.8–5.4 while strontium is extracted quantitatively above pH 8.6. The sudden drop in the extraction of yttrium above pH 5.4 is probably due to hydrolysis. The quantitative extraction of strontium and yttrium at different pH values allows the separation of these two elements from each other.

Rubidium is not extracted at all and therefore does not interfere. On the basis of the data presented various radiochemical procedures were devised as follows.

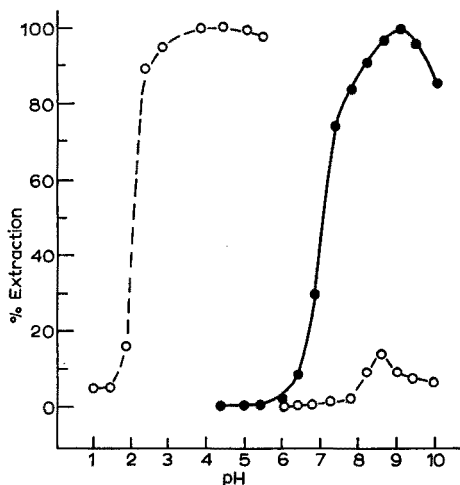


Fig. 1. Effect of pH on the extraction of yttrium (○--○) and strontium (●—●) with PMCyP in MIBK.

TABLE I

% EXTRACTION AT VARIOUS pH VALUES

Elements	pH = 1.0	pH = 2.3	pH = 5.0	pH = 7.3	pH = 9.0	pH = 10
^{90}Y	4.7	90.9	100	3.6	9.5	8.0
^{89}Sr	0.0	0.0	1.09	75	100	97.3
^{86}Rb	0.0	0.0	0.0	0.0	0.0	0.0

Separation of ^{90}Y from ^{90}Sr - ^{90}Y mixture

An aliquot of ^{90}Sr - ^{90}Y solution was heated to dryness and the residue was dissolved in 5 ml of aqueous solution preadjusted at pH 3.8 (2.63 ml of 0.1 M HCl + 50 ml of 0.1 M potassium hydrogen phthalate diluted to 100 ml); 25 ml of 1% PMCyP in MIBK was added and shaken for 1 min with a magnetic shaker. The phases were centrifuged and separated.

The aqueous phase was reserved for further production of ^{90}Y . ^{90}Y was back-extracted from the organic phase with 0.4 M hydrochloric acid. Further purification of ^{90}Y was done by evaporating the solution to dryness and fuming with concentrated nitric acid to destroy any organic matter. The final carrier-free $^{90}\text{YCl}_3$ solution was stored in 0.1 M hydrochloric acid.

Separation of ^{89}Sr from the irradiated yttrium oxide target

The irradiated target was dissolved in 3 ml of 6 *M* hydrochloric acid and the solution evaporated to dryness. ^{90}Y was removed by the method described above. The aqueous solution free from yttrium activities was evaporated to dryness and the residue was dissolved in 25 ml of aqueous solution preadjusted at pH 9.0 (21.30 ml of 0.1 *M* NaOH + 50 ml of 0.1 *M* H_3BO_3 diluted to 100 ml); 25 ml of 1% PMCyP in MIBK was added and the mixture shaken for 1–2 min. The phases were then centrifuged and separated. The aqueous phase was discarded and ^{89}Sr from the organic phase was stripped with 0.2 *M* hydrochloric acid. Further purification was done by heating to dryness and fuming with concentrated nitric acid to destroy organic matter. The final solution of $^{89}\text{SrCl}_2$ was stored in 0.1 *M* hydrochloric acid.

DISCUSSION

The radiochemical procedure for ^{90}Y from ^{90}Sr – ^{90}Y mixtures was tested by separating ^{90}Y from a synthetic mixture containing 50 μC ^{90}Y and 50 μC ^{85}Sr . An aliquot of purified ^{90}Y on radioassay gave no γ -peak. The radiochemical separation of ^{89}Sr was tested by making synthetic mixture containing 50 μC ^{90}Y , 15 μC ^{86}Rb and 50 μC ^{85}Sr . The purified ^{85}Sr gave no hard β -radiation due to ^{90}Y . The decontamination factor for yttrium from strontium and *vice versa* was found to be very good and no interference could be observed in either of the activities. The whole procedure took only a few minutes apart from the time required for the evaporation of the solutions. More than 95% of the calculated activities were recovered.

The extraction system with 1-phenyl-3-methyl-4-caprylpyrazolone-5 thus appears to be useful for the separation of strontium from yttrium and *vice versa*. The easy preparation of this reagent and stability during the storage are also big advantages.

The author is grateful to B. S. JENSEN for his help in the preparation of the reagent and to K. HEYDORN, B. KRUSE and U. JACOBSEN for providing the facilities. The award of a fellowship by the Danish Atomic Energy Commission under a bilateral agreement with the Pakistan Atomic Energy Commission is gratefully acknowledged.

SUMMARY

The extraction of strontium(II) and yttrium(III) ions from aqueous solutions at various pH values into methyl isobutyl ketone containing 1-phenyl-3-methyl-4-caprylpyrazolone-5 is described. Quantitative extraction of Sr and Y at pH 8.6–10 and pH 2.8–5.4 respectively is utilized for the carrier-free production of ^{90}Y from ^{90}Sr – ^{90}Y mixtures and ^{89}Sr from neutron-irradiated yttrium oxide. A clean separation of these elements from each other and more than 95% calculated activities were recovered.

RÉSUMÉ

On décrit une extraction du strontium et de l'yttrium en solution aqueuse à divers pH, au moyen de méthylisobutylcétone, renfermant de la 1-phényl-3-méthyl-4-

caprylpyrazolone-5. Une extraction quantitative du strontium et de l'yttrium à pH 8.6–10 et pH 2.8–5.4, respectivement, est utilisée pour la production de ^{90}Y d'avec les mélanges ^{90}Sr – ^{90}Y et ^{89}Sr à partir d'oxyde d'yttrium irradié aux neutrons. On a obtenu une bonne séparation de ces éléments les uns des autres et plus de 95% d'activités calculées.

ZUSAMMENFASSUNG

Die Extraktion von Strontium(II)- und Yttrium(III)-Ionen aus wässrigen Lösungen bei verschiedenen pH-Werten mit Isobutylketon, das 1-Phenyl-3-methyl-4-caprylpyrazolon-5 enthält, wird beschrieben. Die quantitative Extraktion von Strontium und Yttrium bei pH 8.6–10 bzw. 2.8–5.4 wird zur trägerfreien Herstellung von ^{90}Y aus ^{90}Sr – ^{90}Y -Mischungen und ^{89}Sr aus neutronenbestrahltem Yttriumoxid verwendet. Eine saubere Trennung dieser Elemente von jedem anderen und eine Rückgewinnung von mehr als 95% der berechneten Aktivität wurde erreicht.

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LIQUID-LIQUID EXTRACTION METHODS FOR THE PRODUCTION OF CARRIER-FREE ^{115}Cd AND $^{89,90}\text{Sr}$ FROM FISSION PRODUCTS

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^{90}Sr is extensively used as a β -emitter. It occurs near one of the peaks of the mass-yield distribution curve during the fission of ^{235}U . The commonest method for separation is based on the precipitation of strontium nitrate although some ion-exchange and solvent-extraction techniques have been described¹. Cadmium is also formed during the fission and its presence acts as a poison in the fuel element. Various procedures for its separation from spallation^{2,3} and fission products⁴ have been reported in the literature. The most rapid one, devised by DEVOE AND MEINKE⁵, utilised dithizone solution in chloroform for extracting carrier-free activities in strongly basic solution. The extraction^{6,7} of cadmium from hydrochloric acid with triisooctylamine and its separation from its spallation products using high-molecular-weight amines has been reported in the literature⁸. The present investigation was undertaken to study the liquid-liquid extraction behaviour of 1-phenyl-3-methyl-4-caprylpyrazolone-5 (PMCyP) for fission product elements. The method of synthesis of 4-acyl derivatives of 1-phenyl-3-methylpyrazolone-5 and their physical and chemical properties as chelating agents has been reported by JENSEN^{8,9}. The use of PMCyP in methyl isobutyl ketone (MIBK) has been previously reported for the production of ^{90}Y from ^{90}Sr - ^{90}Y mixture, ^{89}Sr from irradiated Y_2O_3 ¹⁰ and also for the carrier-free production of ^{54}Mn , ^{58}Co , ^{59}Fe from irradiated iron, nickel and cobalt¹¹. This paper describes a simple and rapid procedure for separating carrier-free ^{115}Cd and $^{89,90}\text{Sr}$ from fission products.

The separation of ^{115}Cd and $^{89,90}\text{Sr}$ is based on their quantitative extraction with PMCyP at pH 5.4 and pH 9.0 respectively. The interfering ions, *i.e.* rare earths along with other trivalent ions, are removed at pH 1-2.8. Further purification of ^{115}Cd is achieved by repeating the extraction cycle in the presence of thiocyanate ions while $^{89,90}\text{Sr}$ is extracted in the presence of ammonium sulphate. More than 90% ^{115}Cd and 80% added strontium activities with good decontamination factors can be recovered. The procedures require only a few minutes in addition to the time required for evaporating the solutions.

EXPERIMENTAL

Reagents and apparatus

These were the same as described previously¹¹. The radio-assay procedure was

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also done in the same way. The fission product mixture was provided by the Health Physics Division.

Extraction procedure

To 2 ml of a buffered solution containing tracer concentrations of the radio-nuclides (10,000 counts/min), 2 ml of 1% PMCyP in MIBK were added and shaken for 1 min. The phases were centrifuged, separated and counted. The activities in the organic phase were measured before and after equilibration by counting the characteristic radiations. The activities in the aqueous phase were also measured for material balance.

Recovery of ^{115}Cd from the fission products

To an aliquot of fission product, 2 ml of aqua regia were added and evaporated to dryness. The residue was dissolved in aqueous solution buffered at pH 2.8 (26.42 ml 0.1 M HCl + 50 ml 0.1 M potassium hydrogen phthalate diluted to 100 ml); 25 ml of 1% PMCyP in MIBK were added and shaken for 1 min. The extraction cycle was repeated and the organic layer was discarded. The aqueous layer was evaporated to dryness and the residue was dissolved in aqueous solution buffered at pH 5.4 (35.45 ml 0.1 M NaOH + 50 ml 0.1 M potassium hydrogen phthalate diluted to 100 ml); 25 ml of 1% PMCyP in MIBK were added and the phases were shaken for 1 min, centrifuged and separated. The aqueous layer was reserved for $^{89,90}\text{Sr}$ (Solution A). From the organic layer ^{115}Cd activities were stripped with 1 M hydrochloric acid. The acid solution was evaporated to dryness and the residue dissolved in a mixture containing 8 ml of aqueous solution buffered at pH 5.4 and 2 ml of 5 M ammonium thiocyanate. The ^{115}Cd activity was extracted by shaking with 25 ml of PMCyP in MIBK for 1 min. From the organic layer the cadmium activity was back-extracted with 5 ml of 1 M hydrochloric acid. Further purification was done by heating the solution with aqua regia to dryness to destroy any organic matter. The final solution of $^{115}\text{CdCl}_2$ was stored in 0.1 M hydrochloric acid.

Recovery of $^{89,90}\text{Sr}$ from fission products

Solution A was evaporated to dryness and dissolved in a mixture containing 8 ml of aqueous solution buffered at pH 9.0 (21.30 ml 0.1 M NaOH + 50 ml 0.1 M boric acid, diluted to 100 ml) and 1 ml of 2 M ammonium sulfate. Then 10 ml of 1% PMCyP in MIBK were added and the phases were shaken for 1 min, centrifuged and separated. The strontium activity was back-extracted from the organic phase with 0.1 M hydrochloric acid. The extraction cycle was repeated to obtain a better decontamination factor. The final solution of $^{89,90}\text{SrCl}_2$ was stored in 0.1 M hydrochloric acid.

RESULTS AND DISCUSSION

The activities of the aqueous and organic phases indicate the concentrations of the elements in the respective phases. The results shown in Table I are the mean of 4 runs and refer to the percentage extraction (E) of the elements into the organic phase at different pH values of the aqueous phase. The extraction curves of various elements are shown in Figs. 1-4.

TABLE I

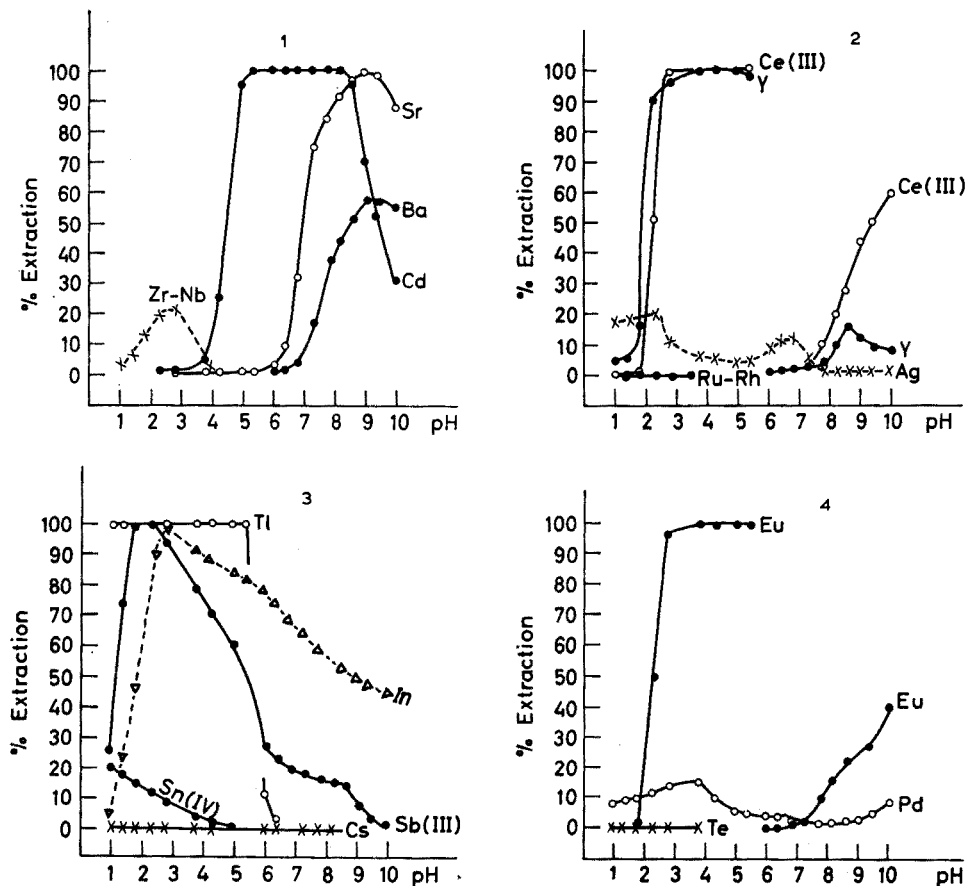
% EXTRACTION OF VARIOUS ELEMENTS WITH 1-PHENYL-3-METHYL-4-CAPRYLPYRAZOLONE-5 IN MIBK FROM AQUEOUS SOLUTIONS AT VARYING pH VALUES

	pH						
	1.0	2.8	3.8	5.4	7.3	8.2	9.0
Sr	0.0	1.8	1.06	1.09	75	91.2	100
Cd	0.0	3.0	5.0	100	100	100	70
Zr-Nb	4.0	21.5	0.2	0.0	0.0	0.0	0.0
Cs	0.0	0.0	0.0	0.0	3.6	0.0	0.0
Eu	0.5	100	100	100	0.0	18	25
Sb	26	96	78	50	19	15	14
Sn	20	9.0	4.8	0.01	0.0	0.0	0.0
Se	0.01	1.0	0.5	0.0	0.0	0.0	0.0
Ba	0.0	0.25	0.11	0.45	17.04	44.7	58.2
Y	4.7	96.5	100	98.5	3.6	10.4	9.5
Pd	8.0	14.7	15.1	5.2	1.0	0.6	1.0
Ag	17.4	10.0	6.0	5.0	5.2	0.8	0.3
Tl	100	100	100	100	3.6	0.0	0.0
Ce	0.2	100	100	100	3.6	20	44
Ru	0.0	0.0	0.0	0.0	0.0		
Rh	0.0	0.0	0.0	0.0	0.0		
Te	0.0	0.0	0.0	0.0	0.0		
In	4.7	99.5	89.2	77.7	62.9	54.0	48.0

From the extraction data it is obvious that among the major fission product elements, Cs, Ru, Rh are not extracted over the whole range of pH while zirconium and niobium are extracted up to 21.5% at pH 2.3 without showing any significant contribution at higher pH. Trivalent ions like yttrium, rare earths, indium and antimony are extracted almost quantitatively at pH 2.8. Palladium, silver, strontium, and cadmium are extracted up to 14.7, 10.0, 1.8 and 3.0% respectively at pH 2.8. Thus the final yield of strontium and cadmium is not badly affected. Cadmium can be recovered quantitatively at pH 5.4 with a little contamination from strontium, palladium and silver which are masked with thiocyanate in the reextraction cycle. The radiochemical procedure was tested by separating the ^{115}Cd activities from a synthetic fission product mixture containing $50\ \mu\text{C}$ ^{115}Cd , $10\ \mu\text{C}$ ^{95}Zr - ^{95}Nb , $10\ \mu\text{C}$ ^{137}Cs , $8\ \mu\text{C}$ ^{90}Sr - ^{90}Y , $4.8\ \mu\text{C}$ ^{106}Ru - ^{106}Rh , $10\ \mu\text{C}$ ^{103}Pd , $15\ \mu\text{C}$ ^{111}Ag , $20\ \mu\text{C}$ ^{141}Ce , $8\ \mu\text{C}$ ^{125}Sb , $8\ \mu\text{C}$ ^{113}Sn , $10\ \mu\text{C}$ $^{114\text{m}}\text{In}$, $8\ \mu\text{C}$ $^{123\text{m}}\text{Te}$, $10\ \mu\text{C}$ ^{152}Eu , and $8\ \mu\text{C}$ ^{133}Ba . More than 90% of the added cadmium activity was recovered. The γ -spectrum of ^{115}Cd separated from all the above elements and the supplied fission products showed no contamination from foreign ions when compared with the standard source.

The radiochemical separation of $^{89,90}\text{Sr}$ is based on the removal of almost all the foreign ions at pH 2.8 and 5.4. Palladium and silver show negligible extraction at pH 9.0 while up to 58.5% of barium is extracted. The extraction of strontium at pH 9.0 in the presence of ammonium sulfate decreases the barium contamination to 4% in the single extraction and this is further decreased in the reextraction cycle. Since the fission products used were 6 months old, all the barium activities had decayed and no interference could be observed but in a freshly prepared synthetic fission product mixture, the final ^{89}Sr activities on γ -analysis showed very weak γ -rays due to ^{133}Ba . The radiochemical procedure was tested by separating ^{89}Sr

activities from a mixture containing $20 \mu\text{C}$ ^{89}Sr , $20 \mu\text{C}$ ^{133}Ba , $10 \mu\text{C}$ ^{137}Cs , $5 \mu\text{C}$ ^{95}Zr - ^{95}Nb , $5 \mu\text{C}$ ^{106}Ru - ^{106}Rh , $10 \mu\text{C}$ ^{90}Y , $5 \mu\text{C}$ ^{103}Pd , $10 \mu\text{C}$ ^{111}Ag , $20 \mu\text{C}$ ^{115}Cd , $8 \mu\text{C}$ ^{113}Sn , $7.5 \mu\text{C}$ $^{123\text{m}}\text{Te}$, and $10 \mu\text{C}$ ^{125}Sb . More than 80% of the added strontium activity was recovered and the time required to obtain the final product was 1.5 h.



Figs. 1-4. Effect of pH on the extraction of (1) Sr, Ba, Cd, Zr-Nb, (2) Ce(III), Y, Ag, Ru and Rh, (3) In, Tl, Sb(III), Sn(IV) and Cs, (4) Eu(III), Pd(II) and Te, with 1% PMCyP in MIBK.

Decontamination study

Decontamination factors were calculated by mixing inactive cadmium and strontium with a known activity of the foreign tracer. The values obtained are shown in Table II. In the cases of ^{115}Cd and ^{89}Sr no activity was observed for Y, Ru, Rh, Cs, Zr-Nb, Ce(III), Eu(III), In or Te. In the case of strontium, no activity was observed with cadmium present.

The losses of activity occurring in different parts of the procedures were estimated to be as shown in Table III.

A very good separation of ^{115}Cd and $^{89,90}\text{Sr}$ from fission products was achieved with PMCyP in MIBK from aqueous solution. The extraction of about 30 elements with this reagent was studied from the viewpoint of utilization of the data obtained

to resolve radiochemical problems. In most of the cases, the equilibrium was established in less than 1 min and it was found that PMCyP in MIBK is a very effective extractant for alkaline earths, rare earths, many trivalent metals and divalent metals. The factors of economy, easy extractability, easy preparation of the reagent, stability during storage and working efficiency are other points in favour of this reagent.

TABLE II
DECONTAMINATION FACTORS

	^{115}Cd	^{89}Sr		^{115}Cd	^{89}Sr
Sr	$1.5 \cdot 10^6$	—	Sn(IV)	$6 \cdot 10^7$	$1 \cdot 10^7$
Ba	$6 \cdot 10^6$	$1 \cdot 10^3$	Pd(II)	$1 \cdot 10^5$	$1 \cdot 10^4$
Sb(III)	$1 \cdot 10^6$	$1 \cdot 10^6$	Ag	$3 \cdot 10^6$	$1 \cdot 10^6$

TABLE III
ESTIMATED ACTIVITY LOSSES IN PROCEDURES

Steps	% losses of ^{115}Cd	% losses of ^{89}Sr
Removal of rare earths and trivalent ions etc.	4	1.8
Removal of cadmium	—	1.0
Extraction	1.3 ^a	5.0 ^b
Miscellaneous	3.0	3.0

^a In presence of thiocyanate.

^b In presence of ammonium sulphate.

The author is grateful to B. S. JENSEN for his help in the preparation of the reagent and important discussions and to K. HEYDORN, B. KRUSE and U. JACOBSEN for providing the facilities. The award of a fellowship by the Danish Atomic Energy Commission under a bilateral agreement with the Pakistan Atomic Energy Commission is gratefully acknowledged.

SUMMARY

The extraction of fission product elements with 1-phenyl-3-methyl-4-capryl-pyrazolone-5 at various pH values has been investigated. The quantitative extraction of cadmium at pH 5.4 and that of strontium at pH 9.0 is utilised in devising procedures for the recovery of ^{115}Cd and $^{89,90}\text{Sr}$ from the fission products. Good decontamination factors and more than 90% ^{115}Cd and 80% $^{89,90}\text{Sr}$ activities were recovered.

RÉSUMÉ

On a examiné l'extraction des éléments de produit de fission à l'aide de 3-méthyl-4-capryl-pyrazolone-5 à divers pH. L'extraction quantitative du cadmium à pH 5.4 et celle du strontium à pH 9.0 sont utilisées pour la récupération du ^{115}Cd et du $^{89,90}\text{Sr}$ dans des produits de fission. On obtient ainsi de bons facteurs de décontamination et des activités supérieures à 90% ^{115}Cd et 80% $^{89,90}\text{Sr}$.

ZUSAMMENFASSUNG

Die Extraktion von Spaltproduktelementen mit 1-Phenyl-3-methyl-4-capryl-pyrazolon-5 bei verschiedenen pH-Werten wurde untersucht. Die quantitative Extraktion von Cadmium beim pH 5.4 und von Strontium beim pH 9.0 wird für die Entwicklung eines Verfahrens zur Rückgewinnung von ^{115}Cd und $^{89,90}\text{Sr}$ aus Spaltprodukten verwendet. Gute Dekontaminationsfaktoren und mehr als 90% der ^{115}Cd - und 80% der $^{89,90}\text{Sr}$ -Aktivitäten wurden gewonnen.

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CONSTRUCTION OF DEMOUNTABLE HOLLOW-CATHODE LAMPS FOR STIMULATING EMISSION OF ORGANIC COMPOUNDS

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The hollow cathode has been eminently successful as a source of radiation for atomic absorption spectroscopy. It provides a spectrum with very narrow emission lines, and this fact has contributed significantly to the sensitivity and selectivity of atomic absorption spectroscopy. It was decided to study the same system as a source of radiation for molecular emission. It was anticipated that the process of excitation would be similar to that encountered with atoms; *i.e.*, ionization and acceleration of the filler gas causing excitation through collision with the cathode surface.

The commercially available elemental hollow cathode is usually sealed. An abundant supply of excitable sample element is available in the cathode. This is usually sufficient for several hundred hours of operation. However, it was not expected that this would be true if molecules were used in place of atoms in the cathode, particularly the more volatile organic compounds. It was therefore decided to design a demountable hollow cathode in which the sample compound could be readily replaced. The demountable hollow-cathode lamp reported by KOIRTYOHANN AND FELDMAN¹ for use with metals and metal salts was adopted for the basic design of the first demountable units to be used on this project. A model was therefore constructed which was very similar to that described by these workers.

It was found experimentally that this lamp was not well suited for stimulating the emission of organic compounds for several reasons, the most important one being that of electrical shorting. The dimensions of this lamp were quite small; the distance from anode to cathode was short, and sparking took place between them.

Upon introduction of organic solids, this problem was compounded by deposition of carbonaceous materials on sides, electrodes, and upon the small quartz window. In general, spectra obtained from this lamp were unstable and erratic, and exceedingly difficult to reproduce.

Therefore, this lamp was discarded and a series of demountable all-glass lamps were constructed. Their performance is described below.

EXPERIMENTAL

Equipment

The schematic diagram of the equipment is shown in Fig. 1. All data reported here were obtained using a Jarrel-Ash Atomic Absorption Spectrophotometer with modifications. A coarse and fine gain control was installed in the amplifier and the

optical lens mounts were reversed to eliminate the triple-pass system normally used in atomic absorption work. The DC power supply to the hollow cathode was the same as that used by the Jarrel-Ash instrument in atomic absorption work.

Reagents

All chemicals employed were of reagent-grade quality and, with the exception of distilling triethylphosphate, no further purification steps were taken.

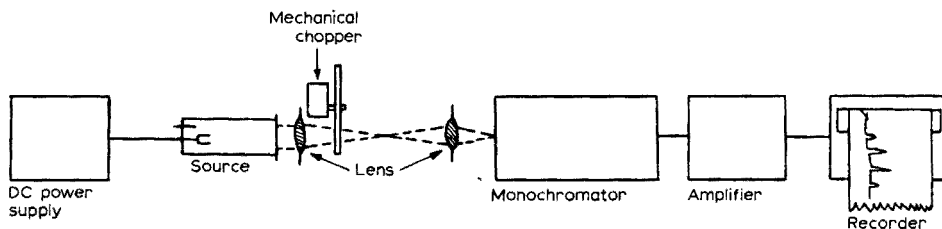


Fig. 1. Schematic diagram of equipment.

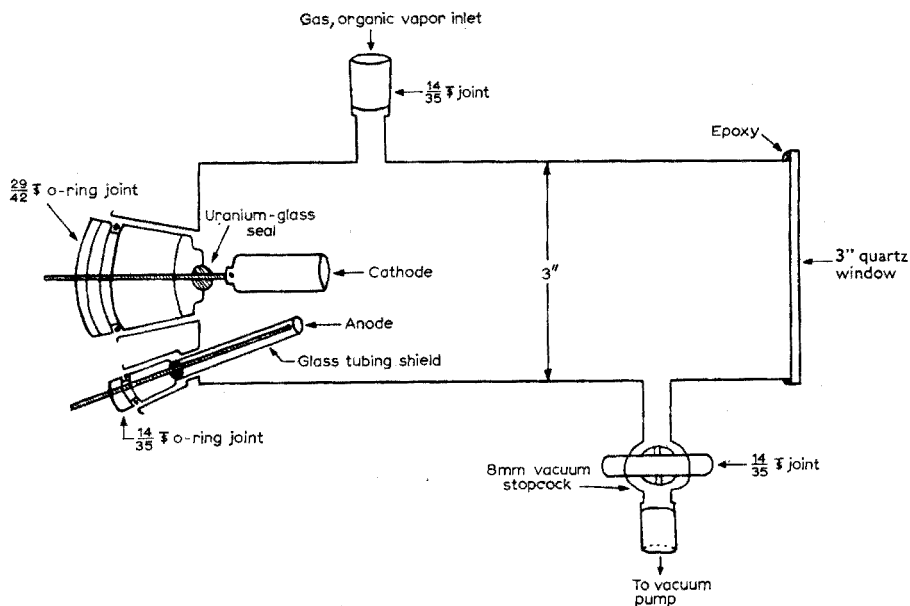


Fig. 2. Demountable hollow-cathode lamp, Model I.

Construction of demountable hollow-cathode lamps

The lamp illustrated in Fig. 2 was constructed to have maximum flexibility. It consisted of a 10-in section of Pyrex glass tubing of 3 in diameter, which had been fitted with a quartz window, vacuum stopcock, and ASCO o-ring joints. The cathode was nickel-plated steel and the anode was nickel. Uranium glass bead seals were employed for sealing cathode and anode in the glass joints. The quartz window was sealed to the tube via low vapor pressure epoxy (Varian Associates). The anode and cathode were made removable to facilitate cleaning and replacement. Although the

lamp was designed to be operated under continuous pumping, the use of the vacuum stopcock allowed operation without pumping when necessary.

A later model was altered to permit operation under highly controlled conditions. The number of joints was reduced and it employed a side stem sealed directly to the chamber to contain organic liquids. Although the flexibility of this lamp was reduced, it was found that air leakage was reduced to a low level. This lamp is illustrated in Fig. 3.

Operation of lamps

The lamp illustrated in Fig. 2 was employed for the preliminary investigation

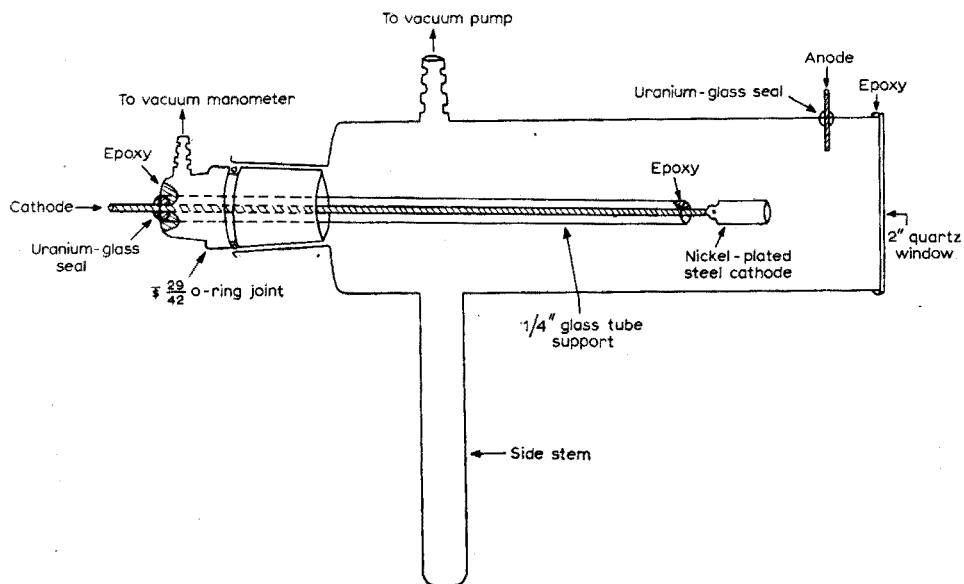


Fig. 3. Demountable hollow-cathode lamp. Model II.

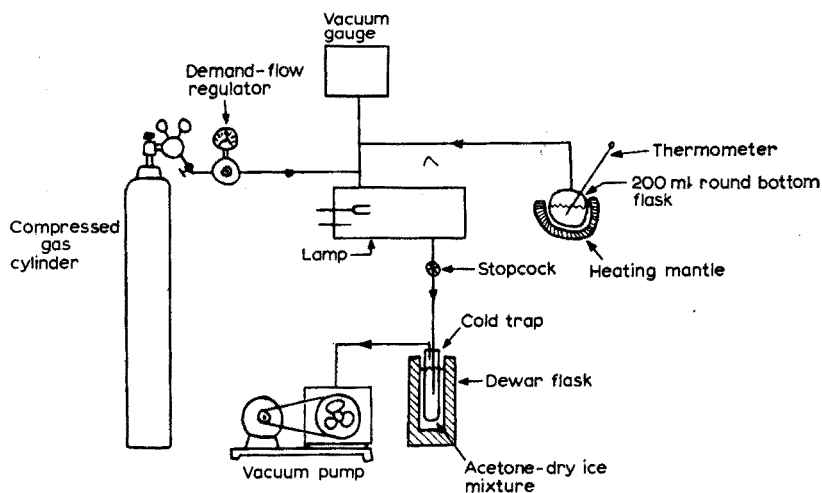
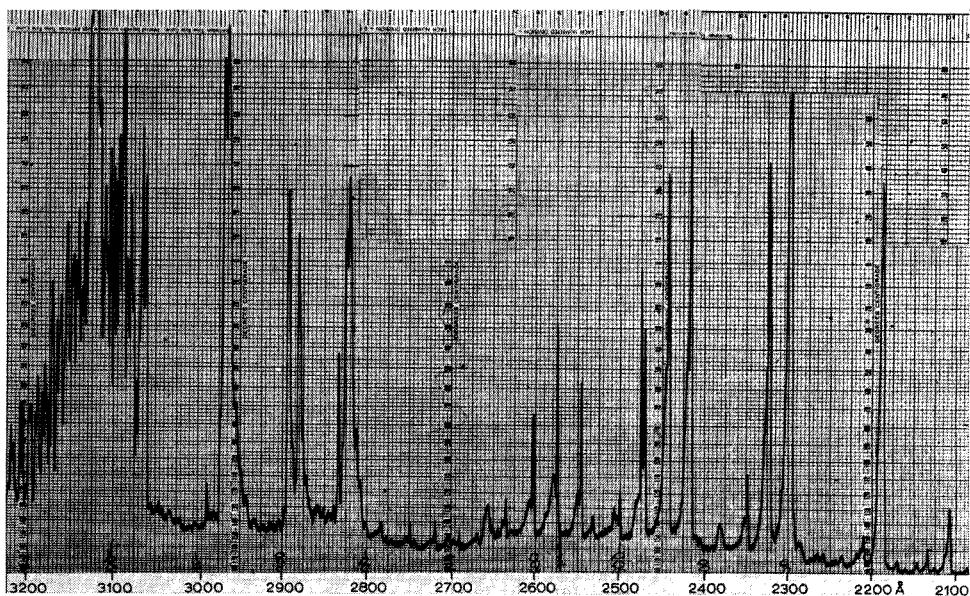


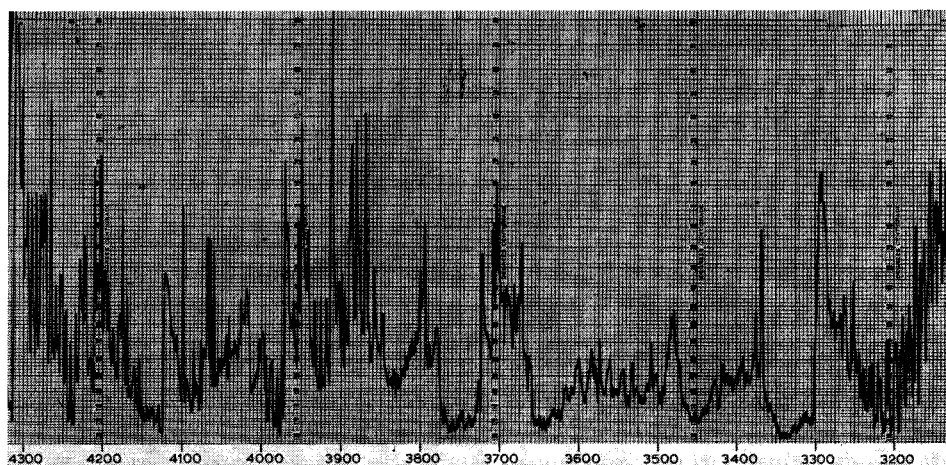
Fig. 4. Sample flow system.

of organic phosphates. A schematic diagram of the sample flow system is shown in Fig. 4. All vacuum lines were thick-walled tygon tubing, and all connections to the lamp were via o-ring seal joints. The organic vapor was introduced by heating the liquid in the round-bottom flask. The lamp was then evacuated and continuously pumped to a low vacuum. Vapor of the organic sample compound was bled into the lamp through a constricted line, thus providing a continuous supply for emission. The gas demand regulator connecting the compressed tank of argon to the system remained tightly closed. These techniques were then applied to obtain the emission spectra of the compounds listed under RESULTS.

a



b



RESULTS

Emission spectra

Triethyl phosphate. The liquid in the round-bottom flask was mixed with glass beads to prevent spattering. The operating conditions were: room temperature, 26°; temperature in flask, 30°; applied voltage, 560 V; current, 20 mA; pressure, 1.5 mm Hg.

The emission spectrum obtained under these conditions is shown in Fig. 5.

It was found that if the pressure of the vapor changed, the applied voltage had to be changed to maintain optimum signal level. As can be seen there are numerous bands which can be assigned to air impurities (N_2, CO_2, H_2O , etc.) and to PO, POH, CO, CO_2 and various CH fragments. However, there are numerous lines that could not be assigned. It is possible that these came from larger molecular fragments.

Tri-n-butyl phosphate. The operating conditions were: room temperature, 27°; temperature in flask, 80°; applied voltage, 425 V; current, 21 mA; pressure, 1.7 mm Hg.

The emission spectrum obtained under these conditions was essentially the same as that of triethyl phosphate. This suggested decomposition of the molecules and subsequent excitation and emission of the fragments. The most interesting fragment emissions were those of POH (band head at 5200 Å) and PO (3420–3300 Å), both of which were observed with each compound.

Figures 6 and 7 show the PO emission between 3200 and 3300 Å for ethyl and butyl phosphate. The large band around 3369 Å (Fig. 7) was due to emission from air impurities. The spectra were very similar but differed slightly in peak intensity.

Inorganic phosphates. A series of inorganic phosphates was examined. In these studies, the inorganic phosphorus salt was mixed with approximately 10% graphite to render them electrically conducting. The mixture was placed inside the nickel-

c

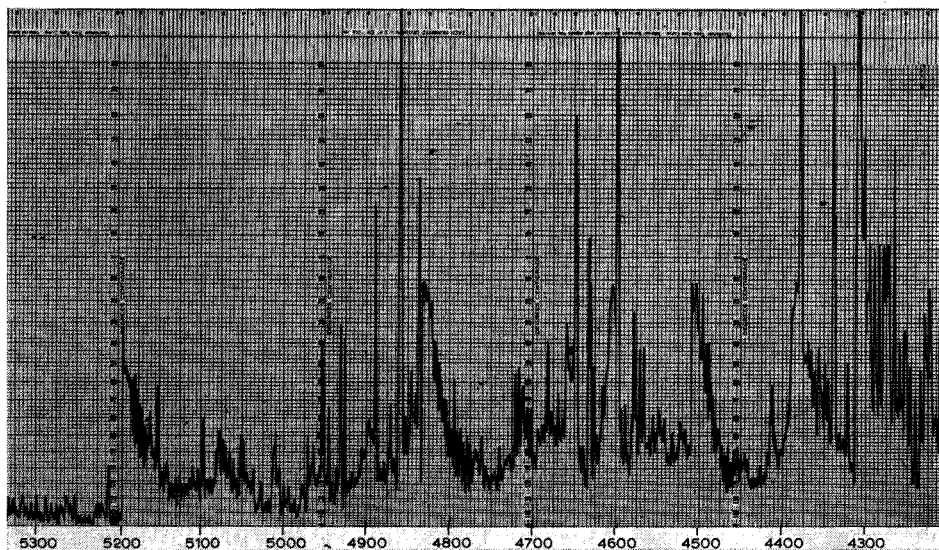


Fig. 5. Emission spectrum of triethyl phosphate.

plated steel cathode. Because the inorganic salts had little or no vapor pressure to sustain a discharge between the electrodes, a continuously flowing atmosphere of argon at a pressure between 2–6 mm Hg was maintained using the demand flow regulator. Helium or argon was found to be satisfactory as carrier gas.

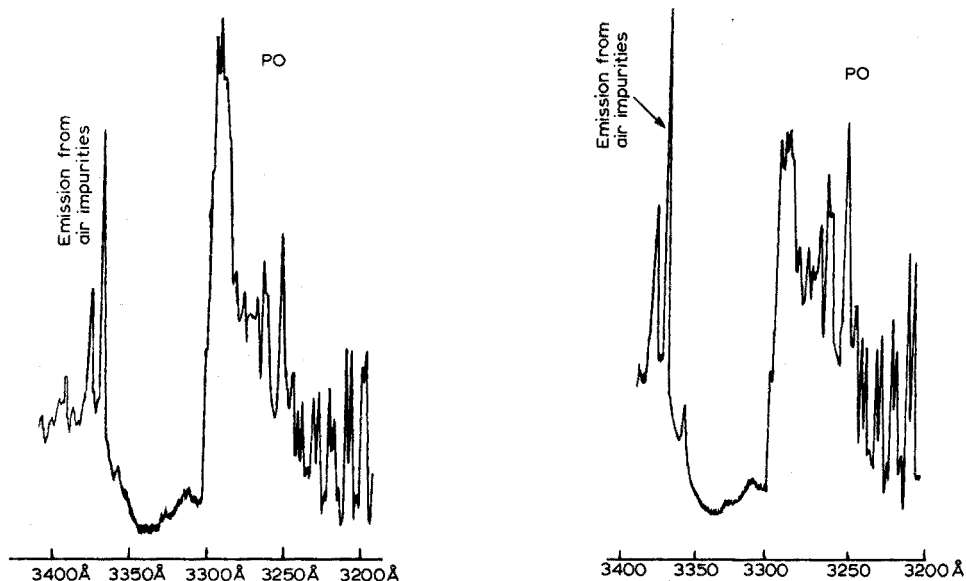


Fig. 6. PO emission from triethyl phosphate.

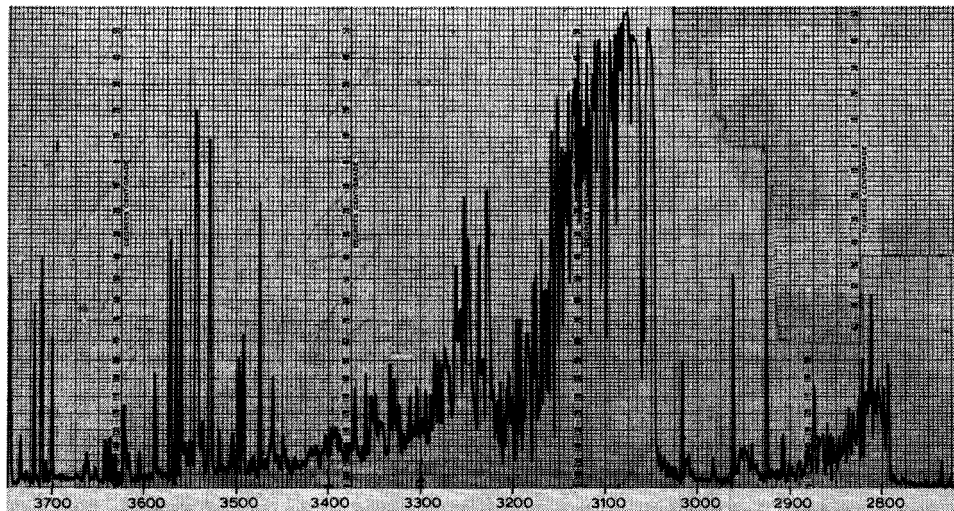
Fig. 7. PO emission from tri-*n*-butyl phosphate.

The compounds tested were $\text{NH}_4\text{H}_2\text{PO}_4$, NaH_2PO_4 , KH_2PO_4 , and P_2O_5 . All showed strong emission of PO bands between 3200 and 3300 Å, plus numerous argon lines. The emission of KH_2PO_4 is shown in Fig. 8. This spectrum showed the presence of PO bands, argon, water and a trace of air. It was of interest to note that no emission was identified as originating from the nickel hollow cathode. This may be caused by the nickel surface being coated by the salt. It was noted that many of the lines which presumably originated with argon did not coincide in wavelength with those listed in the literature. The spectra of the other phosphates were almost identical.

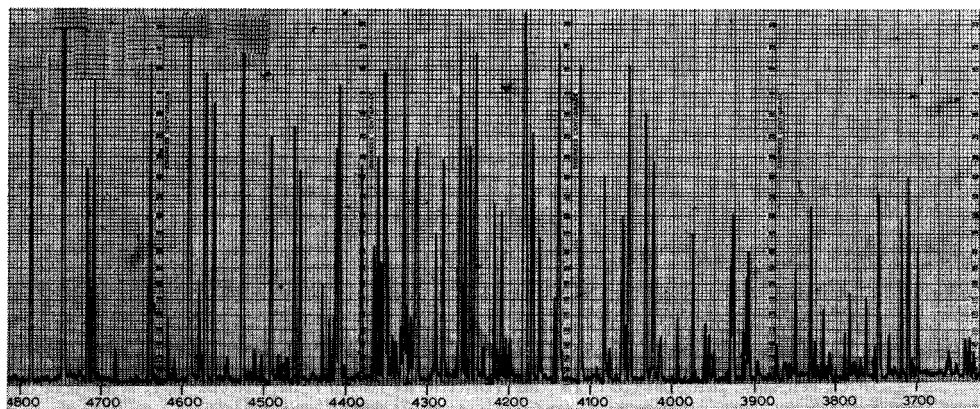
With the exception of P_2O_5 , all inorganic compounds employed exhibited sample decomposition and charring, bubbling and sputtering during the initial period. During this time, water was removed. Eventually, the lamp failed after several hours of operation due to loss of sample. This presented little or no problem in these preliminary studies because the lamp was easily dismantled, cleaned and recharged with a fresh quantity of material. Decomposition of the sample caused the cathode to become coated. A replacement cathode was then required. The demountable feature of the lamp greatly facilitated this step.

In order to compare with the spectrum emitted by organic phosphates, the spectral region from 3200 to 3300 Å is shown in greater detail for KH_2PO_4 (Fig. 9). Note the presence in all cases of the same bands, differing only in relative intensities. Similar spectra were obtained for KH_2PO_4 and P_2O_5 . It was noted that numerous

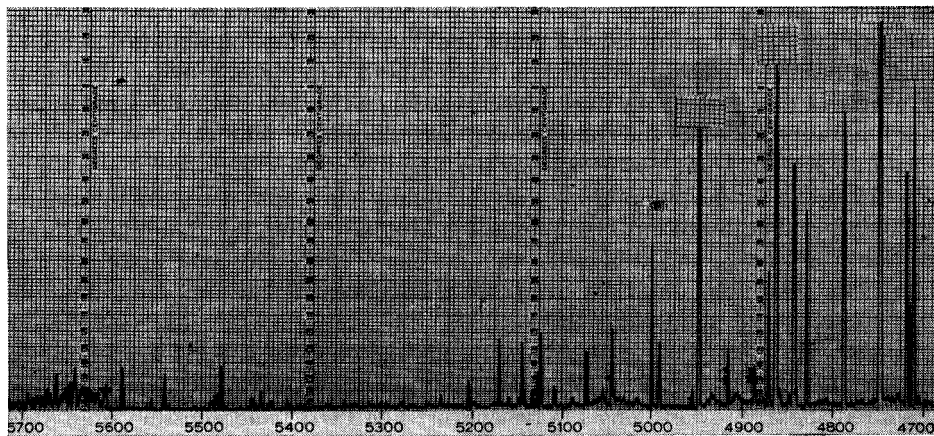
a



b



c

Fig. 8. Emission spectrum of KH_2PO_4 .

lines attributable to argon did not coincide with the wavelengths indicated in other texts².

With a demountable hollow cathode, there are necessarily various joints and connections. This led to air leaks and the emission of spectra from the components of the air. In the emission of butyl phosphate (Fig. 7) taken under static conditions, a strong emission band with a peak at 3369 Å was observed. However, when the lamp was used under continuously flowing conditions, such as employed with the inorganic salts, air emission was substantially reduced to a fraction of its former intensity (see Fig. 9). This may be because air probably leaks into the system at a constant rate, but the continual evacuation system removes most of the air on a continuous basis.

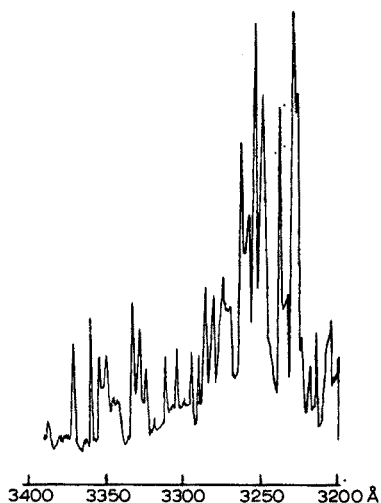


Fig. 9. PO emission from KH_2PO_4 . Note decrease in intensity of emission from air impurities.

Emission from triethyl phosphate under reduced pressure

Since triethyl phosphate is rather volatile at room temperatures, it was decided to obtain its spectra under controlled conditions. The multi-jointed lamp operated satisfactorily under flowing conditions, but was subject to air leaks. Thus, the lamp shown in Fig. 3 was constructed and employed. Liquid triethyl phosphate was mixed with glass beads to reduce spattering, and introduced into the side stem of the lamp. The lamp was then fitted with the hollow cathode, and the vacuum pump and manometer lines were sealed to the chamber with gliptol cement. The chamber was then pumped for several hours down to 0.020 mm Hg.

After the initial pumping period, the pump line was constricted by using a screw clamp and adjusted until the pressure held steady at 0.5 to 0.6 mm Hg. During operation, the voltage varied between 640 and 660 V with a current of *ca.* 13 mA. Under these conditions, multiple striations (*i.e.*, concentric rings of light) were observed between the anode and the cathode. The emission spectrum under these conditions was simpler than that obtained using the previous lamp. The spectrum is shown in Fig. 10. The region of PO emission at about 3300 Å was changed in shape and shifted slightly toward longer wavelengths. The POH band emission from 5150 to 5200 Å appeared to be at the same wavelength as before but was now considerably

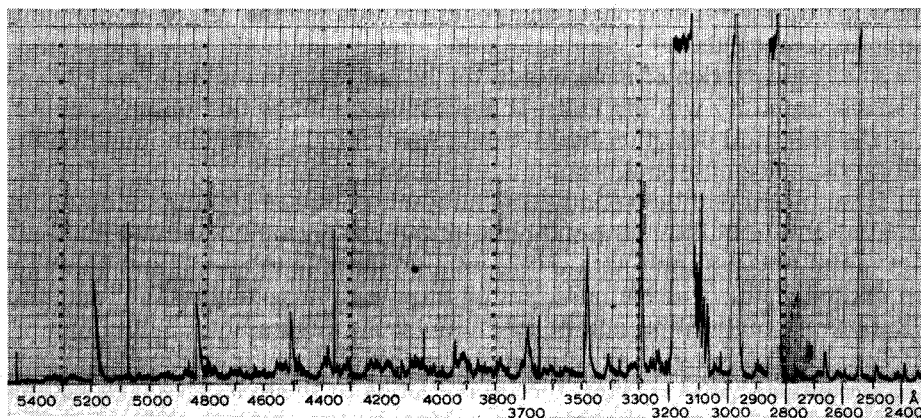


Fig. 10. Emission spectrum of triethyl phosphate under reduced pressure.

stronger than that observed earlier (Fig. 5). A very strong, sharp emission line was observed at 2535 Å. This band was assigned to phosphorus. Mercury lines were noted at 5461, 4358, 4046, 3663 Å and originated from the fluorescent mercury lights in the laboratory. The Hg line at 2536.5 Å was also observed with reduced strength. It probably originated from traces of mercury from the manometer in the vacuum system. This line was very close to the 2535 Å phosphorus line observed earlier.

Numerous other bands were observed which were not identified but which appeared to be molecular in origin. In particular were the bands at 2800 Å, 2980 Å and 3150 Å. These bands coincide with OH emission bands, but their intensity and shape indicate that they originate from a different species.

Other bands were observed at 3490 Å, 3700 Å, 3900 Å, 4515 Å, 4840 Å and a sharp emission line at 5080 Å.

ORIGIN OF SPECTRA AND ANALYTICAL APPLICATION

It was noted that with the more volatile organic compounds, such as triethyl phosphate, the radiation originated (1) from the striations between the electrodes of the hollow cathode, and (2) from the surface of the cathode itself. This indicated that at least part of the spectrum originated in the gas phase. Electron bombardment and excitation of the molecules may occur giving rise to emission spectra from the ionized molecules. Under these circumstances, the mean free path, and therefore the emission intensity, would be very sensitive to pressure changes. This was observed to be so experimentally. Emission was also observed from the inside of the hollow cathode. The mechanism of excitation was probably similar to that encountered in elemental hollow cathodes; *i.e.*, ionization of the filler gas, acceleration of the cathode, and collision and excitation of the cathode material.

It was observed in these preliminary studies that the P line, 2535 Å, was emitted strongly from the gas phase excitation, but not from the inside of the cathode. This sharp line does not originate from the ionic valence electrons of phosphorus, but probably from outer *n* electrons of the phosphorus atom. Its intensity was such as to allow the detection of trace quantities of triethyl phosphate. The same line was ob-

served with tri-*n*-butyl phosphate and could be used for the detection of organic phosphorus compounds.

The concentration of molecules in the hollow cathode was $1.65 \cdot 10^{-5} M$ and the emission intensity was 177 units. It is probable therefore that under these conditions the analytical detection limits were $3 \cdot 10^{-7} M$. The emission intensity was stable over a period of several hours.

It was noted that both organic and inorganic phosphorus compounds could be detected by this technique. It was also noted that the organic portions of the molecule gave rise to emission spectra. These were presumably caused by transition between excited states of whole molecules or fragments of molecules. The analytical implications are considerable and we intend to pursue this research.

The authors wish to express their appreciation to Mr. L. M. DUNLAP who constructed the glass lamps, and to the Army Chemical Center for providing financial assistance to this project under Research Contract No. DA. 18-35 AMC 378(A).

SUMMARY

A demountable hollow cathode has been constructed which provides emission spectra of organic compounds. The construction and operation of the hollow cathode is described. The emission spectra of organic and inorganic phosphates are illustrated and discussed.

RÉSUMÉ

On a construit une cathode creuse démontable permettant d'obtenir les spectres d'émission de composés organiques. On décrit sa fabrication et son utilisation. Les spectres d'émission de phosphates organiques et inorganiques sont présentés.

ZUSAMMENFASSUNG

Es wurde eine demontierbare Hohlkathodenlampe zur Bestimmung der Emissionsspektren organischer Verbindungen konstruiert. Die Bau- und Arbeitsweise der Lampe wird beschrieben. Die Spektren organischer und anorganischer Phosphate werden gezeigt und diskutiert.

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AN ULTRASENSITIVE CATALYTIC METHOD FOR METAL IONS AND CYANIDE-CONTAINING ORGANIC COMPOUNDS

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In a previous paper¹ GUILBAULT AND KRAMER described an ultrasensitive, specific method for the detection and determination of cyanide using *p*-nitrobenzaldehyde and *o*-dinitrobenzene. *p*-Nitrobenzaldehyde reacted specifically with cyanide to give an active reductant capable of effecting the reduction of *o*-dinitrobenzene to give a highly colored product. Additional experiments were performed to extend the general applicability of this reaction to organic compounds which contain cyanide, such as benzoyl cyanide, tetracyanoethylene (TCNE), and *p*-chlorobenzylidene malononitrile (*p*ClBM); and to very low concentrations of metal ions that complex cyanide, such as silver(I), mercury(II), copper(II), cobalt(II), nickel(II), zinc(II) and cadmium(II). These substances could be determined in the concentration range of 0.006–10 μg per ml of solution with deviations of about 2–3%.

EXPERIMENTAL

Reagents

All solutions were prepared from reagent-grade chemicals of the highest available purity, using triply distilled deionized water and spectral grade solvents. A mixed reagent solution of *p*-nitrobenzaldehyde and *o*-dinitrobenzene was prepared by dissolving the C.P. compounds (Eastman Organics, Rochester, N.Y.) in methyl cellosolve. The final concentration of the solution was 0.1 *M* in each reagent.

Apparatus

A Beckman model DB recording spectrophotometer was used in all experiments. A constant temperature of 25° was maintained for all determinations.

PROCEDURES

Qualitative detection of cyanide-containing organic compounds

To 1 ml of the unknown solution, add 0.2 ml of 0.5 *M* sodium hydroxide, and 1.0 ml of the mixed reagent solution. If a purple color develops, an organic compound that contains cyanide (or cyanide ion itself) is present.

Determination of cyanide-containing organic compounds

To a 1.0-ml solution of the compound to be determined, containing 0.1–10 μg

of compound, add 0.2 ml of 0.5 *M* sodium hydroxide, and adjust the absorbance of the solution to read zero. At zero time, add 1.0 ml of the mixed reagent solution, and record the change in the absorbance of the solution *versus* time. From calibration plots of $\Delta A/\text{min}$ *vs.* concentration, establish the quantity of the required compound (Fig. 1).

Determination of metal ions

To a solution of the unknown to be determined (containing 0.18–0.9 μg of Cu(II), 0.5–5.0 μg of Ag(I) or Hg(II), 1.8–10 μg of Co(II), 30–200 μg of Zn(II) or Ni(II), or 90–450 μg of Cd(II)), add 0.1 ml of a $7.5 \cdot 10^{-5}$ *M* solution of potassium cyanide, 0.2 ml of 0.5 *M* sodium hydroxide and 2.0 ml of the mixed *p*-nitrobenzaldehyde–*o*-dinitrobenzene solution. Record the change in the absorbance of the

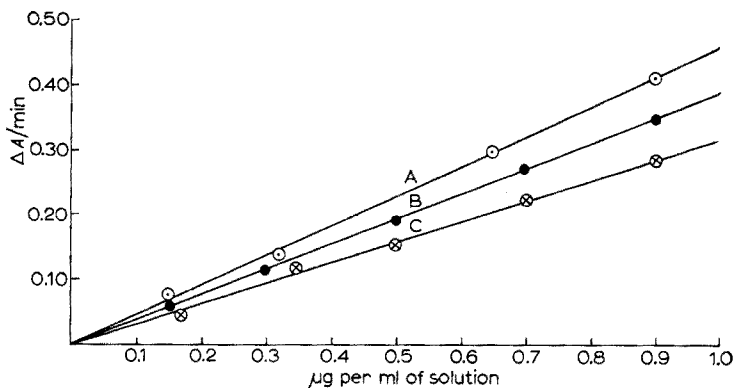


Fig. 1. Variation of $\Delta A/\text{min}$ with concentration of cyanide-containing organic compound. 0.2 ml of 0.5 *M* NaOH added, followed immediately by 2.0 ml of reagent solution (except as noted). A = TCNE. B = benzoyl cyanide. C = *p*-CIBM—30 sec before addition of reagent.

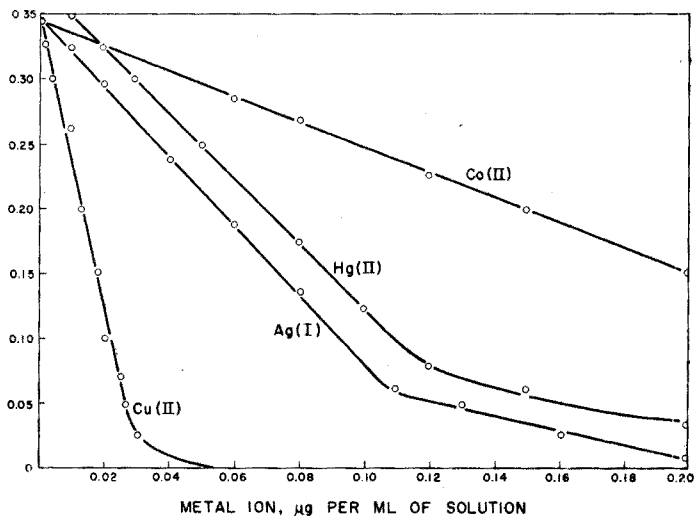


Fig. 2. Variation of $\Delta A/\text{min}$ with metal ions added to $2.5 \cdot 10^{-6}$ *M* CN^- , 2.0 ml of reagent solution and 0.2 ml of 0.5 *M* NaOH.

solution with time. Run a blank, which contains only cyanide, hydroxide and reagent, to determine the base $\Delta A/\text{min}$. From calibration plots of $\Delta A/\text{min}$ vs. the metal ion concentration, establish the amount of these materials (Fig. 2).

RESULTS

The results of the determination of three cyanide-containing organic compounds are listed in Table I. In general, 0.1–10 μg of these compounds could be analyzed

TABLE I

DETERMINATION OF CYANIDE-CONTAINING ORGANIC COMPOUNDS

TCNE			<i>p</i> -ClBM			Benzoyl cyanide		
Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)	Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)	Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)
0.100	0.102	+2.0	0.250	0.255	+2.0	0.100	0.102	+2.0
0.320	0.316	-1.2	0.500	0.506	+1.2	0.500	0.496	-0.8
0.650	0.635	-2.3	1.00	0.985	-1.5	1.00	1.01	+1.0
1.30	1.33	-2.3	1.65	1.70	+3.0	2.50	2.47	-1.2
5.00	5.03	+0.6	3.30	3.26	-1.2	5.00	5.05	+1.0
		s.d. ± 2.0			s.d. ± 2.1			s.d. ± 1.4

TABLE II

DETERMINATION OF CATIONS

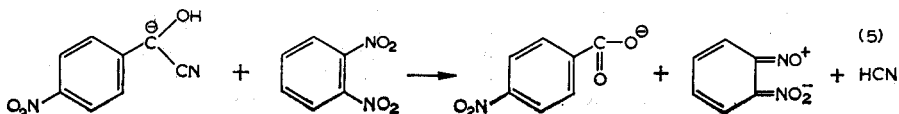
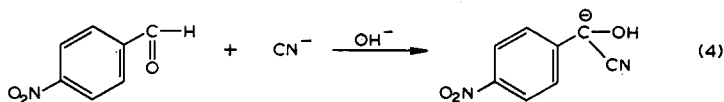
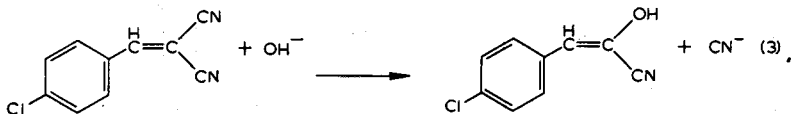
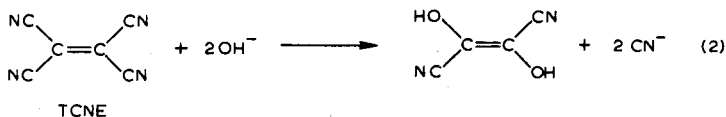
Mercury(II)			Silver(I)		
Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)	Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)
0.0200	0.0204	+2.0	0.0150	0.0147	-2.0
0.0500	0.0510	+2.0	0.0300	0.0303	+1.0
0.100	0.0980	-2.0	0.0600	0.0614	+2.3
0.1500	0.152	+1.3	0.101	0.103	+2.0
0.200	0.196	-2.0	0.200	0.197	-1.5
		s.d. ± 2.1			s.d. ± 2.0
Copper(II)			Cobalt(II)		
Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)	Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)
0.00300	0.00297	-1.0	0.0300	0.0306	+2.0
0.00600	0.00612	+2.0	0.0600	0.0594	-1.0
0.0100	0.0102	+2.0	0.100	0.0998	-2.0
0.0200	0.0197	-1.5	0.200	0.203	+1.5
0.0300	0.0307	+2.3	0.400	0.396	-1.5
		s.d. ± 2.1			s.d. ± 1.9
Nickel(II)			Zinc(II)		
Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)	Present ($\mu\text{g}/\text{ml}$)	Found ($\mu\text{g}/\text{ml}$)	Error (%)
1.05	1.03	-1.9	1.00	1.03	+3.0
2.10	2.15	+2.4	2.00	1.94	-3.0
4.00	4.10	+2.5	4.10	4.22	+2.9
6.10	6.00	-1.7	5.00	4.90	-2.0
7.00	7.21	+3.0	8.00	8.16	+2.0
		s.d. ± 2.6			s.d. ± 2.8

with a deviation of about 2%. Mercury(II) and silver(I), in concentrations of 0.015–0.20 μg per ml, and copper(II) and cobalt(II) in concentrations of 0.003–0.030 and 0.03–0.40 μg per ml were analyzed with a deviation of about 2.1%. Zinc(II) and nickel(II) in the range 1–8 $\mu\text{g}/\text{ml}$ and cadmium(II) in the range 3–15 $\mu\text{g}/\text{ml}$ were assayed with a deviation of about 3% (Table II).

DISCUSSION

In a previous paper¹, GUILBAULT AND KRAMER reported that cyanide ion reacts rapidly with *p*-nitrobenzaldehyde to form the cyanohydrin anion, which is a strong reducing agent, and rapidly effects the reduction of the colorless *o*-dinitrobenzene to the purple dianion of *o*-nitrophenylhydroxylamine. A number of cyanide-containing organic compounds were found to hydrolyze rapidly in the presence of base to give sufficient cyanide to be rapidly detected by this technique. In fact, the addition of base to tetracyanoethylene (TCNE) and benzoyl cyanide immediately converted these compounds to hydrolyzed product and cyanide ion in almost quantitative yield (Table III and eqns. (1)–(3)). The reaction with *p*-chlorobenzylidene malononitrile (*p*ClBM) is slower, (eqn. (2)), and requires reaction with base for about 30 sec before addition of the cyanide reagents for best results. In all 4 reactions, 0.2 ml of 0.5 *M* sodium hydroxide was found to be optimum.

The cyanide formed then reacts with the aldehyde (eqn. (4)) to form the cyanohydrin anion, which then reduces *o*-dinitrobenzene to the purple compound (eqn. (5)). The rate of change in the absorbance of the solution at 560 nm with time was proportional to the concentration of each material (Fig. 1).



This technique should be applicable to any organic compound that is easily hydrolyzed to give cyanide ion, so that only compounds of this type would be expected to interfere in any procedure for the above compounds, or the qualitative test for such materials. It has been found that the test is totally specific for cyanide ion¹, so that no other anion or cation would be expected to interfere.

TABLE III

EFFECT OF SODIUM HYDROXIDE CONCENTRATION AND INCUBATION TIME ON THE RATE OF HYDROLYSIS OF TCNE AND *p*-CIBM

Compound	Base (ml) (NaOH, 0.5 M)	Time ^a (sec)	$\Delta A/\text{min}$
TCNE	0.2	0	0.13
TCNE	0.2	30	0.12
TCNE	0.2	60	0.12
TCNE	0.1	0	0.040
TCNE	0.3	0	0.130
TCNE	0.5	0	0.110
<i>p</i> -CIBM	0.2	0	0.092
<i>p</i> -CIBM	0.2	30	0.130
<i>p</i> -CIBM	0.2	60	0.130

^a Time between addition of base to TCNE or *p*-CIBM and addition of *p*-nitrobenzaldehyde-*o*-dinitrobenzene reagent solution.

TABLE IV

COMPARISON OF CONCENTRATION OF METAL IONS NEEDED TO CAUSE A 50% DECREASE IN $\Delta A/\text{min}$ WITH STABILITY CONSTANTS OF METAL ION-COMPLEX REPORTED ([CN⁻] = $2.5 \cdot 10^{-6}$ M; 0.1 M mixed reagent solution)

Metal ion	Conc. (M)	$K_{\text{form}}(\text{exp})$	Metal ion	Conc. (M)	$K_{\text{form}}(\text{exp})$
Hg	$4 \cdot 10^{-7}$	$1 \cdot 10^{42}$ ^a	Co	$3.24 \cdot 10^{-6}$	$1 \cdot 10^{19}$ ^c
Cu	$2.3 \cdot 10^{-7}$	$1 \cdot 10^{25}$ ^a	Cd	$5 \cdot 10^{-5}$	$1.29 \cdot 10^{17}$ ^a
Ni	$4.4 \cdot 10^{-5}$	$1 \cdot 10^{22}$ ^a	Zn	$6.0 \cdot 10^{-5}$	$2.5 \cdot 10^{13}$ ^a
Ag	$5 \cdot 10^{-7}$	$6.3 \cdot 10^{20}$ ^b			

^a 4:1 CN⁻:M²⁺ complex.

^b 2:1 CN⁻:M⁺ complex.

^c 6:1 CN⁻:M²⁺ complex.

Mercury(II), silver(I), copper(II), cobalt(II), zinc(II), nickel(II) and cadmium(II), form strong complexes with cyanide ion, and hence inhibit the catalytic reaction sequence (4) and (5). Thus a decrease in the rate of production of the purple dianion with time, $\Delta A/\text{min}$, results. Since the method for cyanide is catalytic and very sensitive (as little as 10 ng can be determined), this procedure permits the determination of very low concentrations of these metal ions (Fig. 2). Likewise, any other metal ion that forms cyanide complexes (iron, etc.) may be determined by this technique.

The order of sensitivity for different metal ions roughly parallels the order of stability of the cyanide complexes formed. The concentration of metal ion needed to effect a 50% decrease in $\Delta A/\text{min}$ (or a 50% decrease in the total free cyanide ion available for reaction) is indicated in Table IV, together with the stability constant of the metal ion-cyanide complex formed. The sensitivity is best for the determination

of those metal ions that form strong cyanide complexes, such as Hg, Cu, Ag and Co. The lack of sensitivity in the case of nickel is unexpected, though the low sensitivity for cadmium and zinc is not unexpected since these ions form weak cyanide complexes.

Finally, the influence of various cations and anions on the determination of silver(I) is indicated in Table V. As would be expected, Hg, Cu, Fe and Co interfered seriously, with lesser interference noted from Zn, Ni and Cd (10^{-5} M concentrations needed). Other cations that do not form cyanide complexes (alkali metals, alkaline earths, aluminum) did not interfere, nor did any common anion except periodate.

TABLE V

EFFECT OF INTERFERENCES ON THE DETERMINATION OF SILVER
($\text{CN}^- = 2.5 \cdot 10^{-6}$ M; $\text{Ag}^+ = 5 \cdot 10^{-7}$ M)

<i>Interfering ion</i>	<i>Concn.</i>	$\Delta A/\text{min}$	<i>Interfering ion</i>	<i>Concn.</i>	$\Delta A/\text{min}$
None	0	0.20	Cl^- , Br^- , I^-	$1 \cdot 10^{-4}$	0.20
Zn^{2+}	$3 \cdot 10^{-5}$	0.18	IO_4^-	$1 \cdot 10^{-4}$	0.04
Co^{2+}	$3 \cdot 10^{-5}$	0.15	Cd^{2+}	$3 \cdot 10^{-5}$	0.19
Ni^{2+}	$3 \cdot 10^{-6}$	0.20	Fe^{3+}	$3 \cdot 10^{-6}$	0.10
Mg^{2+} , Ca^{2+}	$1 \cdot 10^{-4}$	0.20	SO_4^{2-}	$1 \cdot 10^{-4}$	0.20
K^+ , Na^+	$1 \cdot 10^{-4}$	0.20			

The reaction could be made more selective for the determination of any metal ion by the use of masking agents such as EDTA, Trien, fluoride, etc., provided that the element to be masked forms a stronger complex with the masking agent than it does with cyanide.

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SUMMARY

Ultrasensitive methods are described for the detection and determination of cyanide-containing organic compounds and of various metal ions. The methods are based either on the hydrolysis of the organic compounds to give cyanide ion, which then catalyzes the reduction of *o*-dinitrobenzene via formation of the cyanohydrin anion of *p*-nitrobenzaldehyde, or on the inhibition of this catalytic reaction by silver(I), mercury(II), copper(II), cobalt(II), nickel(II), zinc(II) and cadmium(II) which form cyanide complexes. By these methods, tetracyanoethylene, *p*-chlorobenzylidene malononitrile, or benzoyl cyanide (0.1–10 $\mu\text{g}/\text{ml}$) may be determined with a deviation of about 2%, and Ag(I), Hg(II) (0.02–0.2 $\mu\text{g}/\text{ml}$), Cu(II) (0.003–0.030 $\mu\text{g}/\text{ml}$), Co(II) (0.06–0.40 $\mu\text{g}/\text{ml}$) and Ni(II), Zn(II) and Cd(II) (1–10 $\mu\text{g}/\text{ml}$) can be determined with a deviation of about 3%.

RÉSUMÉ

On décrit des méthodes ultrasensibles pour déceler et doser des composés organiques renfermant du cyanure et pour l'analyse de divers métaux. Ces procédés

sont basés soit (1) sur l'hydrolyse des composés organiques pour donner des ions cyanures qui catalysent la réduction de l'*o*-dinitrobenzène via formation d'anion cyanohydrine, soit (2) sur l'inhibition de cette réaction catalytique par l'argent, le mercure, le cuivre, le cobalt, le nickel, le zinc et le cadmium, formant des complexes cyanés. Par ces procédés les composés suivants: tétracyanoéthylène, *p*-chlorobenzylidène malononitrile ou le benzoylcyanure (0.1–10 µg/ml) peuvent être dosés avec un écart d'environ 2%; Ag(I) et Hg(II) (0.02–0.2 µg/ml), Cu(II) (0.003–0.03 µg/ml), Co(II) (0.06–0.4 µg/ml) et Ni(II), Zn(II) et Cd(II) (1–10 µg/ml) sont dosés avec un écart d'environ 3%.

ZUSAMMENFASSUNG

Es wird eine ultraempfindliche Methode zum Nachweis und zur Bestimmung von cyanidhaltigen organischen Verbindungen und von verschiedenen Metallionen beschrieben. Die Methode beruht entweder auf der Hydrolyse der organischen Verbindung zur Bildung des Cyanidions, welches dann die Reduktion von *o*-Dinitrobenzol zur Bildung des Cyanhydrinanions von *p*-Nitrobenzaldehyd katalysiert oder zur Verzögerung dieser katalytischen Reaktion durch Silber(I), Quecksilber(II), Kupfer(II), Cobalt(II), Nickel(II), Zink(II) und Cadmium(II), welche Cyanidkomplexe bilden. Durch diese Methoden können Tetracyanoäthylen, *p*-Chlorobenzylidinmalononitril oder Benzoylcyanid (0.1–10 µg/ml) mit einer Abweichung von etwa 2% bestimmt werden, ferner können Ag(I), Hg(II) (0.02–0.2 µg/ml), Kupfer(II) (0.003–0.030 µg/ml), Co(II) (0.06–0.40 µg/ml) und Ni(II), Zn(II) und Cd(II) (1–10 µg/ml) mit einer Abweichung von etwa 3% bestimmt werden.

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Anal. Chim. Acta, 40 (1968) 251–257

TITRAGES "THERMOCHIMIQUES" PAR FORMATION DE FLUORURES COMPLEXES DE FER, ALUMINIUM, ANTIMOINE, ETAIN ET PLOMB

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(Reçu le 5 juin, 1967)

La stabilité des complexes fluorés de l'aluminium et du fer tels que Na_3FeF_6 ou Na_3AlF_6 est très grande. Celle des complexes analogues d'antimoine, d'étain, de plomb (dont on connaît une combinaison très peu soluble PbClF) est beaucoup moins grande.

Les variations de l'enthalpie au cours de la formation ou de la destruction des complexes est en relation directe avec la constante d'équilibre. Cependant on ne peut déterminer rigoureusement cette constante d'équilibre que si l'on connaît la variation de l'enthalpie libre $\Delta G = \Delta H - T\Delta S$ et par conséquent la variation d'entropie S , celle-ci n'étant en général qu'une fraction de la première.

Des travaux assez nombreux sont relatifs aux enthalpies de formation de complexes de sels de nombreux métaux avec l'EDTA ou l'éthylène diamine¹⁻⁵. Certains auteurs déterminent les constantes de stabilité à partir des variations de ΔG et ΔS —d'autres font l'inverse. Pour notre part, nous avons simplement entrepris l'étude des courbes de titrage donnant les variations de la température en fonction de la quantité de complexant ajouté. Nous avons cependant pu déterminer approximativement, les enthalpies de formation dans le cas de l'aluminium et dans celui du fer. Nous avons en outre étudié l'effet de l'acide borique sur les complexes: destruction des complexes par formation de fluoborates (l'emploi de l'acide borique est courant en électrolyse et dans les fluoborates le métal serait à l'état^{6,7} d'ion simple).

Les courbes si l'on ne tient pas compte des effets de la dilution* devraient avoir un aspect sensiblement linéaire. Comme pour les courbes conductimétriques, on détermine des "indices linéaires"⁸. Le passage d'une combinaison complexe à une autre ou à un sel simple se traduit par un point anguleux. Quand il se forme une combinaison insoluble (cas du plomb), le point anguleux est particulièrement marqué et souvent mobile car l'équilibre en milieu hétérogène est lent et le titrage est mauvais. La méthode "thermochimique" a été appliquée depuis déjà longtemps aux titrages de sels de métaux lourds par l'ammoniaque ou les cyanures^{9,10}. Parmi les travaux plus récents, citons ceux de BYE⁸ sur le titrage de métaux lourds par les bases fortes et formation de sels basiques ou d'hydroxydes—ceux de LINDE¹¹ sur des titrages acidimétriques ou par précipitation, avec un appareil à thermistance à enregistrement, et ceux de RINGBOM ET WILKMAN¹², de BERTON¹³ et de DAVIES *et al.*³.

RASMUSSEN ET TORBEN¹⁴ ont étudié plus particulièrement l'action du cyanure

* Il est possible d'effectuer une correction de volume si celui-ci varie trop au cours du titrage; il faut noter aussi que la chaleur d'ionisation varie avec la dilution mais ces variations sont néanmoins négligeables.

de potassium sur les sels de nickel, argent, mercure. ZENCHELSKY¹⁵ qui signale aussi l'analogie entre les courbes conductimétriques et les courbes calorimétriques a effectué de nombreux titrages avec un appareil mesurant non les températures mais les dérivées premières ou secondes (par rapport à la quantité de réactif) comme l'ont fait également TYSON et ses collaborateurs¹⁶. JORDAN marque sa préférence pour l'expression "titrage thermo-chimique" au lieu de thermométrique ou thermique¹⁷. Quoiqu'il en soit la méthode est donnée comme précise—en phase homogène: elle a l'avantage de permettre dans certains cas des séparations et l'inconvénient de nécessiter des concentrations assez élevées, surtout en compleximétrie.

TECHNIQUES EXPÉRIMENTALES

Notre but étant d'obtenir des "courbes de titrage" et non de mesurer des variations d'enthalpie, nous nous sommes contenté d'un montage simple et sensible.

Les thermistances* sont utilisées directement pour la mesure des températures, alors que dans la technique employée il y a déjà longtemps par PITZER¹⁸, on rétablit à l'aide d'un "réchauffeur" l'équilibre des thermistances—et des températures.

La réponse des thermistances n'est pas du tout linéaire puisque leur résistance suit une loi exponentielle de la forme $R = R_0 e^b (1/T - 1/T_0)$ mais pour de petites variations de température—inférieures à 0.01, on peut au moins en première approximation admettre une loi linéaire¹⁹.

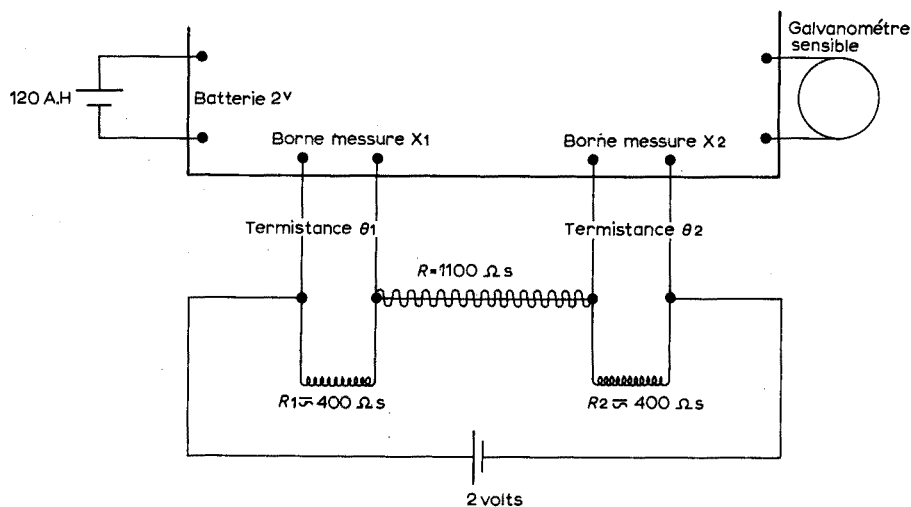


Fig. 1. Potentiomètre.

L'emploi d'un montage en pont de Wheatstone dont les résistances des bras sont judicieusement choisies a d'ailleurs donné de bons résultats à certains auteurs^{15,17}.

Nous avons, pour notre part, donné la préférence à la simple méthode potentiométrique signalée comme la plus précise¹⁹. Les variations de résistance sont déterminées par la mesure de la différence de potentiel aux bornes des thermistances mises sous tension par l'intermédiaire de résistances très élevées (voir Fig. 1). Le

* Nous avons utilisé des thermistances Fenwall type 74001-001 dont la résistance est de 400 Ω et le coefficient de température $3 \cdot 10^{-4} \text{ C}^{-1}$.

potentiomètre est alimenté par un accumulateur de très forte capacité (100 A.h.). Le courant est suffisamment constant au cours d'un titrage pour qu'on puisse, soit suivre la variation de température sur le galvanomètre sensible, soit "interpoler" entre deux valeurs des potentiels différents de 0.1 mV pour obtenir une sensibilité de 0.01 mV.

Deux mesures peuvent être faites à peu près simultanément sur deux thermistances identiques dont l'une peut servir de témoin. L'appareil peut être étalonné en effectuant un titrage d'un acide fort par une base forte (titrages simultanés ou successifs).

La calorifugation indispensable est assurée par deux Dewar qui contiennent chacun une thermistance. L'ensemble est placé dans une cuve de verre remplie d'eau, elle-même protégée par un revêtement de polystyrène expansé. Il est important que la solution titrante de fluorure de sodium par exemple soit à la même température que la solution du sel à titrer. Au sortir de la burette mécanique à vis micrométrique, la solution est conduite par un long tube étroit et mince, en téflon, qui plonge dans l'eau de la cuve.

Appelons ΔX_1 et ΔX_2 les variations de potentiel aux bornes du potentiomètre. En première approximation on peut écrire :

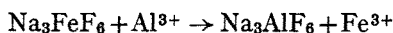
$$\frac{\Delta X_1}{\Delta X_2} = \frac{\Delta t_1}{\Delta t_2}$$

t_1 et t_2 représentant les températures.

FORMATION DE FLUORURES COMPLEXES

Complexes du fer et de l'aluminium

Parmi les complexes de l'aluminium les "fluoro-aluminates" sont bien caractéristiques et le plus souvent de coordinence 6. La liaison serait d'ailleurs partiellement ionique. Le composé dont il sera question plus loin de formule Na_3AlF_6 (cryolithe) aurait une structure octaédrique chaque ion Na^+ étant entouré de 6 F^- . La stabilité de ces complexes est telle que le complexe ferrique déjà très stable est détruit suivant :



L'insolubilité du fluoro-aluminate de sodium a été mis à profit pour le titrage des ions F^- par acidimétrie, formation de laques avec l'alumine ou conductimétrie. Un excès de sel d'aluminium ou de sodium est nécessaire²⁰⁻²³. Nous retrouverons dans nos expériences les accidents des courbes dus à la formation d'un précipité (milieu concentré). L'électrode (rotative) d'aluminium présente avec les ions F^- des variations importantes, signe d'une profonde modification ionique, d'où une méthode pour doser des traces de fluorures. L'acide fluorhydrique n'étant pas un acide très fort, le pH du milieu est loin d'être sans influence²⁴. Nos expériences ont été faites en milieu relativement concentré (voisin de la normale) et neutre.

On connaît l'intérêt analytique de la séparation aluminium-fer : il ne nous a pas été possible de séparer l'aluminium du fer comme cela l'a été pour, par exemple, le calcium et le magnésium⁵. Les différences de pente sont beaucoup plus marquées pour le fer et l'aluminium que même dans le cas du cuivre (Figs. 2, 3). Nous avons

également obtenu des courbes de titrage nettes par destruction du complexe avec l'acide borique. La Fig. 3 représente* les courbes de titrage de NaF à diverses concentrations. On observe toujours un point anguleux. Ce point marque le passage de l'ion Al^{3+} à l'ion complexe $(\text{AlF}_6)^{3-}$. Les différences de pente sont un peu moins marquées en solutions plus diluées. Les abscisses correspondent bien à la coordinence 6 comme le montrent les valeurs obtenues pour les rapports $(\text{Al}^{3+})/\text{F}^-$ et $(\text{Fe}^{3+})/\text{F}^-$ soit:

$$1.95 \times 3 - 2.02 \times 3 - 2.03 \times 3 - 2.03 \times 3 - 2.03 \times 3 \text{ (Fig. 4)}$$

$$1.96 \times 3 - 1.92 \times 3 \text{ (Fig. 7).}$$

Il apparaît parfois des accidents très marqués (Fig. 3) dus à des précipitations (ferrifluorures de sodium ou fluoro-aluminates). L'abscisse de ces points particuliers est variable et ne présente pas d'intérêt analytique pour nous.

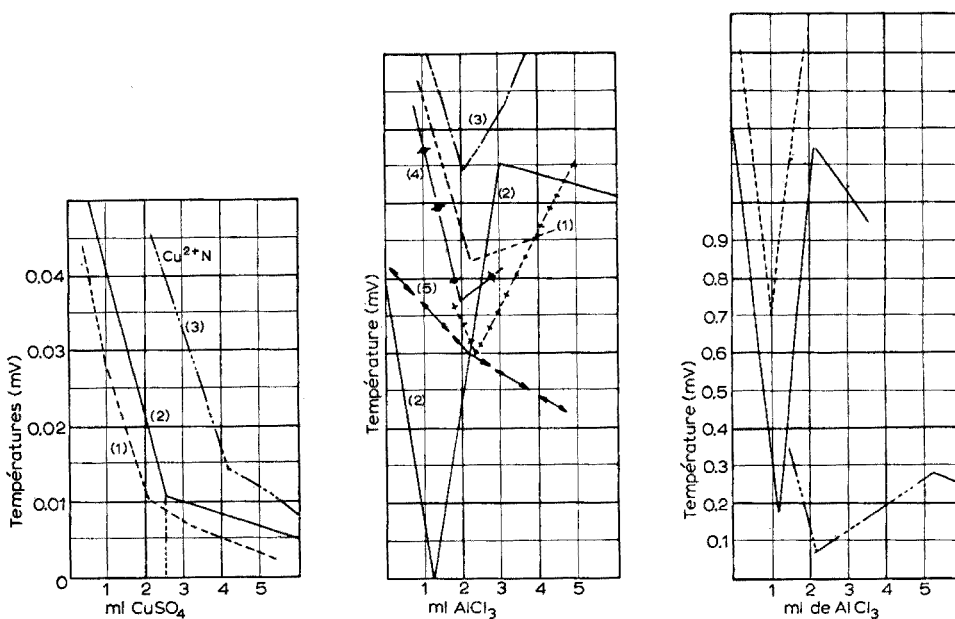


Fig. 2. Titrage de CuSO_4 par NaF. (1) 5 ml NaF 0.42 N par Cu^{2+} 0.42 N; (2) 5 ml NaF 0.84 N par Cu^{2+} 0.86 N; (3) 1 ml NaF 0.84 N par Cu^{2+} N.

Fig. 3. Titrage de NaF par AlCl_3 . (1) 5 ml NaF 0.84 N par Al^{3+} 0.93 N; (2) 5 ml NaF 0.84 N par Al^{3+} 1.85 N; (3) 5 ml NaF 0.42 N par Al^{3+} 0.46 N; (4) 5 ml NaF 0.21 N par Al^{3+} 0.23 N; (5) 5 ml NaF 0.105 N par Al^{3+} 0.116 N.

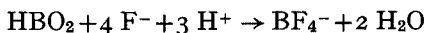
Fig. 4. Titrage de NaF par FeCl_3 2.02 N. (1) 5 ml NaF 0.82 N; (2) idm. dilué 2 fois.

Les courbes de la Fig. 4 sont relatives au fer. Le ferrifluorure de sodium est également peu soluble et susceptible de précipiter. Ces accidents sont marqués très nettement sur les courbes. L'action du mélange à peu près équimoléculaire sur NaF (Figs. 5, 6) ne donne pas lieu à des points anguleux distincts pour la formation des

* Les courbes sont décalées pour rendre la Fig. plus lisible. Ce sont les différences des pentes des diverses branches qui sont importantes.

complexes du fer et de l'aluminium. On observe également un maximum très marqué dû à la formation d'un complexe insoluble. Le titrage inverse présente les mêmes accidents.

Il est à remarquer que l'action de l'acide borique sur les fluorocomplexes (Figs. 8, 9) fournit d'excellentes courbes de titrage mais là encore, il n'est pas possible de séparer le fer de l'aluminium. De plus le rapport des ions $(F)^-/(BO_2)^-$ n'est pas 4 comme on pouvait s'y attendre d'après la réaction²⁵



mais très voisin de 3 (courbes Fig. 8). Nous n'opérons pas en milieu fortement acide. Dans ces conditions une hydrolyse est possible: totale suivant



ou par étape et on obtient des composés tels que $NaBF_3 OH$.

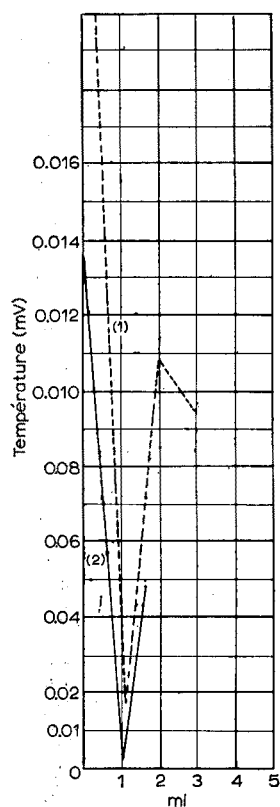


Fig. 5. Titrages successifs de 5 ml NaF 0.82 N par $AlCl_3$ et $FeCl_3$. (1) par Al^{3+} 0.92 N; (2) par Fe^{3+} 1.01 N.

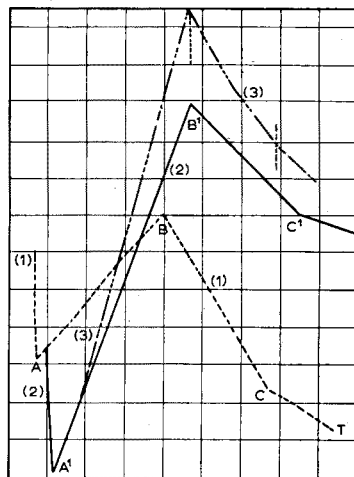


Fig. 6. Titrage de NaF par le mélange $AlCl_3$, $FeCl_3$. (1) 5 ml de NaF 0.84 N par Al^{3+} 0.925 N, Fe^{3+} 1.01 N; (2) identique; (3) le mélange est dilué 2 fois.

Comparaison des effets thermiques

La formation des complexes de fer et d'aluminium provoquent des effets

thermiques assez voisins soit ΔH_1 et ΔH_2 . Il est commode de prendre pour étalon l'effet thermique soit ΔH_0 produit par la neutralisation de l'acide acétique par la soude avec des conditions identiques à celles du titrage. La simple mesure des différences de potentiel permet de déterminer le rapport $r = \Delta H_1/\Delta H_0$. On trouve dans le

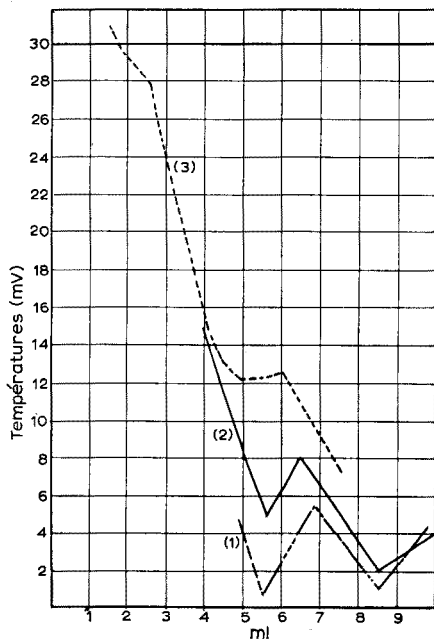


Fig. 7. Titration par NaF 0.82 N du mélange FeCl_3 , AlCl_3 . (1) 5 ml du mélange Fe^{3+} 1.01 N, Al^{3+} 0.93 N; (2) identique; (3) 2 ml du mélange Fe^{3+} 1.39 N, Al^{3+} 0.62 N.

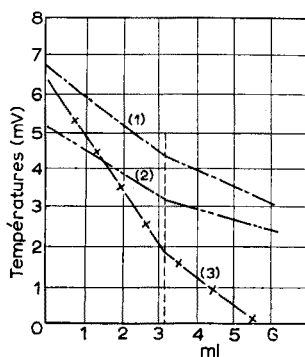


Fig. 8. Titration de AlF_6^{3-} et FeF_6^{3-} par H_3BO_3 . (1) 1 ml AlF_6^{3-} par H_3BO_3 (sol.N); (2) idem; (3) 1 ml FeF_6^{3-} .

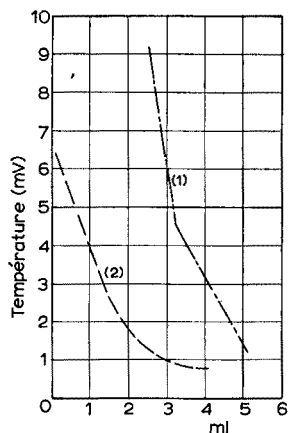


Fig. 9. Titration de NaF par Sb^{5+} . (1) 1 ml Sb^{5+} par NaF 0.84 N; (2) action de H_3BO_3 sur le complexe.

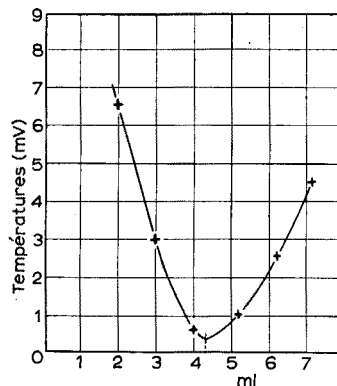


Fig. 10. Action de $\text{Pb}(\text{CH}_3\text{CO}_2)_2$ sur NaF (5 ml sol.N et NaF 0.84 N).

cas de l'aluminium: $r = 0.55$ et 0.53 (titrages simultanés) et dans le cas du fer: $r = 0.354$. Cela confirme le fait que les complexes de l'aluminium sont les plus stables et laisse prévoir l'impossibilité d'une séparation.

Complexes du cuivre

Les complexes halogénés du cuivre sont du type $(\text{CuX}_3)^-$ et $(\text{CuX}_4)^{2-}$ où X représente l'halogène et existent à l'état solide. La dissolution et la dilution amènent leur destruction. Les complexes du deuxième type sont les plus stables et avec nos conditions opératoires, c'est ceux-ci qui se forment. Les courbes de titrage (Fig. 3) se rapportent à l'action du sulfate de cuivre sur le fluorure de sodium.

En accord avec la formation de l'ion $(\text{CuF}_4)^{2-}$ la position du point anguleux pour les rapports $(\text{F}^-)/(\text{Cu}^{2+})$ $2 \times 1.99 - 2 \times 2.00$. Il est nécessaire d'ajouter une petite quantité d'acide sulfurique (5% en volume) dans la solution de sulfate de cuivre pour empêcher la formation de l'oxyfluorure CuFOH : celui-ci, très insoluble en milieu neutre ou alcalin, ne précipite pas en milieu acide.

Effet thermique. L'effet thermique est encore assez marqué et la mesure du rapport r dans les mêmes conditions que dans le cas du fer et de l'aluminium a donné $r \approx 0.055$.

Complexes d'étain et d'antimoine

Les courbes obtenues avec l'étain(II) et l'antimoine(III) sont difficiles à interpréter car pour éviter l'hydrolyse on est obligé d'opérer en milieu très acide. Un point anguleux d'ailleurs peu net correspondrait au composé: SnFCl ; le rapport $(\text{F}^-)/(\text{Sn}^{2+})$ étant voisin de 1. La formation de fluorostannite KSnF_3 n'a pas été mise en évidence²⁶.

Dans le cas de l'antimoine, le point anguleux correspondrait à NaSbF_4 .

Il n'est pas non plus possible de séparer l'antimoine de l'étain et l'action de l'acide borique ne fournit plus que des courbes très peu nettes.

Action des sels de plomb (précipitation)

Les courbes relatives au plomb sont surtout nettes dans le cas de l'acétate, seules représentées sur la Fig. 10. Elles se compliquent dans le cas du nitrate: on observe non pas un mais deux points anguleux probablement dus à la formation de composés mixtes tels PbNO_3F^* . Les équilibres en phase hétérogène sont d'ailleurs beaucoup plus lents. Dans le cas de l'acétate, le rapport $(\text{F}^-)/(\text{Pb}^{2+})$ est égal à 2, ce qui correspond bien à PbF_2 .

CONCLUSION

Au point de vue purement analytique et avec les inconvénients inhérents à la méthode "thermochimique", c'est-à-dire nécessité d'opérer en milieu assez concentré (voisin de la normale) de bons résultats ont été obtenus pour le dosage de l'aluminium, du fer, du cuivre, par formation des ions complexes: $(\text{AlF}_6)^{3-}$, $(\text{FeF}_6)^{3-}$, $(\text{CuF}_4)^{2-}$, dans l'ordre des "stabilités" décroissantes.

Les "constantes de stabilité" sont trop voisines pour qu'il soit possible de séparer aluminium et fer par l'emploi du fluorure. La méthode paraît susceptible

* Analogue à PbClF .

d'une précision suffisante (1%), ne nécessite pas un appareillage coûteux et permet un dosage rapide. Elle peut être appliquée au dosage des fluorures. Il semble également que l'on puisse l'appliquer au dosage de l'acide borique par destruction des complexes fluoborés et formation d'acide fluoborique.

Des résultats moins bons ont été obtenus pour les sels antimonieux et stanneux. Enfin la formation d'un précipité très peu soluble avec les sels de plomb se traduit par un point anguleux marqué reproductible bien qu'on soit en phase hétérogène. On note seulement une certaine distorsion des courbes.

RÉSUMÉ

Une étude thermochimique du titrage de sels d'aluminium, de fer, de cuivre, de plomb, d'étain et de l'antimoine par le fluorure de sodium a été entreprise. La destruction des complexes fluorés par l'acide borique a également été étudiée. L'appareil de mesure comporte deux thermistances mises sous tension et un pont potentiométrique. Des points anguleux nets sont obtenus pour le fer, l'aluminium, le cuivre, le plomb (précipitation) sans qu'une séparation aluminium-fer ait été possible. L'action de l'acide borique donne également des points anguleux nets.

SUMMARY

A thermochemical study of the titration of aluminium, iron, copper, lead, tin and antimony salts with sodium fluoride is described. The destruction of fluoride complexes by boric acid has been studied. The measurement apparatus consists of two thermistors and a bridge. Clear breaks were obtained for iron, aluminium, copper and lead but no separation of iron and aluminium was possible. The action of boric acid also gave clear breaks in the curves.

ZUSAMMENFASSUNG

Es wird eine thermochemische Untersuchung der Titration von Aluminium-, Eisen-, Kupfer-, Blei-, Zinn- und Antimonsalzen mit Natriumfluorid beschrieben. Die Zerstörung des Fluorid-Komplexes durch Borsäure wurde untersucht. Die Messapparatur besteht aus 2 Thermistoren und einer Brücke. Eindeutige Knickpunkte wurden für Eisen, Aluminium, Kupfer und Blei erhalten, aber eine Trennung von Eisen und Aluminium war nicht möglich. Borsäure ergibt ebenso Knickpunkte in den Kurven.

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A SIMPLE, SENSITIVE, AND SPECIFIC COLORIMETRIC ASSAY FOR DIHYDROXYUREA

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The synthesis of dihydroxyurea (HOHN-CO-NHOH) has recently been accomplished by BOYLAND AND NERY¹, who also described a colorimetric assay for this compound by means of sodium aminoprusside and magnesium chloride in phosphate buffer. Although sensitive, this method also measures hydroxyurea¹, N-hydroxycarbamates², and arylhydroxylamines³. Since hydroxyurea is one of the decomposition products arising from dihydroxyurea, the method presents some difficulties in the measurement of dihydroxyurea alone. We have been interested in studying the possibility that dihydroxyurea may be a substrate for urease, as has been shown to be the case with hydroxyurea⁴, and in this instance it is essential that the assay for dihydroxyurea be insensitive to hydroxyurea, and to hydroxylamine, a reaction product. NERY has recently reported a very sensitive assay for hydroxamic acids, hydroxyureas, and hydroxylamine⁵. The present paper describes an extremely simple colorimetric assay, involving only alkali and alcohol, that is specific for dihydroxyurea and at the same time provides a sensitivity greater than that of the sodium aminoprusside reaction. The details of the method are described below along with its application in demonstrating urease catalysis of dihydroxyurea hydrolysis.

EXPERIMENTAL

Materials

The dihydroxyurea used in this study was a gift from Dr. E. BOYLAND, The Chester Beatty Research Institute, London, England. The white crystalline solid was markedly hygroscopic and was kept vacuum-desiccated until use. On paper and thin-layer chromatography with several solvent systems described below the material showed about 3–5% contamination with hydroxyurea, but no evidence of hydroxylamine salts or other compounds. Aqueous 10 mM solutions were stable for 2–3 weeks at 4°C. The other compounds used in this study were all reagent grade. The hydroxyurea was obtained from the E. R. Squibb & Sons, New York, and the jackbean urease, type VI, 7 Sumner units/mg, was obtained from the Sigma Chemical Company, St. Louis, Missouri.

Apparatus

Spectral absorption curves were performed on the Perkin-Elmer Model 202 double-beam spectrophotometer using silica cells with a 1-cm light path. Individual

absorption readings were carried out in a Beckman model DU spectrophotometer. Whatman #1 chromatography paper and Eastman silica gel chromatogram sheets were used for chromatographic studies, and densitometric quantitation was performed on a Photovolt Model 542 Densicord with Integrator.

Chromatographic procedures

Chromatography was carried out in water-saturated *n*-butanol, and in 4:1:5 *n*-butanol:acetic acid:water; the R_F values for dihydroxyurea, hydroxyurea and hydroxylamine were 0.13, 0.23, 0.04 in the former, and 0.17, 0.32, 0.07 in the latter. The spots were developed by spraying with iron(III) chloride, which gives greenish-purple stains with dihydroxyurea and hydroxyurea with gradual fading, and a delayed pink spot with hydroxylamine; or by chlorination followed by heating, which gives permanent brown colors with all three compounds on paper chromatograms⁶. Densitometry was carried out with a 545-nm filter for iron(III) chloride-sprayed chromatograms, and a 445-nm filter for chlorinated-heated chromatograms.

Assay procedure

Potassium hydroxide (0.5 ml of 12% w/v solution) was mixed with 7 ml of absolute ethanol. Up to 2.5 ml of aqueous sample containing dihydroxyurea was then added with mixing, and the final volume adjusted to 10 ml with water. After 3–5 min, the absorption was read at 400 nm against a reagent blank. The molar extinction coefficient for dihydroxyurea in this system was 6200, and absorption was linear with concentration to an optical density of 2.0, so that final concentrations of dihydroxyurea from 10–320 μM could be read directly.

RESULTS AND DISCUSSION

A yellow color appears rapidly upon mixing the dihydroxyurea with the alkaline ethanol. The time dependence of its appearance is shown in Fig. 1, as recorded

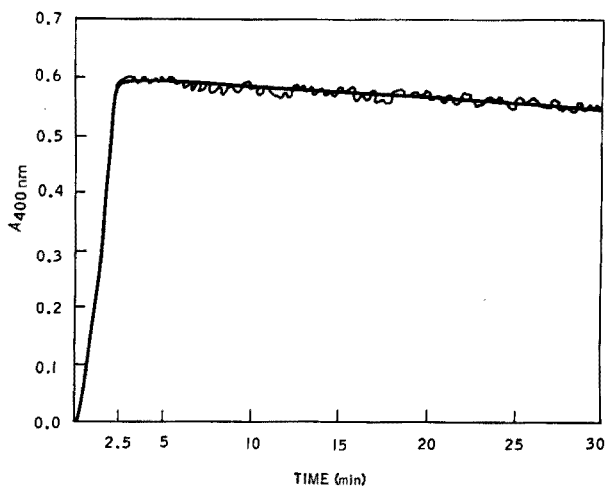


Fig. 1. Effect of time on the 400-nm absorption peak upon alkalization of 0.1 mM dihydroxyurea in 70% ethanol.

on a Gilford automated spectrophotometer at 400 nm. Color development is essentially complete in 2.5 min and is stable thereafter for several hours, the decay rate being less than 0.3% of the initial color per min. No absorption is given by 1-mM concentrations of hydroxyurea, hydroxylamine, N-hydroxyurethane, aceto-hydroxamic acid, propionohydroxamic acid, isobutyrohydroxamic acid, potassium cyanate, urea, or ammonium sulfate. Solutions containing moderate amounts of protein may be added directly to the assay without affecting the dihydroxyurea absorption after the precipitated protein has been centrifuged. The time for maximum color formation is increased under these circumstances, however, so that a 30-min waiting period is included before the optical density is read. If opalescence is a problem, the sample may be added first to the absolute alcohol and, after centrifugation and decanting of the supernate, the potassium hydroxide may be added subsequently. Concentrations of phosphate in excess of 2 mM produce turbidity, whereas 10 mM Tris-HCl or Tris-maleate do not.

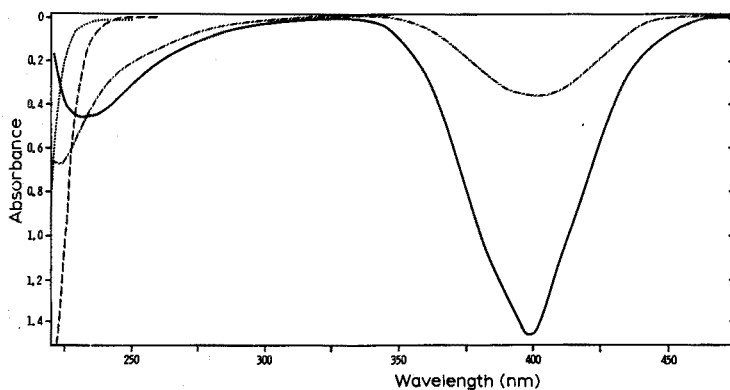


Fig. 2. Spectral absorption curves of 0.3 mM dihydroxyurea in aqueous and in alcoholic alkali. (—) 0.3 mM DHU in 0.6% KOH-70% ethanol; (---) 0.6% KOH-70% ethanol vs. water; (- · - ·) 0.3 mM DHU in 0.6% KOH; (.....) 0.6% KOH vs. water.

The spectral absorption curve of 0.30 mM dihydroxyurea in aqueous and ethanolic alkali is shown in Fig. 2. The reagent blanks in both cases show no absorption peak beyond 220 nm. In the presence of dihydroxyurea two absorption peaks appear, one in the ultraviolet region and one in the visible. The ultraviolet peak is at 225 nm in aqueous solution and is shifted to 235 nm and slightly decreased in the presence of 70% ethanol. The visible peak has a maximum at 400 nm and is increased severalfold in the presence of 70% ethanol. In neutral solutions of ethanol or water, dihydroxyurea fails to produce an absorption spectrum.

Effect of varying reaction conditions

The effects of varying the percentage of alcohol on the absorption at 400 nm is shown in Fig. 3. Seventy percent ethanol by volume gives maximum absorption, which subsequently falls with still higher concentrations. Methanol gives essentially the same effect as ethanol, while *n*-propanol is only about half as effective. Isopropanol, however, is even more effective than ethanol or methanol, with the maximum effect being noted at 60% (v/v). Should the added sensitivity be required, the reac-

tion carried out in 60% isopropanol would provide a molar extinction coefficient of 7700.

A final concentration of 0.6% potassium hydroxide (0.11 *N*) was found to be the most suitable, lower concentrations giving decreased absorption and higher concentrations leading to more rapid fading of the color complex. Equimolar concentrations of sodium hydroxide gave the same absorption as potassium hydroxide, indicating that the color complex is dependent only on the pH and not on the cation involved. The color complex was absent in solutions with a pH less than 12.

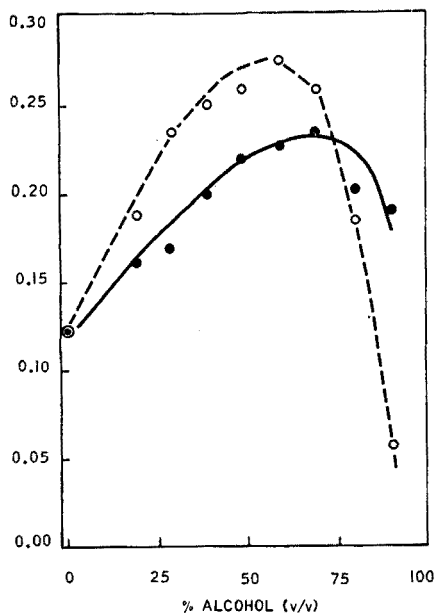


Fig. 3. Effect of varying concentrations of ethanol (—) and isopropanol (---) on the absorption by an alkaline solution of 0.04 mM dihydroxyurea at 400 nm.

Origin of the color complex

Since the color complex is generated in strong alkali, two possibilities present themselves as to the nature of the reaction. The first is that the dihydroxyurea is rapidly destroyed, giving rise to another product which is responsible for the formation of the yellow color. The second possibility is that the color complex arises from a reversible form of dihydroxyurea, the most likely being the doubly ionized hydroxamate ion. This would provide a reasonable explanation for the specificity of the reaction, since dihydroxyurea is the only hydroxamic acid which can generate a dibasic anion of this nature, and would explain the pH requirement since the pK_a is 10.5 for hydroxyurea⁷, and it is reasonable that the second hydroxamate ionization point would be even higher. If this is so, then dihydroxyurea should be recoverable, upon reacidification, for the same time period that the yellow color persists in alkali. This was tested in the following way: a 0.2 *M* solution of dihydroxyurea was made alkaline in 70% ethanol, and aliquots diluted for absorption readings at 400 nm at various time intervals. Other aliquots were reacidified, chromatographed, and stained by the iron(III) chloride or chlorination procedures described above. The

amount of chromatographically identified dihydroxyurea recovered was determined densitometrically. The results are shown in Fig. 4, where it may be seen that essentially complete recovery of the initial dihydroxyurea could be obtained for 2 h after the mixture had been made alkaline. The fall-off in recoverable dihydroxyurea thereafter occurred fairly synchronously with the decline in absorption at 400 nm in alkaline ethanol. This indicates that the assay method measures dihydroxyurea itself or some rapidly reversible form of the compound, presumably the dibasic anion.

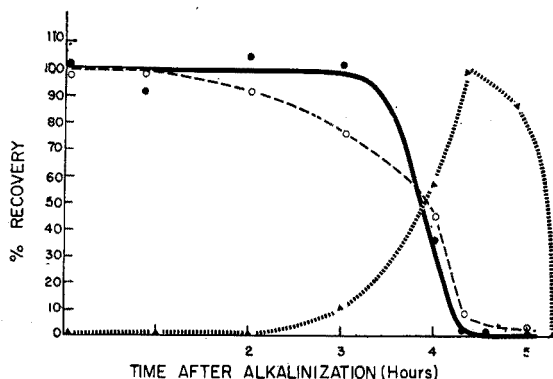


Fig. 4. Correlation between 400-nm absorption (●) by dihydroxyurea in alkali and chromatographically identified dihydroxyurea (○) after reacidification. The appearance of an unidentified new product (▲) on paper chromatograms is also shown.

During the period 4–5 h after alkalization, when the absorption at 400 nm and chromatographically recoverable dihydroxyurea were both declining rapidly, a new spot appeared on the chromatograms, reached its maximum concentration at about 4.25 h and then declined over the following hour. This apparently represented some new and irreversible by-product of dihydroxyurea breakdown which is itself relatively unstable, and whose R_F (0.51) does not match that of hydroxyurea (0.32) in this solvent system. Since the compound stains with the chlorination-heat procedure, it apparently contains the amido (–CO–NH–) grouping⁶; it is attractive to consider the possibility that it may be N-hydroxycarbamic acid but there are no data to substantiate this.

Stability of dihydroxyurea

BOYLAND AND NERY¹ noted that dihydroxyurea is rather labile in solution at all pH levels. However, our chromatographic recovery suggests that dihydroxyurea is stable for several hours in 0.1 M alkali in 70% ethanol, and that the color reaction described here is due to the intact molecule itself and hence serves as a convenient assay for stability of the compound in various solutions. With this assay, 10 mM solutions of dihydroxyurea in water were found to be stable within 10% of their initial reading for 2–3 weeks at 4°C. However, boiling in hydrochloric acid or standing in aqueous alkali resulted in a loss of most of the compound (Table I). In addition, the rate of breakdown of dihydroxyurea appeared to be greater at pH 7.4 than at 6.0 and to be accelerated by the presence of Tris buffers (Table I), although not by phosphate.

TABLE I

PERCENTAGE RECOVERY OF 1 mM DIHYDROXYUREA IN VARIOUS SOLUTIONS

Solution	Temperature (°)	Hours	% Recovery
0.83 N HCl	95	$\frac{1}{2}$	30
0.54 N KOH	25	16	20
Water (pH 6)	25	24	100
	25	48	100
	25	72	85
	25	72	100
0.1 M PO ₄ (pH 5.7) (pH 7.4)	25	72	100
	25	24	96
	25	48	48
	25	72	20
0.1 M Tris-HCl (pH 7.4)	25	4	82
	25	24	56
	25	48	9
0.1 M Tris-maleate (pH 7.4)	25	2	91
	25	24	68

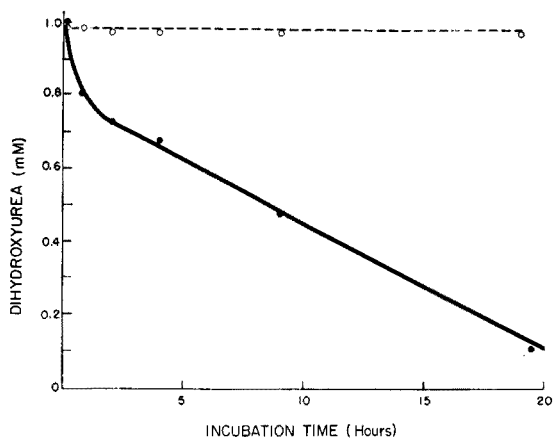


Fig. 5. Disappearance of dihydroxyurea on incubation with 0.36% urease (●) compared to its persistence in the presence of 0.36% albumin (○). Aqueous solutions of pH 6.0 were used in both experiments.

Dihydroxyurea as a substrate for urease

The assay described was used to demonstrate that dihydroxyurea is indeed hydrolyzed by urease. It is apparent from Fig. 5 that dihydroxyurea can be completely decomposed upon long-term incubation with urease, and that the reaction does not occur in the presence of other proteins such as albumin. The decay pattern for dihydroxyurea is quite similar to that of hydroxyurea⁴, in both instances the rate of hydrolysis being more than 100-fold slower than that of urea. The complete stoichiometry, kinetics, and specificity of the enzyme reaction will be described elsewhere⁸.

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We are indebted to Dr. E. BOYLAND, Chester Beatty Research Institute, London, England, for the supply of dihydroxyurea, without which this study could not have been made.

SUMMARY

A simple, sensitive and specific colorimetric assay for dihydroxyurea is described. The assay involves only 0.1 *M* alkali in 70% ethanol, gives a molar extinction coefficient of 6200 for dihydroxyurea, and is insensitive to hydroxamic acids, *N*-hydroxycarbamates, cyanate, ammonium salts, hydroxyurea, and hydroxylamine. The reaction appears to involve dihydroxyurea itself or some rapidly reversible form of the compound, presumably the dibasic anion. The assay has been used to demonstrate that dihydroxyurea is a substrate for the enzyme urease.

RÉSUMÉ

On décrit une méthode colorimétrique simple, sensible et spécifique pour l'analyse de la dihydroxyurée. On utilise une solution d'hydroxyde alcalin 0.1 *M* dans l'éthanol à 70%, donnant un coefficient d'extinction molaire de 6200. Les acides hydroxamiques, les *N*-hydroxycarbamates, cyanate, sels d'ammonium, hydroxyurée et hydroxylamine. Ce procédé est utilisé pour démontrer que la dihydroxyurée est un substrat pour l'uréase.

ZUSAMMENFASSUNG

Es wird eine einfache, empfindliche und spezifische Probe für Dihydroxyharnstoff beschrieben. Die Probe enthält nur 0.1 *M* Alkali in 70% Äthanol, ergibt einen molaren Extinktionskoeffizienten von 6200 und ist unempfindlich für Hydroxamsäuren, *N*-Hydroxycarbamate, Cyanate, Ammoniumsalze, Hydroxyharnstoff und Hydroxylamin. Der Nachweis wurde verwendet, um zu zeigen, dass Dihydroxyharnstoff ein Substrat des Enzyms Urease ist.

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EFFECTS OF γ -RADIATION ON SPECTROPHOTOMETRIC DETERMINATION OF URANIUM AS THIOCYANATE*

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Radiation chemists have been successful in investigating the effects of various types of radiation on many different materials, including many of interest to the analytical chemist. However, aside from studies of the radiation chemistry of relatively dilute and essentially pure aqueous solutions of substances that may serve as analytical reagents, little research has been done to establish the effects of the different types and levels of radiation on the methods of analytical chemistry. In recent years it has become necessary to make analytical determinations in radiation fields and the effects of such fields on the reactions and results have been unknown. The exact effects can be determined only by experiments carried out under the same conditions of radiation under which the analytical procedures must be carried out.

The spectrophotometric ammonium thiocyanate method for uranium¹ yields a relative standard deviation of about 4% when applied to the determination of 0.20–0.80 mg of uranium in a 25-ml final volume. It has been used for the determination of uranium in aqueous or organic media in the presence of relatively large amounts of thorium and small amounts of iron and copper.

The aqueous thiocyanate procedure is subject to many anionic interferences. CROUTHAMEL AND JOHNSON² developed a procedure in which the uranium thiocyanate complex color is developed in an acetone–water medium in order to circumvent these interferences, to increase the color stability and to make the color development relatively independent of pH. Standard deviations of 0.5% were obtained.

In both the uranium procedures, tin(II) chloride is used as a reducing agent for any iron present. The effect of radiation on uranium thiocyanate solutions in the presence and absence of tin(II) chloride was studied.

EXPERIMENTAL

Apparatus

Irradiation of the samples was carried out in 1/2-ounce glass bottles placed in reproducible positions with respect to a 288 or 3914-C cobalt-60 source. The dose rates in these positions, determined by ceric sulfate dosimetry, were of the order of

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$2 \cdot 10^5$ and $2 \cdot 10^6$ R/h initially and were corrected for decay. All irradiations were carried out at room temperature.

Spectral curves were obtained on a Beckman DK-2 recording spectrophotometer. Absorbance measurements at fixed wavelengths were made using a Beckman DU spectrophotometer. Stopped silica cells of 1.00-cm path length were used for all measurements.

Reagents

Solutions were prepared using ACS reagent-grade chemicals and distilled water according to the procedures recommended in the methods studied.

Since this entire study was intended to be one on the effect of radiation on the analytical procedure as normally performed, it was deemed unnecessary to attempt extensive purifications, *e.g.*, of water and glassware, that have become routine preliminary steps to the radiation chemist. It is for this reason that ordinary distilled water and glassware cleaned by normal analytical laboratory methods were used.

PROCEDURES

(A) Uranium thiocyanate in water medium

Presence of tin(II) chloride. To aliquots of a standard solution of uranium(VI) in 100-ml volumetric flasks were added 20 drops of concentrated hydrochloric acid, 20.0 ml of 8 M ammonium thiocyanate, and 4.0 ml of 20% tin(II) chloride dihydrate. The solutions were mixed and diluted to volume with distilled water. The solutions were divided into 10-ml portions, nine of which were irradiated. As soon as possible after removal of the solutions from the cobalt-60 source, the absorbances of the irradiated solutions and of the unirradiated control solution were measured against distilled water at 380 nm.

Absence of tin(II) chloride. The above procedure was repeated except that no tin(II) chloride was added.

(B) Uranium thiocyanate in acetone-water medium

Presence of tin(II) chloride. To aliquots of a standard solution of uranium(VI) in 100-ml volumetric flasks were added 40 drops of concentrated sulfuric acid, 10 ml of distilled water, 4.0 ml of 10% tin(II) chloride dihydrate, 60 ml of acetone saturated with ammonium thiocyanate, and distilled water to volume. The solutions were divided into 10-ml portions, nine of which were irradiated. As soon as possible after removal of the solutions from the source, the absorbances of the irradiated solutions and of the unirradiated control solution were measured against distilled water at 375 nm.

Absence of tin(II) chloride. The above procedure was repeated except that no tin(II) chloride was added.

RESULTS AND DISCUSSION

The major change that occurs in dilute aqueous solutions under the influence of light-particle radiations is in the dissolved material, as a result of the free radicals

H and OH produced from the water by the energy of the radiations. Reaction yields in radiation chemistry are expressed in terms of the number of molecules converted per 100 eV of energy absorbed, called "G"³. Because the analytical chemist probably is more familiar with the terms, the values for radiation effects given in this paper are expressed as concentration change per roentgen, *e.g.*, mmoles/ml/R, which has been designated the "radiation damage factor". In some instances, radiation effects which have been monitored by changes in absorbance have been expressed as "radiation damage", *i.e.*, the percentage change in absorbance of an irradiated solution from that of an unirradiated control solution. Since these radiolytic effects change with such variables as pH, the values are accurate only for the stated conditions.

Effect of radiation on uranium thiocyanate in water medium

In order to determine the effect of γ -radiation on the uranium thiocyanate complex in water solution, a series of samples prepared with and without tin(II) chloride, were subjected to γ -radiation at various levels. The difference between the absorbances of the irradiated solutions and of unirradiated control solutions was taken as a measure of the radiation-produced error.

Aqueous solutions of uranium thiocyanate containing tin(II) chloride showed a slight decrease in absorbance with increasing radiation dose until the appearance of elemental sulfur caused an increase in the absorbance (Fig. 1). The dose at which the absorbance increase first occurred was not the same for the various uranium levels studied, but was in the range $2 \cdot 10^5$ to $4 \cdot 10^5$ R.

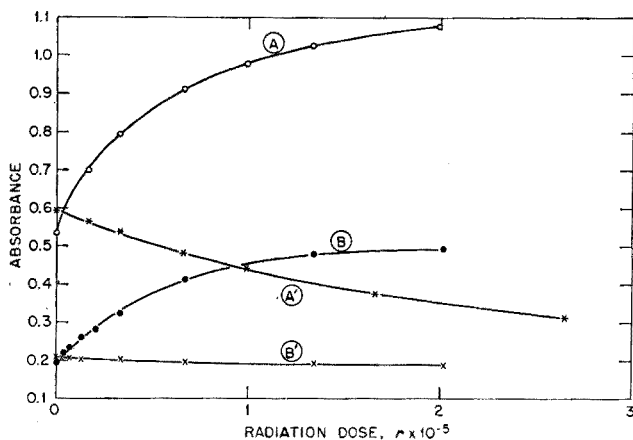


Fig. 1. Absorbance of uranium thiocyanate in various media as a function of radiation dose (see PROCEDURES for composition of test solutions). [U], 20 p.p.m. Dose, as shown. (A) Acetone-water, no SnCl_2 present. (A') Acetone-water, SnCl_2 present. (B) Water, no SnCl_2 present. (B') Water, SnCl_2 present.

The absorbances of a series of aqueous uranium thiocyanate to which no tin(II) chloride was added increased with increasing radiation dose over the entire dose range studied; again, however, the relationship was not linear (Fig. 1). This increase was due again to the turbidity caused by the elemental sulfur produced by the action of the radiation. However, in contrast to the solutions containing tin(II) chloride,

TABLE I
THE EFFECT OF MEDIUM, DOSE, AND URANIUM CONCENTRATION ON SENSITIVITY OF URANIUM THIOCYANATE TO RADIATION

[U] (p.p.m.)	Dose (R · 10 ⁻⁴)	Water medium				Acetone-water medium			
		SnCl ₂ present		No SnCl ₂		SnCl ₂ present		No SnCl ₂	
		RD (%) ^a	RDF (mM/ml/R) ^b (× 10 ¹¹)	RD (%) ^a	RDF (mM/ml/R) ^b (× 10 ¹¹)	RD (%) ^a	RDF (mM/ml/R) ^b (× 10 ¹¹)	RD (%) ^a	RDF (mM/ml/R) ^b (× 10 ¹¹)
10	1.66	0.0	—	—52	—	2.2	5.4	—40	—
	3.36	0.0	—	-104	—	7.2	9.1	-67	—
	9.93	1.8	0.49	-207	—	19.4	8.2	-103	—
20	20.20	5.3	1.1	—	—	31.8	6.7	-140	—
	1.66	2.8	1.4	-37	—	3.6	18	-30	—
	3.36	3.8	9.5	-66	—	8.2	21	-48	—
30	9.93	8.6	7.2	-129	—	24.7	20	-82	—
	20.20	10.5	4.4	—	—	40.4	17	-101	—
	1.66	2.6	20	-23	—	5.5	42	-23	—
40	3.36	4.9	19	-41	—	13.8	50	-39	—
	9.93	9.5	12	-83	—	32.2	41	-67	—
	20.20	12.8	8.0	—	—	48.0	30	-77	—
40	1.66	2.5	25	-17	—	6.0	61	-18	—
	3.36	4.4	22	-31	—	12.5	64	-32	—
	9.93	10.3	17	-62	—	33.9	57	-59	—
20.20	16.5	14	—	—	52.2	44	-65	—	

^a RD = Radiation damage = $\frac{\text{Absorbance of control} - \text{absorbance of irradiated sample}}{\text{Absorbance of control}} \times 100$. Negative values indicate an increase in absorption on irradiation.

^b RDF = Radiation damage factor = $\frac{\text{RD}(\%) \cdot [\text{U}](\text{mmoles/ml})}{\text{Total dose (R)}}$

the sulfur was produced immediately on irradiation, which shows the protection afforded by the tin(II) chloride. The odor of hydrogen sulfide was detected above all the irradiated solutions.

Effect of radiation on uranium thiocyanate in acetone-water medium

In order to determine the effect of γ -radiation on the uranium thiocyanate color in acetone-water solution, series of samples prepared by the procedure of CROUTHAMEL AND JOHNSON², both with and without tin(II) chloride, were subjected to γ -radiation at various levels. Again, the difference between the absorbances of the irradiated solutions and of unirradiated control solutions was taken as a measure of the radiation produced error (Fig. 1).

The absorbance of uranium thiocyanate in acetone-water solution in the presence of tin(II) chloride decreased with increasing radiation dose, markedly at doses less than $3 \cdot 10^5$ R and then more gradually.

Uranium thiocyanate in acetone-water solution containing no tin(II) chloride exhibited an increase in absorbance caused by radiolytic sulfur, with increasing radiation dose, again markedly at low doses and more gradually for doses greater than about $1 \cdot 10^5$ R (Fig. 1).

In Table I the effects of the various parameters are summarized. It is to be noted that the presence of tin(II) chloride acts as a protective agent in both water and acetone-water medium. However, it is less efficient in the acetone-water medium, as can be seen by the relative radiation damage factors for a given uranium concentration and radiation dose. The reason for the difference may well be due to the production of radiolytic organic radicals which may in turn attack the complex and/or the free thiocyanate. The radiolytic damage in the presence of tin(II) chloride in general increases with an increase in uranium concentration and the damage per unit of radiation decreases with increasing dose.

When no tin(II) chloride is present, the radiolytic sulfur causes a negative error, *i.e.*, the absorbance increases with radiation, at all levels of uranium concentration and dose levels studied. The effectiveness of the tin(II) chloride as a protective agent is undoubtedly due to the fact that its reaction rate with the radiolytic solvent products is higher than is that of the thiocyanate ion.

Effect of radiation on ammonium thiocyanate in water medium

In order to determine the effect of γ -radiation on solutions of ammonium thiocyanate under the approximate conditions of the aqueous uranium thiocyanate method, three series of 4 M ammonium thiocyanate solutions were prepared—one approximately neutral, one containing 5 drops of concentrated hydrochloric acid and one containing 2 drops of concentrated sulfuric acid—all in 10-ml total volumes. These solutions were submitted to γ -radiation at levels of $3.50 \cdot 10^4$, $6.70 \cdot 10^4$ and $1.68 \cdot 10^5$ R. All solutions were observed to contain radiolytic sulfur and to give off hydrogen sulfide. The amount of sulfur produced increased with increasing radiation dose. No attempt was made to determine these or any other radiolysis products quantitatively.

DUFLE⁴ has reported some results of work on the radiation chemistry of potassium thiocyanate solutions. His data for the irradiation of neutral solutions in the 0.002–0.1 M range indicate that thiocyanate ion is reduced in concentration as

a result of radiolysis by 1.3 molecules per 100 eV of energy absorbed while cyanide ion and sulfate ion plus free sulfur are produced in approximately the same amounts. These yields are reduced when the solutions are irradiated in a current of air and when degassed. According to DUFLE, no $S(CN)_2$, NO_2^- , NO_3^- , SO_2 , or H_2S is produced; there are some traces of CNO^- and, for very high doses, some NH_3 .

Effect of radiation on uranium(VI) in water medium

In order to determine the effect of γ -radiation on solutions of uranium(VI), portions of a 200 $\mu g/ml$ standard solution of uranium(VI) were submitted to various levels of γ -radiation. After irradiation the uranium(VI) remaining in the solutions was determined by the aqueous thiocyanate procedure⁵. Within the limits of error of the determination, no change in the uranium(VI) concentration was caused by doses from $3.35 \cdot 10^4$ to $1.34 \cdot 10^6$ R.

HAISSINSKY AND DUFLE⁵ have found that γ -radiation oxidizes uranium(IV) with the yield in deaerated solutions increasing toward a value of 2.1 molecules per 100 eV with increasing concentration of uranium(IV); in the presence of air they obtained a much higher yield dependent on the radiation intensity as expected for a chain reaction.

CONCLUSION

The experimental results of this study show the uranium thiocyanate method to be highly susceptible to radiation-caused error. However, the findings also indicate that, under optimum conditions, the method may be used under reasonable levels of radiation with little or no error caused by the radiation. These optimum conditions are as follows.

(1) The uranium content should be kept as low as possible, preferably below 10 p.p.m.

(2) Water medium should be preferred to the acetone-water mixture.

(3) Tin(II) chloride should be used as a protective agent whether or not there is need to reduce any iron present.

(4) The total permissible radiation dose should not exceed *ca.* $3 \cdot 10^4$ R in water medium and *ca.* $1 \cdot 10^4$ R in acetone-water medium following the procedures given. Radiation doses above this level will introduce appreciable positive or negative error dependent upon the dose level.

In conclusion, it should be emphasized that the above conditions and, indeed, all the data presented are applicable only under conditions of γ -radiation.

SUMMARY

The effects of γ -radiation on the spectrophotometric determination of uranium as the thiocyanate complex in water and acetone-water solutions have been studied. When tin(II) chloride is present, the absorbance of uranium thiocyanate in aqueous solution decreases with increasing radiation dose until the appearance of radiolytic elemental sulfur causes an apparent increase. In the absence of tin(II) chloride, the turbidity caused by radiolytic sulfur causes an increase in absorbance over the whole dose range studied. In acetone-water solution, similar but much more severe effects

occur. Observations of radiation effects of some of the individual reagents used in the spectrophotometric determinations are included, as well as indications of the errors caused by specific radiation doses.

RÉSUMÉ

Les auteurs ont examiné l'influence des rayons γ sur le dosage spectrophotométrique de l'uranium comme complexe thiocyanate, dans l'eau et dans des solutions eau-acétone. En présence de chlorure d'étain(II), l'absorption du thiocyanate d'uranium en solution aqueuse diminue avec l'augmentation de la dose de rayons, jusqu'à ce que l'apparition de soufre élémentaire radiolytique cause une augmentation apparente. En l'absence de chlorure d'étain(II), le trouble dû au soufre produit une augmentation d'absorption pour toutes les doses de rayons utilisées. En solution acétone-eau, on observe les mêmes effets, mais plus prononcés encore. On a examiné également les effets sur quelques réactifs individuels utilisés pour des dosages spectrophotométriques.

ZUSAMMENFASSUNG

Der Einfluss der γ -Strahlung auf die spektralphotometrische Bestimmung von Uran als Thiocyanat-Komplex in Wasser und Aceton-Wasser-Lösungen wurde untersucht. Wenn Zinn(II)-chlorid anwesend ist, nimmt die Absorption des Uranthiocyanats in wässriger Lösung mit steigender Strahlendosis ab, bis das Auftreten von radiolytischem elementarem Schwefel ein scheinbares Ansteigen verursacht. Bei der Abwesenheit von Zinn(II)-chlorid wurde ein Ansteigen der Absorption durch die Trübung des radiolytisch verursachten Schwefels über den gesamten untersuchten Dosisbereich festgestellt. In einer Aceton-Wasser-Lösung treten ähnliche, aber bei weitem stärkere Effekte auf. Weitere Beobachtungen der Strahleneinflüsse auf einige Reagenzien, die bei spektralphotometrischen Bestimmungen verwendet werden, wurden durchgeführt, ebenso werden Fehler, die durch spezifische Strahlendosen verursacht werden, aufgezeigt.

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THE SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM WITH
 BISMUTHIOL II AFTER SEPARATION WITH
 4,4'-METHYLENEDIANTIPYRENE AND 1,1,2,2-TETRACHLOROETHANE

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Tellurium can be separated from its most significant interferences, copper and selenium, by the extraction of its complex with 4,4'-methylenediantipyrene (MDAP) into 1,1,2,2-tetrachloroethane. Tellurium can be back-extracted into water and complexed with bismuthiol II, which can be extracted into chloroform. This combination of extractions results in a highly selective and sensitive procedure for the determination of tellurium. A practical lower limit of analysis appears to be 0.5 μg of tellurium. The method has been applied to solutions containing more than 500 mg of copper.

The separation procedure using MDAP is based on the work of BUSEV, BABENKO AND CHEPIK^{1,2} using diantipyrylpropylmethane and 1,2-dichloroethane. This earlier procedure appeared to have the following limitations: very slow separation of phases, inadequate sensitivity for the analysis of present day materials, and

TABLE I
 COMPARISON OF EXTRACTANTS FOR TELLURIUM-4,4'-METHYLENEDIANTIPYRENE

<i>Extractants</i>	$\mu\text{g Te}$	<i>Abs./330 nm</i> <i>(1-cm cell)</i>	<i>Corr.</i> <i>abs.</i>	<i>Comment</i>
1. Chloroform-1,1,2,2-tetrachloroethane (1:1)	0	0.028, 0.024		Separation good
	75	0.175, 0.193	0.149, 0.167	
2. 1,1,2-Trichloroethane	0	0.021, 0.026		Separation fair
	75	0.078, 0.089	0.054, 0.065	
3. 1,2-Dichloroethane	0	0.022, 0.026		Separation poor
	75	0.470, 0.456	0.446, 0.432	
4. 1,1,2,2-Tetrachloroethane	0	0.022, 0.028		Separations excellent
	75	0.724, 0.730	0.699, 0.702	
5. 1,2-Dichloroethane-1,1,2,2-tetrachloroethane (1:1)	0	0.030, 0.026		Separations good
	75	0.510, 0.498	0.482, 0.470	

a probable loss of tellurium in the backwash step (based on data from the procedure using bismuthiol II).

The final determination of tellurium using bismuthiol II is a modification of the procedure of YOSHIDA, TAGA AND HICKIME³. This procedure, like others in which this reagent is used⁴⁻⁷, is lacking in selectivity; copper and selenium in particular are major interferences.

The objective of this investigation was to establish a procedure for the determination of tellurium in small concentrations in the presence of major amounts of copper and lesser amounts of those elements frequently associated with copper including selenium. Previous papers using bismuthiol II reagent indicated that elim-

TABLE II

PERCENT RECOVERY OF 15 μg OF TELLURIUM WITH HCl CONCENTRATION IN THE BACKWASH STEP

<i>Backwash step</i>	<i>Abs./330 nm (5-cm cell)</i>
None	0.720
None	0.734
HCl (1:1) twice	0.455, 0.462
HCl (2:1) twice	0.115, 0.125
HCl (conc) twice	0.054, 0.056
HCl (1:1) and DMAP twice	0.718, 0.719

TABLE III

COMPARISON OF RECOVERY OF TELLURIUM WITH PRIOR SEPARATION TO BISMUTHIOL II STEP ONLY

<i>Procedure</i>	$\mu\text{g Te}$	<i>mg Cu</i>	<i>Corr. abs.</i>	<i>Corr. abs./ 1 $\mu\text{g Te}$</i>
1. Bismuthiol II only	5	0	0.222	0.0444
	10	0	0.448	0.0448
	15	0	0.666	0.0444
2. Bismuthiol and 4,4'-methylene-diantipyrene, without a backwash	5	0	0.226	0.0452
	10	0	0.448	0.0448
	15	0	0.668	0.0445
3. As above but with two backwashes with HCl (1:1)	5	0	0.164	0.0328
	10	0	0.327	0.0327
	15	0	0.497	0.0331
4. As above	5	500	0.157	0.0314
	10	500	0.356	0.0356
	15	500	0.466	0.0311
5. Bismuthiol II and 4,4'-methylene-diantipyrene with two backwashes with [HCl(1:1) and 6% MDAP]	5	0	0.210	0.0420
	10	0	0.439	0.0439
	15	0	0.662	0.0441
6. As above	5	500	0.217	0.0434
	10	500	0.439	0.0439
	15	500	0.670	0.0447
	20	500	0.897	0.0448

ination of interference by copper and selenium would make this reagent feasible in many analyses.

If a quantitative separation could be achieved using MDAP, the bismuthiol II procedure would make an excellent final photometric finish. In Table I, a comparison is made of several potential extractants for the tellurium MDAP complex. In Table II, a comparison is made of variations in the copper backwash step. In Table III, standard curves of bismuthiol II alone and variations of the MDAP separation using

TABLE IV
EFFECT OF COPPER ON THE DETERMINATION OF TELLURIUM

mg Cu	$\mu\text{g Te}$	Abs./330 nm (5-cm cell)	Corr. abs.	Av. abs.	Abs./100 mg Cu
0	0	0.030, 0.030			
100	0	0.032, 0.034	0.002, 0.004	0.0030	0.0030
200	0	0.035, 0.036	0.005, 0.006	0.0055	0.0028
500	0	0.049, 0.046	0.019, 0.016	0.0175	0.0035
1000	0	0.108, 0.111	0.078, 0.081	0.0795	0.0080
500	15	0.716, 0.721	0.668, 0.673	0.670	
0	15	0.706, 0.700	0.676, 0.670	0.673	

TABLE V
THE DETERMINATION OF TELLURIUM IN COPPER

Sample description	Aliq. wt. (g)	Wt% Te	%Te recovered
ASARCO Cu	0.500	0.00006	
+ 1 mg Cu (0.5% Te) ^a	0.500	0.00057	102
+ 2 mg Cu (0.5% Te) ^a	0.500	0.00055	98
+ 3 mg Cu (0.5% Te) ^a	0.500	0.00103	97
		0.00104	98
		0.00152	98
		0.00152	98
Cu with Pb 0.23%, Sb 0.049%, Se 0.026%, Bi 0.056%, Fe 0.033%, Te 0.02%, Ni 0.056%, As 0.039%	0.100	0.016	
Atomic abs. standards 15.1 $\mu\text{g Te}$	0.030	0.052	103
20.2 $\mu\text{g Te}$	0.020	0.104	103

^a Added as solution 0.2 mg per ml.

1,1,2,2-tetrachloroethane are compared in terms of sensitivity, selectivity and adherence to the Beer-Lambert law. In Table IV, there is a closer observance of the effect of copper on the MDAP-bismuthiol II determination of tellurium. The results of analysis using the established procedure are contained in Table V.

EXPERIMENTAL

Apparatus

A Beckman DU Spectrophotometer with a hydrogen lamp and 5-cm cells was used for absorbance measurements.

125-ml separatory funnels with teflon stopcocks were used for all extractions. Because of the importance of preventing leakage of 1,1,2,2-tetrachloroethane, the ground glass stopper penny heads were squashed to provide a firmer gripping surface.

Reagents

Bismuthiol II (1%). Prepare a 1% aqueous solution daily.

4,4'-Methylenediantipylene (5%) MDAP. Dissolve 5 g of the reagent in 100 ml of 1:1 acetic acid.

Buffer solution pH 3.5. Dissolve 1 g of EDTA and 20 g of sodium citrate in 100 ml of water. The pH is then adjusted to 3.5 with hydrochloric acid.

Buffer solution pH 7.5. Dissolve 10 g of EDTA, 10 g of $\text{Na}_2\text{B}_4\text{O}_7$ and 13 g of KH_2PO_4 in 1 l of water. The pH is then adjusted to 7.5 with 20% sodium hydroxide solution.

Matrix backwash solution. Mix 25 ml of MDAP and 400 ml of 1:1 hydrochloric acid.

Copper and tellurium solutions. Dissolve the pure metals in 1:1 nitric acid.

Final procedure

Aliquots containing the tellurium are placed in 100-ml beakers. Add 5 ml of 1:1 sulfuric acid and evaporate to vigorous fumes of sulfur trioxide. Cool and wash down sides of the beaker with 1:1 hydrochloric acid until the volume is approximately 25 ml. Transfer to a 125-ml separatory funnel, using 1:1 hydrochloric acid for rinsing. Add 2 ml of MDAP reagent and let stand for 1 min. Then add 10 ml of 1,1,2,2-tetrachloroethane and shake for 90 sec. Allow the layers to separate and reserve the organic layer in a second separatory funnel. Repeat the extraction with a second 10 ml portion of 1,1,2,2-tetrachloroethane and combine in the second separatory funnel. Discard the aqueous layer and rinse out the separatory funnel. Add 20 ml of the matrix backwash solution to the separatory funnel containing the organic layer and shake for 30 sec. Allow the layers to separate and reserve the organic layer in the first separatory funnel. Discard the aqueous layer and rinse out the separatory funnel. Repeat the backwashing of the organic layer with 20 ml of the matrix backwash solution. Again discard the aqueous layer and rinse out the separatory funnel. Add 15 ml of water to the organic layer and shake for 90 sec. Allow the layers to separate for a few minutes and reserve the organic layer in the other separatory funnel. Transfer the aqueous layer to a 100-ml beaker and rinse the separatory funnel into the beaker. Make a second 15-ml water extraction and combine with the previous aqueous layer in the beaker. Evaporate to 20–25 ml and cool. Add 2 ml of pH buffer 3.5 solution and adjust the pH to 3.0–3.5 (usually 1 drop of 1:1 hydrochloric acid). Transfer to a clean separatory funnel and add 1 ml of bismuthiol II solution. Let stand for 20–30 sec and extract with 22–24 ml of chloroform for 1 min. Reserve the chloroform layer in a second separatory funnel and discard the aqueous layer. Add 25 ml of buffer pH 7.5 solution to the chloroform layer and shake for 1 min. Allow the layers to separate and filter the chloroform layer through coarse filter paper into a dry 25-ml volumetric flask. Make to volume with chloroform. Determine the absorbance at 330 nm in 5-cm cells using the hydrogen lamp in the DU spectrophotometer. Carry a blank through the entire procedure.

For the determination of copper-base samples, 1:1 nitric acid is suitable for

dissolution. Aliquots containing less than 20 μg of tellurium can be treated just as described in the preparation of standard tellurium samples or synthetic copper-tellurium samples.

DISCUSSION AND DATA

The 1,1,2,2-tetrachloroethane is significantly the best extractant for the MDAP-tellurium complex. The extraction is quantitative and since results for samples containing up to 500 mg of high-purity copper are not significantly higher than aqueous blanks, there is no carry over of copper into the bismuthiol II extraction where there would be serious interference. All of the separations of 1,1,2,2-tetrachloroethane and aqueous layers are clean and relatively quick. The only drawback to the use of this reagent is its high level of toxicity (about twice that of carbon tetrachloride). Wherever possible the operations were performed in a hood. The used 1,1,2,2-tetrachloroethane was reserved for special safe disposal.

The use of MDAP in the hydrochloric acid backwash for the removal of copper and other interfering ions appeared to maintain the quantitative retention of tellurium in the organic phase. The standard curve going through the entire procedure showed only a small deviation from the bismuthiol II standard curve. The conformity to the Beer-Lambert law in the range of 5 to 20 μg of tellurium appeared to indicate that extrapolation to small concentrations of tellurium in copper would be feasible. The procedure using MDAP, 1,1,2,2-tetrachloroethane and backwashing with MDAP in 1:1 hydrochloric acid seemed practical for the determination of tellurium in copper. While the procedure had many steps, they were essentially simple and straightforward. The general good agreement in duplicate determinations in samples with and without copper indicates that there are probably no critical steps in the procedure.

The procedure when applied to 100, 200 and 500 mg of copper showed a consistent absorbance of 0.003 per 100 mg of copper, which is equivalent to 0.7 μg of tellurium per 1 g of copper. This may approximate the tellurium content of the high-purity copper used. The 1-g aliquots of copper showed a doubling of the absorbance per 100 mg of copper; this might be improved by a third backwash with MDAP and 1:1 hydrochloric acid.

The determination of tellurium in copper samples when applied to synthetic samples gave reasonable data, deviating by about $\pm 1\%$ from nominal. A special alloy containing 200–500 p.p.m. of Pb, Ni, Fe, Bi, As, Sb and Se gave a reasonable answer of 0.016% tellurium for an original addition of 0.02%.

CONCLUSIONS

The spectrophotometric determination of tellurium using a prior separation with MDAP and 1,1,2,2-tetrachloroethane and final determination with bismuthiol II and chloroform, while lengthy, appeared to be a feasible procedure for the determination of tellurium in copper and other metals and ores. Approximately 8 samples could be analyzed per day. The precision appeared to be approximately $\pm 2\%$ relative at even the 0.0010% level. A sample containing 40 μg of selenium gave the same absorbance as a reagent blank. Though larger amounts of selenium were not checked,

the evaporation from sulfuric acid would volatilize selenium. In the analysis of tellurium in concentrations below the level conveniently analyzed by gravimetric procedures or atomic absorption spectroscopy, this should be a useful procedure despite its apparent length.

SUMMARY

Tellurium can be isolated from most other elements by the extraction of its complex with 4,4'-methylenediantipylene into 1,1,2,2-tetrachloroethane. After isolation tellurium can be determined photometrically as its complex with bismuthiol II in chloroform. The procedure can be applied to copper and copper-based materials in the presence of many elements normally associated with copper, including selenium. The procedure is lengthy but straightforward, precise and subject to few interferences.

RÉSUMÉ

Le tellure peut être isolé de la plupart des autres éléments par extraction de son complexe avec le 4,4'-méthylènediantipyrène dans le tétrachloroéthane. Après séparation, le tellure peut être dosé photométriquement, sous forme de son complexe avec le bismuthiol II, dans le chloroforme. Ce procédé peut être appliqué à l'analyse du cuivre ou d'alliages à base de cuivre, en présence de nombreux éléments généralement associés au cuivre, y compris le sélénium. Cette méthode, bien que peu rapide, est simple, précise et sujette à peu d'interférences.

ZUSAMMENFASSUNG

Tellur kann von den meisten anderen Elementen durch Extraktion seines Komplexes mit 4,4'-Methylenediantipyrin in Tetrachlorkohlenstoff isoliert werden. Nach der Abtrennung wird Tellur spektralphotometrisch als Komplex mit Wis-muthiol(II) in Chloroform bestimmt. Das Verfahren eignet sich zur Untersuchung von Kupfer und Kupferlegierungen in Gegenwart von vielen Elementen, die normalerweise zusammen mit Kupfer vorkommen, einschliesslich Selen. Das Verfahren ist genau und besitzt nur wenige Störungen.

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GLYOXIMES AS REAGENTS FOR THE GRAVIMETRIC DETERMINATION OF BISMUTH

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The reaction of nickel(II) with dimethylglyoxime was reported by TSCHUGAEFF in 1905¹. Since that time numerous papers have appeared on the reaction of this, as well as other oximes, with nickel, palladium and platinum salts^{2,3}. The reaction of bismuth(III) with oximes, however, has been generally neglected and conflicting reports have appeared in the literature. KUBINA AND PLICHTA⁴ observed that bismuth(III) reacted with dimethylglyoxime to form a yellow precipitate which could serve as a qualitative test for bismuth, but could not be employed for the gravimetric determination because of a coprecipitation of bismuth hydroxide under the alkaline conditions needed. PESHKOVA AND SHLENSKAYA⁵ reported the formula of the precipitate of bismuth with dimethylglyoxime to be $\text{Bi}_2\text{O}_3\text{H}_2\text{DMG}$, where H_2DMG represents dimethylglyoxime. CELECHOVSKY AND OKAC⁶ believed that the yellow bismuth dimethylglyoxime precipitate was merely an adsorption compound of dimethylglyoxime with basic bismuth compounds. LOTT AND VITEK⁷ observed that this reaction could be employed for the gravimetric determination of bismuth when they employed EDTA in the procedure to mask the reaction of nickel and palladium with dimethylglyoxime and prevent the formation of basic bismuth compounds. They considered that the reaction occurred through an acid-base mechanism in which dimethylglyoxime ionized at a high pH to form a dibasic acid which reacted with bismuthyl ions, and reported the formula to be $\text{Bi}_2\text{O}_2\text{DMG}$.

Oximes such as 1,2-cyclohexanedionedioxime (nioxime) and α -furildioxime have been reported to show a similar specificity for only nickel and palladium^{2,3}. Accordingly, it was decided to investigate these and several other oximes to establish their reactions with bismuth.

EXPERIMENTAL

Apparatus

X-ray powder patterns were obtained with a General Electric XRD-6 unit using a Phillips powder camera of 114.6 mm diameter.

Tracer studies were conducted with a Baird-Atomic Model 530 Spectrometer using a thallium-activated sodium iodide well probe.

Reagents

Bismuth solution (10.00 mg Bi/ml). This was prepared by dissolving 10.000 g

of 99.999% granular bismuth metal (Fairmount Chemical Co., Inc.) in dilute nitric acid and diluting to 1 l with water.

Radioactive bismuth stock solution. This was prepared by adding 3 ml of ^{210}Bi (0.1 mC) nitrate (Oak Ridge National Laboratory) to 47 ml of 0.0565 *M* bismuth nitrate solution.

Lead solution (10 mg Pb/ml). This was prepared by dissolving 8.00 g of lead nitrate (Mallinckrodt) in water and diluting to 500 ml.

Thallium solution (10 mg Tl/ml). This was prepared by dissolving 1.2202 g of thallium(I) formate (Distillation Products, Inc.) in water and diluting to 100 ml.

Oximes. Bis(biacetylmonoxime)-*o*-phenylenediimine, 4-carboxy-bis(biacetylmonoxime)-1,2-phenylenediimine, and bis(biacetylmonoxime)-2,3-naphthalenediimine were prepared by condensing biacetylmonoxime with 1,2-diaminobenzene, 3,4-diaminobenzoic acid, and 2,3-diaminonaphthalene respectively^{8,9}. About 5 g of the diamine, 5 g of biacetylmonoxime and 10 ml of 10% sodium hydroxide solution were added to 500 ml of water. The reaction mixture was then heated for 30 min on a steam bath and the oxime formed was precipitated on cooling in ice. The product was recrystallized from water or dilute ethanol. Solutions of these oximes (0.1 *M*) were prepared by dissolving the oxime in alcohol or acetone.

Other oximes employed were obtained commercially from Distillation Products, Inc., or Aldrich Chemical Co. Solutions of these oximes (0.1 *M*) were prepared by dissolving the oxime in 0.1 *M* potassium hydroxide solution.

Qualitative reactions

Qualitative tests were undertaken to determine if bismuth would react with various oximes in a manner similar to the reaction with dimethylglyoxime⁷. These tests were performed by adding 10 ml of 0.1 *M* EDTA and 5 ml of 0.1 *M* oxime solution to 2 ml of 0.05 *M* bismuth nitrate solution, and then adjusting the pH to 12 as indicated by universal indicator paper. The positive results are recorded in Table I; there was no reaction with acetoneoxime, cyclohexanoneoxime, 2,3-butanedione-monoxime, 2,4-pentanedionedioxime or 1,4-cyclohexanedionedioxime.

Qualitative interference studies were also conducted to determine the specificity of the reaction between bismuth and 1,2-cyclohexanedionedioxime. These tests were performed as described above with 5 ml of a 0.01 *M* solution of the metal ion instead of bismuth, with the addition of cyanide ion. Similar tests were also performed to determine which foreign ions would interfere by forming hydroxides or hydrous

TABLE I

QUALITATIVE REACTION OF BISMUTH WITH VARIOUS OXIMES AT pH 12 IN THE PRESENCE OF EDTA

<i>Oxime tested</i>	<i>Reaction observed</i>
Dimethylglyoxime	Yellow precipitate formed
1,2-Cyclohexanedionedioxime	Yellow precipitate formed
4-Methyl-1,2-cyclohexanedionedioxime	Yellow precipitate formed
Bis(biacetylmonoxime)- <i>o</i> -phenylenediimine	Yellow precipitate formed
4-Carboxy-bis(biacetylmonoxime)-1,2-phenylenediimine	Yellow precipitate formed
Bis(biacetylmonoxime)-2,3-naphthalenediimine	Yellow precipitate formed
α -Furildioxime	Light yellow precipitate formed
Diphenylglyoxime	Light yellow precipitate formed
5-Methyl-1,2,3-cyclohexanetrionetrioxime	Light yellow precipitate formed

oxides in the presence of 10 ml of 0.1 *M* EDTA at pH 12. No reaction was found under either sets of conditions with Al(III), Au(III), Ba(II), Ca(II), Cd(II), Co(II), Cu(II), Fe(II), Hg(II), K(I), La(III), Na(I), Ni(II), Pb(II), Pd(II), Pt(II), Sn(II), V(III) or Zn(II). White precipitates were formed in both tests with Mg(II) (no reaction at pH 11), Sb(III), Sn(IV), Th(IV), Ti(IV) and Zr(IV), green precipitates with Cr(III), red-brown precipitates with Fe(III), black precipitates with Mn(II) and yellow precipitates with U(VI). With Bi(III) a white precipitate was formed in absence of oxime and a yellow precipitate in its presence.

Recommended gravimetric procedure for bismuth

Add an appropriate amount of EDTA solution to the solution containing 50–500 mg of bismuth. Add enough EDTA to complex both the bismuth and foreign ions present. Adjust the solution to pH *ca.* 7 and then add an excess of potassium cyanide and a 30–40% excess of 0.1 *M* oxime solution. Adjust to pH 12 with potassium hydroxide and then digest the precipitate for 30–60 min on a hot plate. After cooling, filter the precipitate on a previously weighed medium-porosity sintered glass or porcelain crucible, washing the precipitate several times with distilled water. Dry the precipitate to constant weight at 95°–105°.

When Fe(III), Cr(III), Mn(II), Sn(IV) or Sb(III) is present, the above procedure should be slightly modified. Add excess of EDTA to the solution containing bismuth and one or more of the foreign ions. Then adjust to pH 8.0–8.5 by rapidly adding 4 *M* potassium hydroxide to form the hydroxides of these interfering ions. Digest for 15 min on a steam bath and then remove the hydroxides by filtering through a Gooch crucible using fiberglass filter mat. Add potassium cyanide to the filtrate and precipitate the bismuth oxime complex as stated above.

RESULTS

The above procedure was used with five oximes for bismuth and with 1,2-cyclohexanedionedioxime for lead; the results are recorded in Table II. The elemental analyses of two bismuth–dioxime complexes are shown in Table III.

The optimum pH for the gravimetric determination of bismuth using nioxime was determined. These precipitations were made as described above, except that the pH was adjusted to other appropriate values. The results are shown in Fig. 1.

Solubility of bismuth glyoximates

To determine the solubility product of the bismuth glyoximates, isotopic dilution techniques were employed. Approximately 10 ml of the radioactive stock bismuth solution was treated with excess oxime solution and excess EDTA and then adjusted to pH 12 with potassium hydroxide solution. The yellow bismuth glyoximate formed was digested for 45 min on a hot plate and then transferred into 4 centrifuge tubes. The precipitate was centrifuged for several minutes and the filtrate decanted. The precipitate was then washed with 5-ml portions of 0.1 *M* EDTA solution adjusted to pH 12, with centrifuging and decantation after each washing; generally, three washes were required as indicated by a constant count of the filtrate. The precipitate was then allowed to equilibrate for 1–2 h with 5 ml of 0.1 *M* EDTA solution which had been adjusted to pH 12 with potassium hydroxide solution. The precipitate

TABLE II
 GRAVIMETRIC RESULTS

Reagent	Foreign ions	Bi present (mg)	Bi found (mg)
1,2-Cyclohexanedionedioxime	—	49.9	50.7, 50.4
	—	99.9	100.5, 100.6
	—	149.7	150.1, 150.7
	—	250.1	252.0, 252.4, 250.1
	—	499.1	505.5
	Fe, Mn ^a	99.9	100.9, 101.5
	Pd, Ni	99.9	100.9, 101.5
	Ba, Co, Cu, Ca, Pb, Mg	99.8	98.4, 99.9
	Ga, La, Al, Cd, Zn	99.8	99.9
	Sn, Sb ^a	99.8	103.3, 102.6
	Ti, Zr ^a	149.7	152.2, 154.9
	Fe, Cr, Mn ^a	99.8	101.1, 100.6
	Cr, Mn	99.8	100.5, 100.4
	Th, UO ₂ ²⁺ ^a	149.7	150.7, 153.1
	Hg	99.8	100.1
4-Methyl-1,2-cyclohexanedione-dioxime	—	49.9	52.6
	—	99.9	98.4
	—	250.1	247.3
	—	499.1	493.1
Bis(biacetylmonoxime)- <i>o</i> -phenyl-enediimine	—	49.9	31.0
	—	99.9	62.1
	—	250.1	155.2
	—	499.1	312.2
α -Furildioxime	—	99.9	98.0
	—	99.9	90.4
	—	250.1	240.6
	—	250.1	256.8
Diphenylglyoxime	—	99.9	84.1
	—	99.9	76.4
	—	250.1	216.9
	—	250.1	246.5
		<i>Pb present (mg)</i>	<i>Pb found (mg)</i>
1,2-Cyclohexanedionedioxime	—	100.0	98.2
	—	150.0	147.1
	—	200.0	199.9
	—	250.0	249.2

^a Filtration procedure used to remove interfering ions.

was then centrifuged and 3-ml samples of the filtrate were counted for a preset count of 1,000 and the background subtracted. A 3-ml sample of the radioactive stock bismuth solution was also counted and the background subtracted. The concentration of bismuth in the filtrate, and consequently the apparent K_{sp} , were then calculated. The results are recorded in Table IV.

X-ray crystallographic measurements

X-ray crystallographic powder patterns were obtained for the bismuth gly-

TABLE III

MICROANALYSIS OF PRECIPITATES

		<i>C</i>	<i>H</i>	<i>N</i>	<i>O</i>	<i>Bi</i>
<i>Bismuth complexes</i>						
1,2-Cyclohexanedionedioxime (C ₆ H ₈ N ₂ O ₄ Bi ₂)	Exptl.	12.26	1.55	4.87	10.70	70.62
	Theor.	12.20	1.36	4.75	10.85	70.84
4-Methyl-1,2-cyclohexane- dionedioxime (C ₇ H ₉ N ₂ O ₄ Bi ₂)	Exptl.	14.08	1.60	4.64	11.54	68.14
	Theor.	13.93	1.49	4.64	10.61	69.32
<i>Lead complex</i>						
1,2-Cyclohexanedionedioxime (C ₆ H ₈ N ₂ O ₄ Pb)	Exptl.	20.87	2.31	8.49	7.58	60.75
	Theor.	20.74	2.31	8.07	9.22	59.66

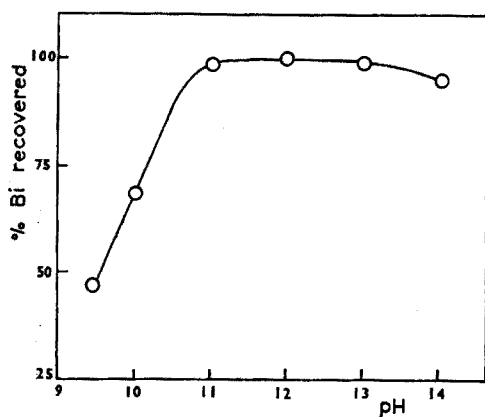


Fig. 1. Recovery of bismuth with nioxime.

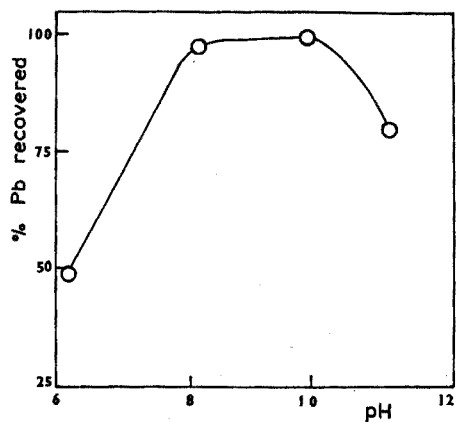


Fig. 2. Recovery of lead with nioxime.

TABLE IV

SOLUBILITY PRODUCTS OF BISMUTH GLYOXIMATES

<i>Oxime</i>	<i>K_{sp}</i>
1,2-Cyclohexanedionedioxime (nioxime)	1 · 10 ⁻¹⁴
Dimethylglyoxime (DMG)	2 · 10 ⁻¹³
4-Methyl-1,2-cyclohexanedionedioxime	1 · 10 ⁻¹⁴
Bis(biacetylmonoxime)- <i>o</i> -phenylenediimine	6 · 10 ⁻¹⁴

oximes formed from dimethylglyoxime, bis(biacetylmonoxime)-*o*-phenylenediimine, 4-carboxy-bis(biacetylmonoxime)-1,2-phenylenediimine, bis(biacetylmonoxime)-2,3-naphthalenediimine, and 1,2-cyclohexanedionedioxime. The bismuth oxime precipitates were found to be extremely insoluble in a host of solvents, and in fact no suitable solvent was found to dissolve them. Consequently, single crystals could not be produced and the powder method was employed. Copper radiation was used with a 2-h exposure time.

Reaction of nioxime with lead and thallium

Since nioxime was found to be an excellent reagent for the gravimetric

precipitation of bismuth(III), its reaction with lead(II) was examined, since the precipitation of lead with dimethylglyoxime has been reported¹⁰. The precipitation of lead with nioxime could be done only in the absence of EDTA.

The optimum pH for the quantitative precipitation of lead was found to be 10 (Fig. 2). To observe if the reaction was quantitative, a 3-4 fold excess of 0.1 M nioxime solution was added to solutions containing 100, 150, 200 and 250 mg of lead, respectively. The acidity of each solution was then adjusted to pH 10.0 and the lead-nioxime precipitate was digested for 30 min on a hot plate, cooled, filtered, dried at 110°, and weighed. The gravimetric results are recorded in Table II and the composition of the complex in Table III.

Both lead(II) and thallium(I) are isoelectronic to bismuth(III). Accordingly, thallium(I) was also tested for any possible reaction with nioxime. By very carefully lowering the pH of a very strongly basic solution of nioxime which contained thallium(I) to pH 10-11, by the addition of perchloric acid, thallium was precipitated with nioxime, but not quantitatively.

DISCUSSION

Although several of the tested glyoximes were observed to react with bismuth, nioxime and 4-methylnioxime were observed to be the most suitable gravimetric reagents. Representing the oximes by the general formula H_2Ox , the general overall reaction for the precipitation of bismuth is:



Nioxime, because of its water solubility, minimizes the "creeping" of the bismuth precipitate and is thus the preferred reagent. It also requires a short digestion period to react completely with bismuth to form the insoluble yellow bismuth glyoximate. It was also observed that nioxime would actually quantitatively precipitate bismuth as the bismuth glyoximate, at pH 10, even if bismuth hydroxide had already formed, and that this precipitation could be performed in the absence of EDTA.

Bismuth was gravimetrically determined in the presence of most common cations using nioxime in the presence of EDTA with a relative standard derivation of 1%. EDTA and cyanide are added as masking agents in the procedure to prevent the reaction of nickel and palladium with the oxime, and also to minimize the precipitation of metal hydroxides upon pH adjustment. Of the foreign cations tested only Sb(III), Cr(III), Fe(III), Mn(II), Hg(II), Th(IV), Sn(IV), Ti(IV), UO_2^{2+} and Zr(IV) interfered in the reaction. These ions caused interference in the gravimetric procedure not because they reacted with nioxime, but because of their tendency to precipitate as oxides or hydroxides in strongly basic solutions. Attempts to prevent this interference with masking agents such as oxalate, tartrate, citrate, fluoride, pyrophosphate, or cyanide ions, as well as triethanolamine or ascorbic acid, failed because these complexing agents either did not prevent precipitation as hydroxides, or also complexed bismuth so strongly to prevent its reaction with nioxime. However, by modification of the gravimetric procedure as stated in the experimental section, Fe(III), Cr(III), Mn(II), Sn(IV) and Sb(III) could be removed.

Of the ions tested only bismuth reacts with nioxime in the presence of EDTA at this pH. Thus from a standpoint of chemical reactivity, this reaction could be con-

sidered just as specific as the "well known specificity" of dimethylglyoxime and nioxime as reagents for only nickel and palladium.

To characterize the precipitates, solubility products of several precipitates were determined by isotopic dilution techniques. Attempts to determine the solubility product of these materials in water by this technique failed because the bismuth-glyoxime precipitate dispersed into such small particles that simple centrifugation did not give a good separation. With 0.1 *M* EDTA adjusted to pH 12 as the solvent (conditions similar to those employed in the precipitation of bismuth), separation by centrifugation became feasible. In this solvent system, the solubility products for the oximes studied were of the order of 10^{-13} – 10^{-15} , which confirms that bismuth is precipitated quantitatively.

The similarity of the X-ray data indicates that these compounds are isomorphous. The exact structural formulae of these precipitates is not known. Several structures have been proposed for the bismuth-dimethylglyoxime precipitate⁵⁻⁷ and these same considerations would also apply to these reported bismuth precipitates. The "d" spacings agreed with those for the bismuth dimethylglyoximate reported by LOTT AND VITEK⁷. However, several additional lines were also resolved for this compound and of special interest is the very intense broad line corresponding to a "d" spacing of 13.34 Å. A similar very intense line was observed for the other bismuth glyoximates as well. Examination of these powder patterns indicates that these compounds are probably monoclinic rather than of cubic structure as reported previously⁷. The X-ray data have been submitted to the A.S.T.M. powder data file.

Qualitative tests were performed to see if monoximes or dioximes separated by more than one carbon atom would also react with bismuth. If the reaction were of an acid-base nature, a bismuth-oxime precipitate should be formed with a structure similar to that proposed by LOTT AND VITEK⁷; however, no reaction was observed. Infrared and X-ray data indicate that the bismuth glyoximates have a definite crystal structure and cannot be adsorption complexes. The necessity for the two oxime groups to be adjacent to each other for the reaction to occur, indicates that the bismuth-oxime precipitates are probably of a chelate structure involving a bismuth-oxygen-bismuth linkage. The gravimetric factor obtained with nioxime and 4-methylnioxime, as well as microanalyses of these precipitates confirms the general formula of Bi_2O_2 (oxime) postulated by LOTT AND VITEK.

Preliminary results show that the isoelectronic elements to bismuth, lead(II) and thallium(I) also react with nioxime and 4-methylnioxime. The reaction of lead(II) with nioxime is quantitative, and a precipitate with the general formula $\text{Pb}(\text{oxime})$ is formed. Further work is under way to investigate the physical properties and possible analytical applications of these findings.

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NOTE ADDED IN PROOF. An article by J. BASSET, T. B. LETOW AND A. I. VOGEL

has recently appeared (*Analyst*, 92 (1967) 279) proposing a polymeric bismuth structure for certain of these compounds.

SUMMARY

Several oximes were investigated for possible use as organic precipitating reagents for bismuth. Of the oximes studied, nioxime (1,2-cyclohexanedionedioxi-*m*) was found to be an excellent gravimetric reagent for 50–500 mg of bismuth. The precipitation of bismuth was carried out in the presence of EDTA at pH 12 in aqueous solution; EDTA was used simultaneously as a masking agent for specificity and to prevent the formation of bismuth hydroxides. Bismuth could be determined in the presence of over 30 cations including Ni and Pd. The determination of lead nioximate was briefly studied.

RÉSUMÉ

Plusieurs oximes sont examinées en vue d'être utilisées comme réactifs organiques de précipitation du bismuth. La nioxime (1,2-cyclohexanedionedioxi-*m*) s'est révélée être un excellent réactif gravimétrique pour le dosage de 50–500 mg de bismuth. On précipite le bismuth en présence d'EDTA à pH 12, en solution aqueuse; EDTA est utilisé simultanément comme agent de masquage et pour empêcher la formation d'hydroxydes de bismuth. On peut ainsi doser le bismuth en présence de plus de 30 cations, comprenant Ni et Pd. On a étudié brièvement le dosage du nioximate de nickel.

ZUSAMMENFASSUNG

Einzelne Oxime wurden als mögliche organische Fällungsreagenzien für Wismut untersucht. Von den untersuchten Oximen zeigte sich Nioxim (1,2-Cyclohexandionedioxi-*m*) als ausgezeichnetes gravimetrisches Reagenz für 50–500 mg Wismut. Die Fällung des Wismuts geschieht in Gegenwart von AeDTE beim pH 12 in wässriger Lösung. AeDTE wurde gleichzeitig zur Maskierung und zur Verhinderung der Bildung von Wismuthydroxid verwendet. Wismut konnte in Gegenwart von über 30 Kationen einschliesslich Ni und Pd bestimmt werden. Die Bestimmung von Bleinioximat wurde kurz untersucht.

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1-(*o*-CARBOXYPHENYL)-3-HYDROXY-3-PHENYLTRIAZENE, A NEW REAGENT FOR THE DIRECT GRAVIMETRIC DETERMINATION OF TITANIUM(IV)

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Titanium has been determined gravimetrically by such reagents as cupferron¹, oxine² and its chloro- and bromo-derivatives^{3,4}, *p*-hydroxyphenylarsonic acid⁵, *N*-benzoyl-*N*-phenylhydroxylamine⁶, and 3-hydroxy-1-*p*-chlorophenyl-3-phenyl-triazene⁷. The use of EDTA and the control of pH increase to a great extent the selectivity of cupferron as a precipitant for titanium, but phosphate, beryllium, uranium(VI), niobium, tantalum and tin(II) interfere⁸. Because of the instability of the reagent itself the titanium precipitate is of uncertain composition and must be ignited to the oxide before weighing. 3-Hydroxy-1-*p*-chlorophenyl-3-phenyltriazene and *p*-hydroxyphenylarsonic acid also need ignition of the titanium precipitate to oxide and are subject to many interferences, like the oxines and *N*-benzoyl-*N*-phenylhydroxylamine which, however, give precipitates of definite composition.

In this paper, the preparation and the use of a new triazene derivative, 1-(*o*-carboxyphenyl)-3-hydroxy-3-phenyltriazene, which forms a highly stable 2:1 complex with titanium(IV), are reported. The compound is moderately soluble in nitrobenzene and in chloroform, less soluble in pyridine and only slightly soluble in benzene, acetone, dioxan, carbon tetrachloride, methanol and ethanol. When re-crystallised from a mixture of chloroform and nitrobenzene, the titanium complex melts with decomposition at 283°–284°. The complex is stable in acid solution (2 *N* hydrochloric acid) and also at the boiling temperature of the reaction medium, but it hydrolyses at pH values above 6.0.

The reagent can be utilised for the direct gravimetric determination of titanium and for its separation in presence of EDTA from almost all ions, except niobium and tantalum. Fluoride, if present, is masked by the addition of an excess of beryllium solution. Hydrogen peroxide in the absence of EDTA has no effect but when present along with EDTA prevents titanium from reacting with the reagent; this effect of peroxide can be easily avoided by boiling the solution with an excess of sodium hydroxide and adjusting the pH to the optimum value before the final precipitation of the element. After precipitation at pH 2.0–5.0, the titanium complex can be weighed after drying at 115–120°. Titanium(IV) can be precipitated quantitatively at pH 1.0–2.0 but then the precipitate must be ignited to oxide before weighing. For the separation of titanium from niobium and tantalum, the procedures described earlier may be followed^{9,10}, and the separated titanium can be determined by this method.

The coloured complexes formed with vanadium(V) and iron(III) are soluble in many organic solvents. Details of the spectrophotometric determination of these

ions and their separation from each other and from other ions will be described in a later publication.

The palladium(II) and copper(II) complexes can be quantitatively precipitated from boiling solutions by the addition of an alcoholic solution of the reagent in the pH ranges of 3.0–6.0 and 3.0–5.5, respectively; the precipitates can be dried at 115–120° and weighed as MRH_2O (where $R=C_{13}H_9O_3N_3$ and M = the bivalent metal ions). The decomposition temperature of these complexes appears to be at 250° and 305°, respectively. The complexes are insoluble in water, fairly soluble in pyridine but slightly soluble in ethanol, chloroform, carbon tetrachloride, acetone, benzene and nitrobenzene. The nickel and cobalt complexes are somewhat soluble in the reaction medium.

In its reaction with palladium or copper, the reagent behaves as a tridentate chelate, but with titanium(IV) the carboxyl group appears to be unreactive. From a study of the infrared spectra of the complexes of palladium, copper and titanium, it is quite clear that while palladium and copper replace the hydrogen atoms of both the salt-forming groups (OH and COOH), titanium does not react with the carboxyl group. In the titanium complex, the asymmetric stretching frequency of the carbonyl group remains unaffected, appearing at 1680 cm^{-1} , whereas for the palladium and copper complexes this frequency shifts to 1613 and 1650 cm^{-1} , respectively. The OH band from the reagent itself is destroyed in all the 3 complexes. Only in the titanium complex, the band due to $Ti=O$ appears at 876 cm^{-1} . The titanium complex probably has the composition $TiO(C_{13}H_{10}N_3O_3)_2$. Further evidence that the carboxyl group does not participate in the reaction with titanium(IV) is provided by the fact that the methyl ester of the reagent gives the same titanium reaction as the free acid. Moreover, its solubility before hydrolysis in water at a pH of 6.0 or higher supports the presence of free carboxyl groups in the complex.

EXPERIMENTAL

Apparatus

A Cambridge pH meter and a Hilger Spectrophotometer with 10-mm glass cells were used, respectively, for pH and absorption measurements.

Preparation of the reagent

Anthranilic acid was diazotised in the cold and coupled with freshly prepared phenylhydroxylamine. The yellowish brown product was crystallised twice from alcohol, m.p. 164–165°. (Found: C 60.78%, H 4.61%, N 16.64%; $C_{13}H_{11}N_3O_3$ requires C 60.70%, H 4.28%, N 16.34%). The reagent is stable to heat, light and air and can be stored indefinitely. It is highly soluble in methanol, ethanol, acetone, nitrobenzene and dioxan, slightly soluble in chloroform, benzene and carbon tetrachloride, very slightly soluble in hot water but dissolves easily in alkaline solution.

A 5% (w/v) solution of the reagent in alcohol was used for the precipitation of titanium.

Standard solutions

A standard solution of titanium(IV) was prepared from potassium titanyl oxalate, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, a weighed amount of which was digested with concentrat-

ed sulphuric acid and then diluted, after cooling, with water to the required volume. The solution of titanium(IV) was standardized gravimetrically as the dioxide in the conventional way¹¹.

Solutions of other ions were prepared from the chloride or the nitrate salts of cations and from the sodium, potassium and ammonium salts of anions. Their concentrations were determined by standard procedures.

A 8% (w/v) solution of EDTA (disodium salt) was used as the complexing agent. The amount of EDTA to be added must not be more than 100 times the amount of titanium present.

General procedure

Dilute an aliquot of titanium solution to 200 ml with water, and add 5 g of ammonium chloride and 4 ml of the reagent solution (20 times the amount of titanium) with stirring. Adjust the pH to 2.0–5.0, and boil for 15–20 min, very cautiously when the reddish-orange precipitate appears. Filter through ashless filter paper, wash with water at room temperature until free from sulphate and ignite to oxide before weighing. Alternatively, filter through a no. 3 Gooch crucible, wash 5–6 times, with 10-ml portions of hot 1:2 ethanol–water at pH 3 and then 2–3 times with water, dry at 115–120° and weigh as the complex.

TABLE I

DIRECT DETERMINATION AND SEPARATION OF TITANIUM FROM OTHER IONS

(Ti taken = 10.49 mg in each case)

<i>Ions added</i>	<i>Added amount (mg)</i>	<i>pH</i>	<i>Wt. of the dried complex (mg)</i>	<i>Ti found (mg)</i>
Fe ³⁺	250	4.0	125.8	10.46
Al ³⁺	250	2.8	126.3	10.51
Cr ³⁺	250	3.5	126.7	10.53
Be ²⁺ , Mg ²⁺	200 (each)	3.0	126.0	10.48
Zn ²⁺ , Cd ²⁺ , Hg ²⁺	100 (each)	3.8	126.6	10.53
Sn ²⁺	250	4.0	127.0	10.56
Mn ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺	100 (each)	4.0	126.8	10.54
Pd ²⁺	100	3.2	126.3	10.51
As ³⁺ , Sb ³⁺ , Bi ³⁺	100 (each)	3.2	126.7	10.53
Th ⁴⁺	100	3.8	125.5	10.43
AsO ₄ ³⁻ , PO ₄ ³⁻	100 (each)	3.5	126.4	10.52
VO ₃ ⁻	250	3.5	126.0	10.48
WO ₄ ²⁻	200	3.0	126.5	10.52
MoO ₄ ²⁻	200	3.0	126.6	10.53
SeO ₃ ²⁻ , TeO ₄ ²⁻	100 (each)	3.5	125.7	10.45
Lanthanides	100	3.5	126.5	10.52
UO ₂ ²⁺	200	4.0	125.7	10.45
Ce ³⁺	200	4.2	125.9	10.47
Ce ⁴⁺	200	3.5	126.8	10.54
Zr ⁴⁺	200	2.5	126.5	10.52
Oxalic acid	1000	4.0	126.6	10.53
Citric acid	1000	4.0	126.0	10.48
Tartaric acid	1000	3.5	126.6	10.53
F ⁻	250	3.0	126.6	10.53
H ₂ O ₂	5 ml. "20 vol"	3.5	126.5	10.52
Nb ⁵⁺	20	3.5	182.3	15.16
Ta ⁵⁺	20	4.0	194.0	16.14

Effect of pH

The effect of the pH of precipitation was examined for 3.6 and 10.2 mg of titanium(IV), with ignition to the oxide. Results were slightly low when the initial acidity was 0.2 N; precipitation was quantitative from solutions of pH 1.0–5.5 and results were low when the initial pH was 5.8.

Composition of the titanium complex

The titanium complex was precipitated at pH 2.0–5.0, filtered on a crucible, and washed and dried as described above. The titanium content of the dried complex was determined by carefully igniting a weighed amount of the complex to TiO_2 . The nitrogen content was determined by the Dumas method. The composition found agreed with the formula $\text{TiO}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3)_2$ (Found: Ti 8.25%, N 14.56%; calculated Ti 8.32%, N 14.58%). The conversion factor for the titanium content is therefore 0.08316.

Separation from foreign ions

Solutions containing known amounts of different foreign ions plus known amounts of titanium (as sulphate) were mixed with an 8% (w/v) EDTA solution. The amount of EDTA was 10–15 times the amount of total ions. Addition of ammonium chloride and reagent solution (20 times the amount of titanium) and the adjustment of pH were done as in the *General Procedure*, the complex being weighed as such. When tungstate and molybdate were present, the titanium solution was boiled after the addition of EDTA to dissolve the precipitate formed by the corresponding acids and then the usual procedure was followed. Results are shown in Table I.

SUMMARY

A direct gravimetric method for the determination of titanium with a new reagent, 1-(*o*-carboxyphenyl)-3-hydroxy-3-phenyltriazene, is proposed. The titanium is precipitated at the pH range 2.0–5.0 and weighed as $\text{TiO}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3)_2$ after drying at 115–120°. In the presence of EDTA, only niobium and tantalum interfere.

RÉSUMÉ

On propose une méthode gravimétrique directe pour le dosage du titane à l'aide d'un nouveau réactif, le 1-(*o*-carboxyphényl)-3-hydroxy-3-phényltriazène. Le titane est précipité au pH 2.0–5.0 et pesé sous forme de $\text{TiO}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3)_2$ après séchage à 115–120°. En présence d'EDTA, seuls Nb et Ta gênent.

ZUSAMMENFASSUNG

Es wird eine gravimetrische Methode zur Bestimmung von Titan mit dem neuen Reagenz 1-(*o*-Carboxyphenyl)-3-hydroxy-3-phenyltriazen vorgeschlagen. Das Titan wird im pH-Bereich von 2.0–5.0 gefällt und als $\text{TiO}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3)_2$ nach Trocknen bei 115–120° gewogen. In Gegenwart von AedTE stört nur Niob und Tantal.

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A SPECIFIC METHOD FOR THE SEPARATION OF MERCURY(II) USING A WEAKLY BASIC CELLULOSE ION EXCHANGER

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The paper-chromatographic behavior and separation of many metal ions on the cellulose anion-exchanger DEAE (diethylaminoethylcellulose) in different media have been widely investigated¹⁻¹¹. KAUFMAN AND KEYES¹² have used DEAE to separate the anionic chromium-thiocyanate complexes, including the geometric isomers $\text{Cr}(\text{SCN})_4(\text{H}_2\text{O})_2^-$ by chromatography on a DEAE column. It has also been shown that the column-chromatographic separation of rhenium(VII), molybdenum(VI) and tungsten(VI) can be achieved in dilute thiocyanate media¹³.

A systematic investigation of the behavior of metal ions on DEAE in thiocyanate media revealed that very few metal ions show any marked adsorption on DEAE, while mercury(II) exhibits a pronounced adsorption. This behavior allows the development of a very selective method for the separation of mercury(II).

EXPERIMENTAL

Reagents and apparatus

Cellulose exchanger. A weakly basic cellulose anion-exchanger, DEAE (diethylaminoethylcellulose; Serva; Gallard-Schlesinger Chemical Manufacturing Corp.) was purified and converted to a thiocyanate form and stored in a desiccator over saturated potassium bromide solution as described before¹³. Where necessary, the chloride form was used.

Stock solution of metal ions. The stock solution of mercury(II) was prepared by dissolving an appropriate amount of mercury(II) chloride in water to give *ca.* 10 mg Hg(II) per ml. For other metals, stock solutions were prepared by dissolving the respective oxide, chloride or oxysalt to give a solution containing *ca.* 10 mg of each metal ion per ml of 0.1–0.5 *M* hydrochloric acid solution. The acid concentration was raised to 3 *M* for stock solutions of antimony(III) and tin(IV). Nitrates of bismuth(III), lead(II) and thallium(I) were used to obtain solutions containing 10 mg of the metal per ml of 0.1 *M* nitric acid. Distilled, deionized water was used throughout, unless otherwise mentioned. The stock solutions were standardized by conventional methods.

Buffer solution. Mixtures of 0.1 *M* hydrochloric acid–0.1 *M* potassium chloride and of 0.1 *M* acetic acid–0.1 *M* sodium acetate were used as buffer solutions, respectively, in the pH ranges 1–2 and 3–6.

Ion-exchange column. DEAE (1 g) was slurried with water and poured into a

conventional glass column, I.D. 1.0 cm, pulled to a tip and plugged with glass wool at the outlet. The resulting bed was usually 6 cm long.

Equilibrium studies

The distribution coefficient, K_d , of mercury(II) was determined by a batch equilibrium method. DEAE in the desired form (0.5-g batches) was weighed out and placed in glass-stoppered conical flasks containing 1-ml portions of a standard mercury(II) solution (1.11 mg Hg(II)) and 40 ml of a desired buffer solution of varying thiocyanate or chloride concentrations. After shaking for 15 h at $25.0 \pm 0.1^\circ$, the equilibrium pH of the aqueous phase was recorded and the two phases were separated by filtration. An aliquot of the filtrate was analyzed for mercury(II) colorimetrically with dithizone. The K_d was computed from the following formula:

$$K_d = \frac{\text{Amounts of ion in DEAE phase/g of DEAE}}{\text{Amounts of ion in solution phase/ml of solution}}$$

Column separation procedure

About 10 ml of the sample solution adjusted to 0.01 *M* in ammonium thiocyanate and 0.1 *M* in hydrochloric acid [or nitric acid for separating bismuth(III), lead(II) or thallium(I)] is loaded on the top of the column previously treated with the same acid thiocyanate solution as above. When the sample solution almost reaches the top of the column bed, non-adsorbable metal ions are washed out of the

TABLE I

ANALYTICAL METHODS USED

Cation	Method
Al(III) ^a , Ga(III) ^a , Ni(II) ^a , V(IV) ^a As(III) ^a	Titration with EDTA using Cu-PAN as indicator Colorimetrically with ammonium molybdate
Bi(III), Co(II) ^a , In(III), La(III), Lu(III), Sc(III), Sm(III), Th(IV), Tl(I), Y(III), Zn(II)	Titration with EDTA using xylenol orange as indicator
Ca(II)	Titration with EDTA ^b
Cd(II), Mg(II), Mn(II), Pb(II), Sr(II)	Titration with EDTA using eriochrome black T as indicator
Cr(III) ^a	Colorimetrically as chromate
Cu(II) ^a	Titration with EDTA using PAN as indicator
Fe(III) ^a	Titration with EDTA using variamine blue B as indicator. Colorimetrically with NH ₄ SCN for traces
Ge(IV)	Colorimetrically with phenylfluorone
Hg(II)	Colorimetrically with dithizone
Mo(VI), Re(VII)	Colorimetrically with KSCN-SnCl ₂
Pd(II) ^a	Colorimetrically with α -nitroso- β -naphthol
Sb(III) ^a	Colorimetrically with KI after decomposition of tartaric acid
Se(IV), Te(IV)	Colorimetrically with SnCl ₂
Sn(IV) ^a , W(VI) ^a	Colorimetrically with dithiol
U(VI) ^a	Colorimetrically with hydrogen peroxide
Zr(IV)	Colorimetrically with quercetin

^a Determined after decomposition of thiocyanate with HNO₃.

^b With 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid as indicator.

column by about 30 ml of 0.01 *M* ammonium thiocyanate–0.1 *M* hydrochloric acid solution [0.01 *M* ammonium thiocyanate–0.1 *M* nitric acid for bismuth(III), lead(II), thallium(I)]. Mercury(II) is then stripped from the column by elution with about 30 ml of 0.5 *M* perchloric acid solution.

When mercury(II) is accompanied by molybdenum(VI) and/or tungsten(VI), the column should be pretreated with several column volumes of pH 3 acetate buffer solution adjusted to 0.01 *M* in ammonium thiocyanate and 1 *M* in potassium chloride. Approximately 10 ml of sample solution, adjusted also as above, is soaked into the column. Mercury(II) is quantitatively eluted by 50 ml of the same thiocyanate–chloride solution. Molybdenum(VI) and/or tungsten(VI) can easily be stripped from the column by elution with 50 ml of 0.1 *M* sodium hydroxide–0.1 *M* sodium chloride solution.

Analytical methods used for effluent analysis are listed in Table I.

RESULTS AND DISCUSSION

K_d values for mercury(II) in thiocyanate media on DEAE (thiocyanate form) are tabulated in Table II as functions of the thiocyanate concentration and of acidity. At each thiocyanate concentration, the K_d values for mercury(II) do not vary to any great extent with pH within the range 1–3 (see Series A). However, the concentration of thiocyanate/or chloride exhibits a marked effect on K_d for mercury(II). In the pH range tested, the K_d values for mercury(II) tend to show a slight maximum at 0.01 *M* in ammonium thiocyanate concentration, decreasing rapidly with increasing concentration of thiocyanate. The presence of chloride ions also decreases the K_d values for mercury(II), as can be seen by comparison between the two sets of data at pH 3. The values for mercury(II) in 1 *M* perchloric acid of varying thiocyanate concentrations are distinctly lower and exhibit no dependence on chloride concentration.

The chloride dependence of K_d values for mercury(II) is also demonstrated in Table III, where K_d values for mercury(II) on DEAE (thiocyanate form) are listed as a function of chloride concentration. Within the lower chloride concentration range (<0.10 *M*) the K_d values for mercury(II) are well above $2 \cdot 10^3$, but decrease sharply as the concentration of chloride increases.

TABLE II

DISTRIBUTION COEFFICIENTS FOR MERCURY(II) AS FUNCTIONS OF THIOCYANATE CONCENTRATION AND pH*

Series	pH	Concn. of NH_4SCN (<i>M</i>)						Total concn. of Cl^-
		0	0.010	0.050	0.10	0.50	1.0	
A	3.0	$2.3 \cdot 10^3$	$2.8 \cdot 10^3$	$1.8 \cdot 10^3$	$9.7 \cdot 10^2$	$1.0 \cdot 10^2$	43	0.10(KCl)
	2.0	$2.3 \cdot 10^3$	$2.5 \cdot 10^3$	$2.1 \cdot 10^3$	$1.2 \cdot 10^3$	$1.1 \cdot 10^2$	37	0.10(KCl–HCl)
	1.0	$2.2 \cdot 10^3$	$2.9 \cdot 10^3$	$2.5 \cdot 10^3$	$1.2 \cdot 10^3$	$1.1 \cdot 10^2$	43	0.10(KCl–HCl)
	1.00 <i>M</i> HClO_4	18	23	29	18	41	24	0.10(NaCl)
B	3.0	$> 10^4$	$> 10^4$	$\sim 10^4$	$4.6 \cdot 10^3$	$1.2 \cdot 10^2$	37	None
	1.00 <i>M</i> HClO_4	19	23	30	22	37	20	None

* DEAE in a thiocyanate form.

TABLE III

EFFECT OF TOTAL CHLORIDE CONCENTRATION ON THE DISTRIBUTION COEFFICIENT OF MERCURY(II)

pH	Concn. of Cl ⁻						
	0	0.010	0.030	0.10	0.30	0.50	1.0
<i>With DEAE-SCN⁻ form^a</i>							
3.0 ^b	> 10 ⁴	> 10 ⁴	> 10 ⁴	2.8 · 10 ³	3.0 · 10 ²	1.2 · 10 ²	34
1.0 ^c				2.9 · 10 ³	3.3 · 10 ²	1.2 · 10 ²	28
<i>With DEAE-Cl⁻ form^a</i>							
3.0 ^b	9.1 · 10 ²	1.1 · 10 ³	1.2 · 10 ³	6.8 · 10 ²	2.0 · 10 ²	87	27
1.0 ^c				6.3 · 10 ²	2.2 · 10 ²	95	28

^a The concentration of NH₄SCN was kept at 0.010 M throughout.

^b KCl was added to pH 3 acetate buffer solution to give the chloride concentration listed.

^c To KCl solution of the listed chloride concentration, HCl solution of the same chloride concentration was added to give the chloride buffer solution of pH 1.

^d No thiocyanate present.

The form of DEAE is of particular importance in keeping the K_d values for mercury(II) sufficiently high. For comparison K_d values for mercury(II) in chloride media on DEAE in the chloride form are also listed in Table III. These are generally much lower than those involving DEAE in the thiocyanate form in thiocyanate and chloride media, particularly if the chloride concentration is kept less than 0.1 M.

To prevent a breakthrough of mercury(II) and a hydrolysis of many other metal ions, it was decided that 0.01 M ammonium thiocyanate solution of ca. pH 1 should be used for most purposes to achieve chromatographic separation of mercury(II) and other ions. The K_d value for mercury(II) in this medium comes close to $3 \cdot 10^3$, which is sufficiently high to retain mercury(II) on a small column.

The study of the elution and batch equilibrium behavior of individual metal ions indicates that Al(III), As(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ga(III), Ge(IV), In(III), La(III), Lu(III), Mg(II), Mn(II), Ni(II), Re(VII), Sc(III), Se(IV), Sm(III), Sn(IV), Sr(II), Te(IV), Th(IV), V(IV), Y(III), Zn(II), Zr(IV) do not exhibit any marked adsorption from 0.01 M ammonium thiocyanate-0.1 M hydrochloric acid solution, so that they can be quantitatively recovered from the column in the first 30-ml fraction of the effluent. Only Mo(VI), Pd(II), Pt(IV) and W(VI) ions are among those that show a pronounced adsorption from thiocyanate media. The complete separation of mercury(II) and platinum(IV) was unsuccessful because of the complex behavior of platinum(IV) on DEAE in thiocyanate media.

For the separation of mercury(II) from bismuth(III), lead(II) or thallium(I), the sample solution should be adjusted to 0.01 M ammonium thiocyanate-0.1 M nitric acid to avoid chloride precipitation. The same solution may be used as eluent. Proper amounts of tartaric acid must be present for the separation of antimony(III) both in sample solution and eluent to prevent hydrolysis of antimony(III). Common anions, nitrate, sulfate and phosphate, do not interfere with the separation, but a large excess of chloride should be absent. The results on quantitative separation are given in Table IV.

The effectiveness of the method presented allows widely varying proportions of mercury(II) and iron(III), at least mercury(II):iron(III) = 100:1 and mercury(II):iron(III) = 1:8,000, to be separated very easily. The method may be extended

TABLE IV
 SEPARATION OF MERCURY(II)

Hg(II) (μg)		Foreign ions (mg)		
Taken	Found	Taken	Found	
III	114	Al(III)	9.23	9.25
III	109	As(III)	9.99	9.99
III	111	Bi(III)	9.87	9.88
III	113	Ca(II)	9.38	9.37
III	109	Cd(II)	10.1	10.0
III	114	Cd(II) ^a	10.1	10.1
III	114	Cd(II) ^b	10.1	10.1
III	108	Cd(II) ^c	10.1	10.1
III	112	Cd(II) ^d	10.1	10.1
III	109	Co(II)	9.81	9.80
III	109	Cr(III)	8.88	8.93
III	111	Cu(II)	10.1	10.1
III	111	Fe(III)	11.1	11.0
III	109	Fe(III)	876	882
I.II · 10 ⁴	I.II · 10 ⁴	Fe(III)	0.111	0.113
I.II · 10 ⁴	I.II · 10 ⁴	Fe(III)	11.1	11.2
III	114	Ga(III)	12.4	12.4
III	121	Ge(IV)	9.40	9.48
III	110	In(III)	15.1	14.8
III	114	La(III)	19.8	19.9
III	105	Lu(III)	10.2	10.2
III	109	Mg(II)	9.07	9.14
III	111	Mn(II)	9.76	9.65
III	114	Mo(VI)	10.1	10.4
III	111	Ni(II)	9.53	9.65
III	109	Pb(II)	10.3	10.3
III	114	Pd(II) ^e	1.06	1.03
III	108	Re(VII)	0.906	0.924
III	112	Sb(III) ^f	15.3	15.2
III	114	Sc(III)	5.11	5.10
III	111	Se(IV)	10.5	10.3
III	109	Sm(III)	8.94	8.92
III	109	Sn(IV)	15.8	16.0
III	114	Sr(II)	10.0	10.0
III	109	Te(IV)	9.00	9.00
III	111	Th(IV)	8.98	9.03
III	113	Tl(I)	12.0	12.1
III	112	U(VI)	11.3	11.3
III	117	V(IV)	12.5	12.7
III	108	W(VI)	10.0	9.73
III	114	Zn(II)	9.90	9.97
III	111	Zr(IV)	9.96	9.51
III	114	Y(III)	11.1	11.0

^a 10 ml sample solution adjusted to 1 M in NaNO₃.

^b 10 ml sample solution adjusted to 1 M in (NH₄)₂SO₄.

^c 10 ml sample solution adjusted to 1 M in H₃PO₄.

^d 10 ml sample solution adjusted to 1 M in NaCl. Increasing sample volume may cause a breakthrough of Hg(II) from the sample solution.

^e Hg(II) eluted in the effluent from 10 ml of the sample and subsequent 40 ml of wash solution, both 0.01 M in NH₄SCN and 1 M in HCl.

^f 10 ml of sample solution contained 100 mg of tartaric acid to prevent hydrolysis.

to the separation of other metal ions which widely vary in proportion. The accuracy and precision of the method are satisfactory; the mean deviation of the results quoted in Table IV is 2.0% for 111 μg of mercury(II), and the standard deviation was 3.0 μg for 111 μg of mercury(II). In summary, the method presented permits mercury(II) to be separated from about 40 elements with a simple eluent on a column containing only one gram of DEAE.

SUMMARY

A systematic study of the behavior of many metal ions on the weakly basic cellulose exchanger DEAE in dilute thiocyanate media showed that few metal ions are adsorbed. The adsorption of mercury(II) allows a rapid and highly selective separation from about 40 metal ions. Quantitative results are quoted for the separation of ca. 100 μg of mercury(II) from milligram amounts of other metal ions; 100 μg to 10 mg of mercury(II) can be quantitatively separated from iron(III) in proportions of mercury(II):iron(III) = 100:1 to 1:8,000 on a column containing only 1 g of DEAE.

RÉSUMÉ

Une étude sur le comportement de divers métaux avec échangeur cellulose, faiblement basique (DEAE), en milieu thiocyanate dilué, a montré que peu d'ions métalliques sont adsorbés. L'adsorption du mercure(II) permet sa séparation rapide et très sélective d'avec une quarantaine d'autres métaux. On peut ainsi séparer quantitativement 100 μg –10 mg de mercure(II) d'avec le fer(III) en proportions mercure(II)/fer(III):100/1 à 1/8000 sur une colonne contenant 1 g DEAE.

ZUSAMMENFASSUNG

Eine systematische Untersuchung des Verhaltens vieler Metallionen auf schwach basischen Zelluloseaustauscher in verdünntem Thiocyanatmedium zeigte, dass einige Metallionen adsorbiert werden. Die Adsorption von Quecksilber(II) erlaubt seine schnelle und sehr selektive Abtrennung von etwa 40 Metallionen. Für die Abtrennung von ca. 100 μg Quecksilber(II) von Milligrammen anderer Metallionen werden quantitative Ergebnisse angegeben. 100 μg –10 mg Quecksilber(II) können quantitativ vom Eisen(III) im Verhältnis von 100:1 bis 1:8000 auf einer Kolonne, die nur 1 g Austauscher enthält, abgetrennt werden.

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THE NATURE OF LIGHT

PART III. LIGHT AND THE SPECIAL CASE OF RELATIVITY

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None of the concepts of the nature of light provide any explanation for its apparent singular velocity, and therefore, for the deduction of the Special Case of Relativity. It should be pointed out that there is no relationship between the comments in these articles, and previous articles which discussed the nature of light¹. However, it is inevitable that any serious thought on the nature of light will lead to the question, "Why should the Special Case of Relativity exist; what is non-Newtonian about light particles?" No explanation based on light structure has ever been attempted, and this presentation does not attempt such an explanation. Rather, it questions the validity of the Special Case.

THE CASE FOR THE SPECIAL CASE OF RELATIVITY

The Michelson-Morley experiment

The basis for the Special Case of Relativity is the Michelson-Morley experiment. A popular portrayal of this experiment is as follows:

A and B are two swimmers in a river which flows at 4 ft/min. The width of the river is 45 feet. Swimmer A swims directly across the river and back to the same point on the bank. It can be seen from Fig. 1 that to do this he must swim at an angle to the current, and that his velocity *across* the river will be 3 ft/min. The total time

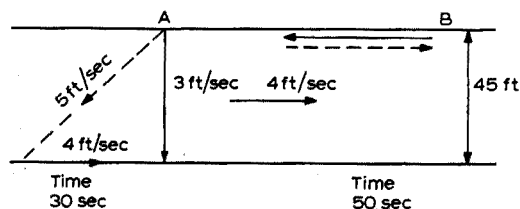


Fig. 1. The swimmer in a river.

taken will be $(45 + 45) : 3 = 30$ min. Swimmer B swims upstream 45 feet, and downstream 45 feet, back to point B. The time taken is $45 : (5 - 4) = 45$ min upstream, and $45 : (5 + 4) = 5$ min downstream. Total time, 50 min.

It can be seen that each travels 90 feet and returns to the same point, but that each takes a different time, because the velocity of the river is superimposed on the velocity of the swimmer.

Similarly, if we take two beams of light, one in the direction of the rotation of the earth, the other across the rotation of the earth, the time taken for each beam to travel an equal distance should be different *if the velocity of the earth is superimposed on the velocity of the light* (originally the experiment was to prove if the velocity of the earth was superimposed on the "ether" which carried the light).

The Michelson–Morley experiment showed no interference patterns arising from two such beams of light, and concluded that the velocity of the earth was *not* superimposed on the velocity of the ether carrying the light (later on the velocity of the light itself). FITZGERALD explained this as a foreshortening of the distances involved. EINSTEIN said that the two beams existed in different time coordinates which are related by the equation

$$T = \tau \sqrt{1 - v^2/c^2} \quad (1)$$

where T and τ are the time coordinates, v is the relative velocity of the source and observer, and c is the speed of light in a vacuum. The optical arrangement of the Michelson–Morley experiment is shown in Fig. 2.

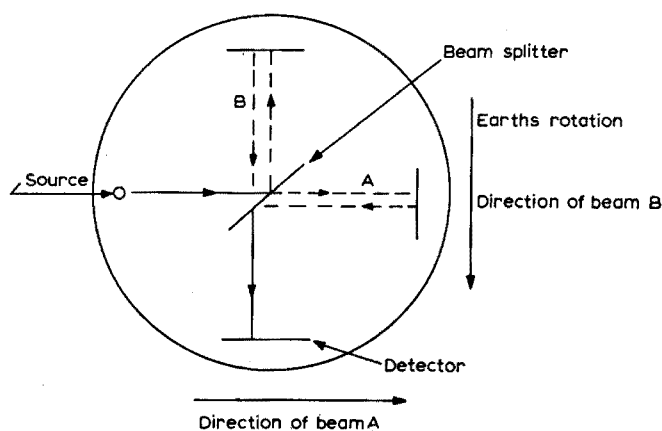


Fig. 2.

Without doubt, this expression and beautiful piece of philosophy has led to some great mathematical advances. However, the concept of a variable time is alien to all of man's instincts. On the other hand, the mathematicians and physicists have used this as another variable and have been able to solve many problems and make many predictions based on this hypothesis. The value to science cannot be over-emphasized. Nevertheless, the physical concept of a variable time, a man-made dimension, is still difficult to comprehend.

Let us re-examine the Michelson–Morley experiment. Consider again the swimmers: swimmer A returned to point A on the bank of the river, swimmer B to point B on the bank of the river, and the mathematics is infallible. However, when we consider the beams of light, they do not return to their original position in space—but they return to their original position on the surface of the earth. The analogy is therefore incorrect. The velocity of the earth changes the points of origin and detec-

tion of the beam of light during the passage of the light beam. To be used as a comparison, the velocity of the river should therefore be superimposed on the points of beginning and ending for the swimmers. This can be done if each swimmer starts from a log floating in the river, and A swims 45 feet across and back to the log; B swims 45 feet upstream and back to a log. In each case, the swimmer travels 90 feet *through relatively still water* at 4 feet/min, and each takes the same time. The effect of the flow of the river is not manifested.

Following the same reasoning, the two beams of light should take the same time to travel their respective paths. The effect of the rotation of the earth should not be apparent because each beam is affected by the earth's movement. No interference fringes would be expected and no conclusions concerning the speed of light should be drawn. It should be noted that this technique does not directly measure the speed of light but it compares the relative velocity of two beams of light.

If the conclusions are correct, the Special Case of Relativity may still be correct, but the Michelson-Morley experiment cannot be used as experimental proof.

SOME PROBLEMS WITH THE SPECIAL CASE OF RELATIVITY

Suppose we have an observer, O, placed on a line between two light sources, A and B, as in Fig. 3.

The light sources are stationary relative to each other, O is moving toward B (and away from A), at velocity, v .

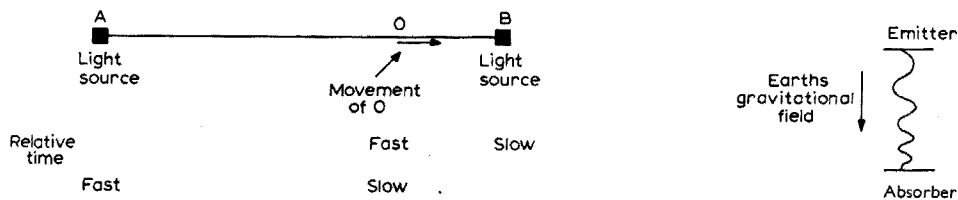


Fig. 3. Observer between two light sources.

Fig. 4.

The time coordinate for O is given by eqn. (1). Figure 3 indicates that light is travelling toward B. If (a) the light was a Newtonian particle and (b) the time flow of O and B were both equal then the apparent velocity to light reaching O would be $c + v$ where v is the relative velocity of O towards B. Velocity is measured as distance: time. To compensate for this expected change in velocity the special case tells us that the time flow has changed so that $distance\ traveled/T = c$ with no motion of O and $distance\ traveled/\tau = c$ with relative motion of O. But, the observer was moving towards O, therefore the Newtonian velocity would be $c + v$. To compensate, τ , the time flow for O must be faster than B.

Simultaneously, with respect to light moving from A and reaching O, the Newtonian velocity of light would be $c - v$ and the time flow for O would be slower than A.

However, A and B are relatively stationary to each other and their time flow is equal. We therefore have the situation that the time flow for O is faster and slower

than the time flow for A and B. This state of affairs may be quite acceptable mathematically, but as a reality it is difficult to accept.

It will be noted in the equation

$$T = \tau \sqrt{1 - v^2/c^2}$$

that the term v is raised to the second power, hence v^2 is constant whether it is approaching or retreating. Hence, the numerical value of T and τ will be equal whatever the sign of v , and τ , the time flow of O, will always be slower than A or B. However, in order to compensate for the Newtonian velocity difference of the light reaching O, it seems reasonable to assign T and τ as suggested.

The Mossbauer effect

The relative mass of a photon is $m = E/c^2$ (from $E = mc^2$). If a photon falls a distance, d , towards the earth with acceleration, g , then its energy will increase by mgd , or Egd/c^2 .

An experiment to test this shift has been carried out using the Mossbauer Effect. The setup is illustrated in Fig. 4.

The emitter gives off γ -rays which are absorbed by the absorber, which is made of the same material as the emitter. If there is any change in the energy of the radiation it will not be absorbed. It was found that the effect of gravity on the radiation was such that the absorber and the radiation were no longer in resonance and absorption was decreased².

By moving the absorber away from the emitter at some relative velocity, v , resonance was re-established and absorption again took place. We have established that the energy of the photon has increased, but since, according to the Special Case of Relativity, c must be a constant, then the frequency of the photon must have increased.

By moving the absorber away from the emitter, at the correct velocity, the Doppler Effect compensates for the frequency shift and resonance is re-established.

This explanation is mathematically quite sound and experimentally demonstrable. However, we have had to accept the proposition that photon is unlike all other particles we know. When it is acted upon by gravity, we must accept that its velocity does not change, but that its frequency does. Further when the absorber is moved away from the emitter until resonance is re-established, the frequency of the radiation is again changed. This is difficult to accept because the radiation is not acted upon by the detector.

For the purpose of argument, let us accept the proposition that the photon was accelerated by gravity and its velocity changes to a velocity other than c . To the stationary absorber, the accelerated stream of photons would pass more quickly, and more crests (or waves) per unit time would be experienced by the absorber. Although the actual frequency (number of revolutions of the photon per unit time)¹ would have remained constant, the number of waves passing the absorber per unit time would seem to increase, indicating an apparent change in frequency. This apparent change in frequency is caused by a change in velocity.

When the absorber was moved away from the emitter, the increased velocity of the photon caused by the attraction of the earth would be compensated. It would

again have a velocity, c , relative to the absorber. The frequency of radiation would appear to be constant and resonance would again be in effect.

This explanation leads the same experimental expectations as before, but does not require that the photon remain at a constant velocity.

The measurement of c

Many measurements of c have been made in the past. These have confirmed that the speed of light is a constant, and is equal to c . For all these results to be in error is almost inconceivable, unless a systematic error has crept into the experimental work or the calculation of the results. Two possible sources of error are listed below.

Possible error from transmitting medium. It is known that if light passes from air to a second medium, such as a glass, that the path changes. The direction of the light path changes again when the light emerges from the glass into the air. This change in path causes dispersion of light and amongst other things it is affected by the change of velocity of light when the medium is changed. The mechanism of this velocity change is not clearly understood. It seems easy to understand that light would travel at a slower velocity through the denser medium (glass), but why its velocity should return to its original velocity when it re-emerges in air is not clearly understood. Possibly, the momentum or kinetic energy of the photon remains constant throughout, but the velocity varies in the different media. This would have to be caused by a difference in some physical property of the media, such as its electrical environment. It is conceivable that the velocity of light through the medium is independent of its initial velocity and therefore the velocity of light emerging from the medium is independent of its incident velocity.

Under these circumstances any equipment which used lenses, windows, etc., would always give the same answer for c because any difference in original velocity would be eliminated by the transmitting medium.

A situation similar to this is encountered with the movement of sound through air or ripples through water. Both are independent of the initial velocity of the sound or ripples.

It is not intended to resurrect the ether theory with these comments.

Calculation of c

One of the common ways to measure c is by use of the expression $c = \lambda\nu$, where λ = wavelength, ν = the frequency (sec^{-1}).

This expression seems to be self-evident. However, let us examine two situations; one in which the observer is stationary to the emitter, the second of which the observer is not stationary relative to the emitter.

Case I—Observer stationary to the emitter. Suppose, for convenience,

(1) The distance of observer to emitter = D .

(2) The wavelength of light = $D/10$.

(3) The time taken for light to travel from E to O is 1 sec.

: ← D → :

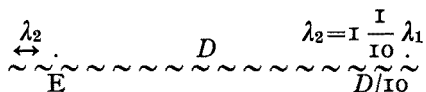
E ~ ~ ~ ~ O

$\lambda_1 = D/10$

$\nu = 10/\text{sec}$

$$c = \lambda \nu = \frac{D \text{ ft per sec}}{10} \times 10 = D \text{ ft/sec} \quad (3)$$

Case II—The observer moves toward the emitter at a velocity $D/10$.



Frequency. During 1 sec the observer will have seen 10 crests of light plus 1 crest of light because it had moved towards the emitter distance $D/10$ ($= 1 \lambda$) during this second. The apparent frequency is therefore $11/\text{sec}$.

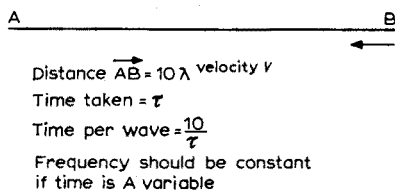
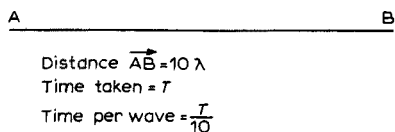


Fig. 5.

Wavelength. The observer measures the wavelength as the distance between crests. However, it is not possible to measure the absolute distance traveled by a given crest in passing two consecutive points even using a crystal lattice or a grating. The light and crystal layer is a moving system; there is a time delay between a given crest interacting with one atomic layer and the next layer. During this time the observer has moved down the light waves and the distance between crests seems to be shorter than it actually is. Suppose the observer moves distance $D/10$ during 1 sec. Then, during this time, $(1 + 1/10)$ of a wave will have passed the observer. If $11/10$ waves pass per sec, the wavelength would therefore appear to be $10D/11$. (It should be noted that the distance between adjacent crests can easily be measured.)

Apply eqn. (3),

$$c = \lambda \nu = 11 \times \frac{10}{11} \times \frac{D}{10} = D$$

This is the identical result to Case I. The effect of the relative motion of the observer and the emitter has been cancelled out and we arrive at the velocity of light *leaving the emitter*. This, of course, could well be a constant, and it is highly probable that it is equal to c . But it may not necessarily be the relative velocity of light to the observer; further if this relative velocity was other than c , we would not detect the difference by using the process outlined above.

Frequency-wavelength relationship

If a beam of light travels from A to an observer O, which is traveling towards A at velocity v , then the time coordinate for O is given by the following expression:

$$T = \tau \sqrt{1 - v^2/c^2}$$



Fig. 6.

The velocity of the light relative to O remains c according to the Special Case of Relativity. This velocity is given by

$$\frac{\text{Distance traveled}}{\text{Time taken}} = c$$

Since c is constant, if D varies then T must vary accordingly.

The electromagnetic field of the light wave (or particles) changes ν times per sec where ν is the frequency of the light. The frequency also is equal to No. of oscillations per unit time.

The time vector for oscillation of the light must be equal to the time vector for linear travel of the light unless the light is existing in two time vectors, one for translational movement and one for oscillation.

Since the time for translational movement is modified to keep c constant, it should also keep ν constant. Therefore relative movement of the observer and the emitter should not result in a change of frequency if the Special Case is valid, *i.e.*, if the speed of light remains constant. The Doppler effect would have no apparent effect on the frequency of the radiation. Experimentally we see that it does.

We have seen that if the speed of light is constant then $c = \text{Distance traveled} / \text{Time taken}$. If the observer approaches the emitter, the D decreases and T must also decrease. If the original distance D was equal to $1000 \times \lambda$ of light, then the time to travel 1λ of light was equal to $T/1000$, when O moves towards A.

Let $D = 1 \lambda$ of light

$$c = \lambda/T = \text{constant},$$

when O approaches A, then T is decreased but c is a constant.

This leads to the conclusion that if an observer approaches an emitter, then the frequency of radiation remains constant, but the wavelength decreases if the Special Case of Relativity is valid. This is in contradiction to the normal interpretation which states that the frequency of radiation changes under these circumstances.

Meson lifetime

It has been shown that the lifetime of a meson is affected by subjecting it to high speed. The change in lifetime indicates that the change in time and the relative velocity of the atom are related by the equation derived for the Special Case (eqn. (1)). This would seem to be unshakable proof of the validity of the equation. However, for the difference in time to be measurable, it is essential that the velocity of the particle should be appreciable compared to the speed of light. This indeed is a high velocity.

Under these circumstances, we must ask the question, "What effect does this very high velocity have on the forces interacting in the nucleus and orbiting particles?" In the case of atoms these forces determine their stability. When an atom is at rest relative to the earth, gravitational forces and the forces exerted by nearby atoms and molecules are small and comparatively constant, and perhaps negligible. However, under conditions of very high velocity it is conceivable that the forces responsible for gravity and molecular interaction are not negligible. They may exert forces on the atomic system sufficient to change its stability and therefore its lifetime. It is possible therefore that the lifetime of the meson is affected by the movement of the system and does not experience a change in time coordination. If this is so, a similar effect should be observable with other forms of radioactivity when the decomposing atom is moving at high velocities. For example, in the case of an electron orbiting a nucleus (as in hydrogen), Bohr postulated that the centrifugal force mv^2/r was equal to the centripetal force Ze^2/r^2 . As is well known, this relationship was used to derive the Rydberg constant as $R = 2\pi^2me^4/h^2c$. The relationship also indicated that there is a direct relationship between m , the mass of the electron, and r , the radius of the orbit. Providing m is constant, then r would remain constant. But, if m is not constant, then r would not be constant, and the atom would change geometry slightly in order for the orbiting electron to stay in equilibrium with the nucleus.

It is possible that if the atom (including the electron) is moving at a very high velocity in the earth's gravitational field that the mass changes. This would lead to an apparent change in the mass of the components. The relationship between mass and velocity is known to be given by the equation

$$m = m_0 / (1 - v^2/c^2) \quad (2)$$

where m_0 = rest mass,

v = relative velocity (between the particle and the earth),

c = speed of light,

m = relativistic mass.

Under these circumstances, when a particle, such as an electron, hydrogen atom or meson, is traveling at a high velocity—approaching the speed of light in the earth gravity, then its mass will increase. This in turn leads to a change r , the radius of the orbit of the electron.

However, we also know that the total path length of a complete orbit should equal a whole number of wavelengths of the electron. This condition is apparently met in a stable atom. Any change in radius would lead to an imbalance in the system and therefore an instability.

In the case of the meson, it has been observed that the half-life is increased at high velocity. The fact that it has a half-life indicates instability, a decrease in the half-life suggests that the system becomes more stable in the new geometry. Such an argument may explain the change in half-life of a meson without calling for a change in its time coordinates.

CONCLUSION

There are numerous other experiments which conclusively prove the Special Case that have not been examined here. For example, the observation of binary stars strongly supports the constancy of the velocity of light.

However, we can see that some of our most reliable proofs can be interpreted in Newtonian concepts without reference to time variation.

SUMMARY

The Special Case of Relativity is examined. Alternative interpretations are proposed for experiments which have been assumed to prove that time flow is a variable.

RÉSUMÉ

Le cas spécial de la relativité est examiné. Des interprétations sont proposées pour des expériences permettant de prouver que le temps écoulé est une variable.

ZUSAMMENFASSUNG

Der spezielle Fall der Relativität wird geprüft. Sich gegenseitig ausschliessende Deutungen werden für Experimente vorgeschlagen, welche angenommen wurden, um zu prüfen, dass der Zeitfluss variabel ist.

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ETUDE THERMOMETRIQUE DE LA FORMATION DES COMPLEXES CITRIQUES ET TARTRIQUES DES LANTHANIDES

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(Reçu le 10 juillet, 1967)

Nous avons déjà eu l'occasion, dans deux mémoires précédents¹, d'indiquer les conditions d'application de la méthode thermométrique à l'étude de la formation des complexes ainsi que les caractéristiques essentielles de l'appareillage utilisé. Nous consacrerons le présent Mémoire à quelques résultats relatifs aux citrates et tartrates de lanthanides afin de compléter nos précédentes études sur la complexation des ions tripositifs.

COMPLEXES CITRIQUES

Les premiers travaux de séparation des lanthanides sur échangeurs d'ions ont fait principalement appel au citrate d'ammonium comme éluant car les différences de stabilité des complexes citriques permettent d'accentuer le facteur de séparation des différents éléments du groupe. Malgré les études de caractère assez empirique qui ont été faites à ce propos, et dont le but était de fixer les conditions optimales de pH et de dilution pour obtenir les éluations les plus efficaces, on ne dispose que d'un petit nombre de données sur les compositions mêmes des complexes susceptibles de se former.

En raison de leur intérêt direct pour notre étude, nous retiendrons d'abord les travaux de TEVEBAUGH^{2,3} qui fut le premier à caractériser, par potentiométrie, deux complexes citriques du lanthane (1:1 et 1:2) que RYABCHIKOV ET TERENT'EVA⁴ ont ensuite isolés ainsi que 4 complexes solubles du néodyme (dont le 1:3). D'autre part, SPEDDING ET POWELL⁵ avaient prévu la formation des complexes 1:3 qui furent identifiés par TOMPKINS ET MAYER⁶. Enfin BÖBTELSKY ET GRAUS⁷ mettent en évidence, par conductimétrie, la formation successive de 3 complexes du cerium(III): 1:1, 1:1.5 et 1:2. Il est cependant à noter qu'on ne relève aucune détermination thermométrique sur la formation des citrates de lanthanides.

Le comportement nettement différent des deux groupes habituels de lanthanides vis à vis des réactions étudiées nous amène, dans l'exposé de nos résultats, à établir une distinction entre les complexes des terres cériques et ceux des terres yttriques.

Complexes citriques des terres cériques

Parmi les lanthanides de ce groupe nous avons limité notre choix au cérium(III) et au praséodyme.

Citrates de cérium(III). Conditions opératoires—Dans les bacs thermométri-

ques: solution de nitrate cerique 0.2491 *M* amené à pH 3 par HNO₃ dilué. Dans la burette: solution de citrate diammonique 2.392 *M* à son pH normal de 4.5. L'addition de sel tel que KNO₃ destiné à accroître la force ionique du milieu s'est avérée inutile. Tension d'alimentation du pont: 1.5 V. Sensibilité de l'enregistreur: 2.5 mV.

Les enthalpogrammes enregistrés ont la forme de la Fig. 1. Ils présentent 4 brisures nettes correspondant aux 4 complexes successifs 1:1; 1:1.5; 1:2 et 1:2.5. Si les 3 premiers étaient déjà connus et décelés, en particulier sur une seule courbe conductimétrique⁷ nous sommes en mesure d'affirmer l'existence d'un nouveau complexe citrique de cérium de rapport *r* égal à 1:2.5.

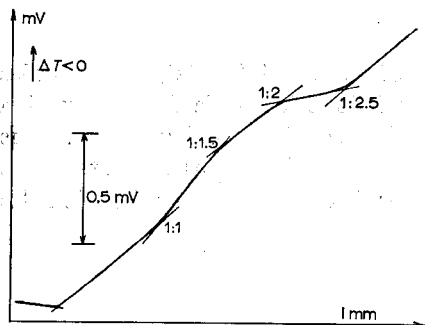


Fig. 1. Citrates de cérium.

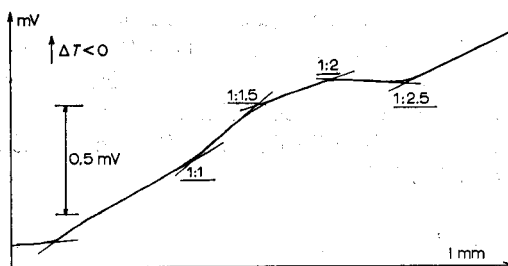


Fig. 2. Citrates de praséodyme.

TABLEAU I

COMPLEXES CITRIQUES DES TERRES CÉRIQUES

Vol. prise d'essai <i>r</i>	10 ml			12.5 ml			15 ml			
	<i>l</i> (mm)	Théor.	Exp.	Δ	Théor.	Exp.	Δ	Théor.	Exp.	Δ
<i>Citrates de cérium(III)</i>										
1:1		51	50	2	63.5	62	1.5	76.5	74.5	2.5
1:1.5		76.5	74.5	2.5	94.5	94.25	0.25	114.5	113.5	1
1:2		102	100.5	1.5	126	125.75	0.5	153	153	0
1:2.5		127.5	130.75	2	158	162	2.5	192	197	2.5
<i>Citrates de praséodyme</i>										
1:1		65	65	0	80.5	81	0.5	97.5	95.75	1.75
1:1.5		97.5	96	1.5	121	121	0	146.5	146	0.4
1:2		130	130	0	161	162	0.75	195	193.5	0.75
1:2.5		162.5	164	1	201.5	204	1.75	244	245	0.4

Les résultats obtenus pour trois prises d'essais sont rassemblés dans le Tableau I. N.B. Dans ce Tableau et les suivants:

vol. prise d'essai: quantité de solution placée dans chacun des bacs thermométriques

r: rapport métal:coordinat

l(mm): longueur des abscisses des brisures (*l* exp. désignant la moyenne de la longueur mesurée pour 2 essais successifs).

Δ = écart en % entre longueurs théoriques et longueurs expérimentales.

Citrates de praséodyme. Conditions opératoires—Dans les bacs thermométriques: solution de nitrate de praséodyme 0.2603 M (obtenue par dissolution à chaud de Pr_6O_{11} dans HNO_3 concentré) à pH 3. Dans la burette: solution de citrate diammonique 2.0544 M à pH 4.5. Tension d'alimentation du pont: 1.5 V. Sensibilité de l'enregistreur: 2.5 mV.

Les enthalpogrammes enregistrés ont la forme de la Fig. 2 et mettent en évidence, comme dans le cas précédent les 4 complexes successifs 1:1, 1:1.5, 1:2 et 1:2.5. Le Tableau I rassemble les résultats pour les 3 prises d'essai utilisées.

Complexes citriques des terres yttriques

Dans ce groupe, nous avons d'abord choisi l'yttrium, (qui n'est pas un véritable lanthanide mais qui leur est généralement assimilé) et l'ytterbium. Il sera en outre fait allusion au comportement du samarium.

Citrates d'yttrium. Conditions opératoires—Dans les bacs thermométriques: solution de nitrate d'yttrium 0.198 M à pH 2. Dans la burette: solution de citrate diammonique 1.5732 M amené à pH 5.5 par de l'ammoniaque. Tension d'alimentation du pont: 1.5 V. Sensibilité de l'enregistreur: 2.5 mV.

Les enthalpogrammes obtenus ont la forme de la Fig. 3 où l'on peut, malgré les raccordements arrondis des segments de droites, déceler, par extrapolation la formation de 3 complexes 1:1, 1:2 et 1:3. Le Tableau II rassemble les résultats pour 3 prises d'essais.

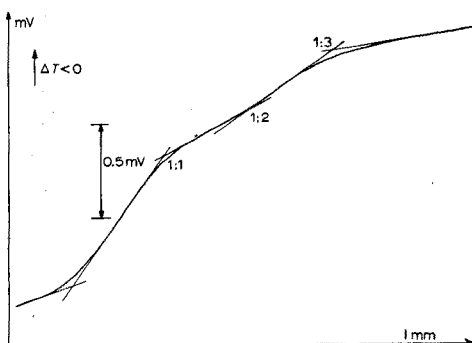


Fig. 3. Citrates d'yttrium.

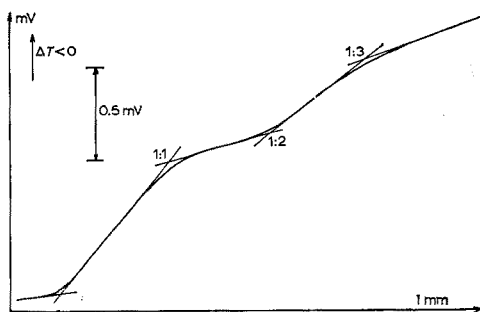


Fig. 4. Citrates d'ytterbium.

TABLEAU II
CITRATES D'YTTRIUM

Vol. prise d'essai l (mm)	5 ml			7.5 ml			10 ml		
	Théor.	Exp.	Δ	Théor.	Exp.	Δ	Théor.	Exp.	Δ
1:1	31.25	31	1	48	47.25	1.5	62.5	63	1
1:2	62.5	62.5	0	96	94	2	125	125.5	0.
1:3	93.75	93.75	0	144	141.5	2	187.5	184.25	1.5

Citrates d'ytterbium. Conditions opératoires—Dans les bacs thermométriques: solution de nitrate d'ytterbium 0.2318 M à pH 2. Dans la burette: solution de citrate diammonique à pH 5.5. Tension d'alimentation du pont: 1.5 V. Sensibilité de l'enregistreur 2.5 mV.

Les enthalpogrammes obtenus ont la forme de la Fig. 4 et permettent de caractériser la formation des complexes 1:1, 1:2 et 1:3, comme dans le cas précédent. Les résultats obtenus pour 4 prises d'essais sont rassemblés dans le Tableau III. Il apparaît en conclusion, que si les citrates complexes 1:1 et 1:2 sont communs pour les terres cériques et les terres yttriques, les deux groupes se distinguent par la formation des autres complexes: tandis que les citrates 1:1.5 et 1:2.5 se forment dans le groupe cérique, c'est le citrate 1:3 qui apparaît pour le groupe yttrique. D'autre part l'allure des enthalpogrammes obtenus permet d'attribuer une plus grande stabilité (brisures plus franches) aux complexes cériques qu'aux complexes yttriques.

TABLEAU III

v vol. prise d'essai (ml)	l (mm)	1:1			1:2			1:3		
		Théor.	Exp.	Δ	Théor.	Exp.	Δ	Théor.	Exp.	Δ
8		45	45	0	90	90	0	135	132	2
10		56.5	57	1	113	113.5	0.5	169.5	168	1
12		68	68.75	1	136	135	1	204	204	0
15		84.5	84.5	0	169	171	2	253.5	248	2

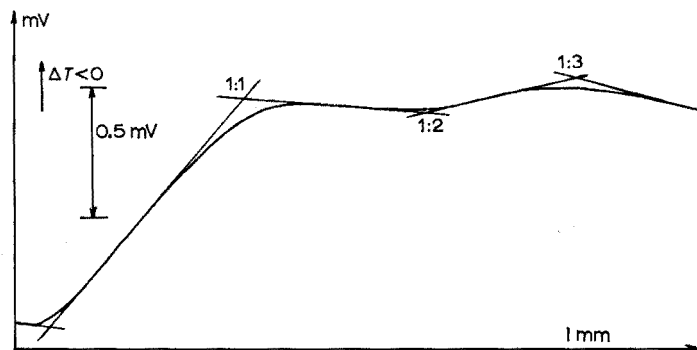


Fig. 5. Citrates de samarium(III).

Enfin, dans le but de déterminer à quel niveau se faisait la coupure entre les deux groupes, nous avons tracé un enthalpogramme dans le cas des citrates de samarium et obtenu (Fig. 5) une allure de courbe tout à fait analogue à celles du groupe yttrique. Ainsi, lorsque l'on considère la formation des complexes citriques, la ligne de démarcation entre les deux groupes de lanthanides se trouve déplacée de l'euprotium-gadolinium au samarium alors que le comportement de ce dernier le fait habituellement classer dans le groupe cérique.

COMPLEXES TARTRIQUES

Moins intéressants, du point de vue pratique, que les complexes citriques correspondants, les complexes tartriques des lanthanides ont naturellement été jusqu'ici moins étudiés. Des quelques publications relatives aux espèces qui se forment nous avons extrait les indications figurant sur le Tableau IV.

TABLEAU IV
ESPÈCES DES COMPLEXES TARTRIQUES

Groupes	Terres rares	Rapports r	Méthodes	Réf.
Cérique	La	1:1.5-1:2	Rayons X	8
		1:1-1:1.5-1:2	Potentiométrie	9
		2:1	Synthèse + analyse	10
		1:3	Synthèse + analyse	11
	Ce(III)	1:2	Synthèse + analyse	12
		1:1-1:1.5	Synthèse + analyse	13
		1:1-1:1.5	Potentiométrie	14
	1:1-1:1.5-1:2	Potentiométrie	15	
Pr et Nd	1:1-1:1.5	Potentiométrie	16	
Yttrique	Eu et Tb	1:1-1:2	Radioactivité	17
	Y	1:1-1:1.5-1:2	Potentiométrie	18

Il apparaît que les complexes 1:1, 1:1.5 et 1:2 se forment pour le lanthane, le cérium et l'yttrium. Si, en outre, on a pu préparer dans ces conditions très particulières (chauffage prolongé à l'ébullition) les complexes 2:1 et 1:3 du cérium, il n'était pas étonnant qu'ils aient échappé à la méthode potentiométrique ou à tout autre méthode d'investigation physico-chimique.

Tous les auteurs s'accordent à reconnaître que les tartrates de terres rares sont des complexes peu stables. Aucune application de la thermométrie n'a été faite dans ce domaine.

Tartrates de cérium(III)

Conditions opératoires—Dans les bacs thermométriques: solution de nitrate céreux 0.251 *M* amené à pH 5 par de l'ammoniaque dilué. Dans la burette: solution de tartrate diammonique 1.3367 *M* amenée à pH 9 par de l'ammoniaque concentrée. Tension d'alimentation du pont: 1 V. Sensibilité de l'enregistreur: 2.5 mV.

Les enthalpogrammes enregistrés ont l'allure de la Fig. 6; ils manifestent 3 brisures (la première étant la plus distinctement marquée) correspondant aux 3 complexes successifs 1:1; 1:1.5 et 1:2. Les complexes 2:1 et 1:3 ne peuvent évidemment se former dans les conditions de l'analyse thermométrique. Les résultats obtenus pour 4 prises d'essais sont rassemblés dans le Tableau V.

Tartrates de dysprosium

Conditions opératoires—Dans les bacs thermométriques: solution de nitrate de dysprosium 0.248 *M* amené à pH 3 par HNO₃ dilué. Dans la burette: solution de

tartrate diammonique 1.3707 M amenée à pH 9 par de l'ammoniaque concentrée. Tension d'alimentation du pont: 1 V. Sensibilité de l'enregistreur: 2.5 mV.

Les enthalpogrammes enregistrés ont l'allure de la Fig. 7. Ils sont caractérisés par 3 brisures suffisamment nettes pour être attribuées aux 3 complexes successifs: 1:1, 1:1.5 et 1:2. Les résultats obtenus pour 3 prises d'essais sont rassemblés dans le Tableau VI.

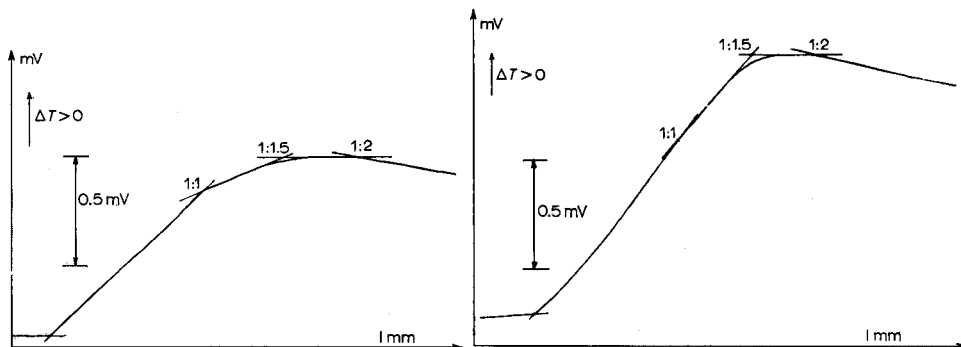


Fig. 6. Tartrates de cérium.

Fig. 7. Tartrates de dysprosium.

TABLEAU V

TARTRATES DE CÉRIUM(III)

<i>r</i>	<i>l</i> (mm)	1:1			1:1.5			1:2		
		<i>Théor.</i>	<i>Exp.</i>	Δ	<i>Théor.</i>	<i>Exp.</i>	Δ	<i>Théor.</i>	<i>Exp.</i>	Δ
<i>vol. prise d'essai (ml)</i>										
4		37	37.5	1.5	55.5	56.5	2	74	75.5	2
5		46	46	0	69	68	1.5	92	91	1
7.5		69	70.75	1.5	104	107	3	138	141.75	2.5
10		92	94	2	138	140	1.5	184	188	2

TABLEAU VI

TARTRATES DE DYSPROSIUM

<i>r</i>	<i>l</i> (mm)	5 ml			7.5 ml			10 ml		
		<i>Théor.</i>	<i>Exp.</i>	Δ	<i>Théor.</i>	<i>Exp.</i>	Δ	<i>Théor.</i>	<i>Exp.</i>	Δ
1:1		45	45	0	67.5	67	1	90	90	0
1:1.5		67.5	67.5	0	101	100.5	0.5	135	135	0
1:2		90	89	1	135	132.5	2	180	176	2

CONCLUSIONS

Ainsi que le montrent les résultats exposés ci-dessus, l'analyse thermométrique permet de caractériser de façon rapide, par l'enregistrement d'un seul enthalpogramme, la formation des complexes successifs des lanthanides avec les anions citrate et tartrate.

Bien que les exemples étudiés aient été limités à quelques éléments, il semble acquis que les complexes tartriques demeurent au nombre de 3 (1:1, 1:1.5 et 1:2) pour les terres yttriques comme pour les terres cériques. Dans le cas des complexes citriques, plus stables que les précédents, il faut par contre distinguer les terres cériques qui donnent lieu à 4 espèces successives (1:1, 1:1.5, 1:2 et 1:2.5) et les terres yttriques qui, à partir du samarium forment seulement 3 citrates (1:1, 1:2 et 1:3).

Ainsi se trouvent confirmées les indications de la littérature concernant les tartrates lanthanidiques; pour les citrates, les conclusions de l'analyse thermométrique infirment l'existence du complexe 1:3 (terres cériques) et lui substituent le complexe 1:2.5.

RÉSUMÉ

Les auteurs montrent qu'un seul enthalpogramme suffit à mettre en évidence toute la série des complexes citriques et tartriques des lanthanides des groupes cérique et yttrique, à condition de réaliser le gradient de pH convenable pour permettre à ces complexes de se former successivement.

SUMMARY

Thermometric measurements make it possible to detect all citrate and tartrate complexes of lanthanides on only one enthalpogram. A suitable gradient of pH must be chosen in order to allow the successive formation of the complexes.

ZUSAMMENFASSUNG

Mit Hilfe von thermometrischen Messungen ist es möglich alle Ziträt- und Tartrat-Komplexe von Lanthaniden zu bestimmen. Durch entsprechende Variierung des pH-Wertes wird die stufenweise Bildung dieser Komplexe ermöglicht.

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SHORT COMMUNICATIONS

Spectrophotometric determination of traces of silicon in pure copper and copper alloys

PAKALNS AND FLYNN¹ have reported a method for the determination of traces of silicon in a variety of salts and standard materials. It involves extracting the yellow silicomolybdate with isoamyl alcohol and subsequent reduction to silicomolybdate blue. The only copper-containing standard material investigated was cupro-nickel. This alloy has a relatively high silicon content (0.11%); hence the dilution factor was large and it was possible to adjust the pH with 9 *N* sulphuric acid before ammonium molybdate addition. The procedure worked very well for large dilution factors, but failed when aliquots of higher acid concentration had to be taken. When ammonia was used to adjust the pH of solutions containing copper and hydroxylamine hydrochloride, copper(II) was reduced to copper(I). This reduced molybdate to molybdenum blue and made the determination of silicon impossible. A reversal in the order of addition of ammonia and hydroxylamine hydrochloride, and the use of acid ammonium molybdate (pH 1.3), enabled the silicon to be determined at low p.p.m. levels in pure copper and copper alloys.

Apparatus and reagents

Apart from the acid molybdate solution, these were the same as described previously¹.

Acid ammonium molybdate solution (pH 1.3.) Prepare 2.5% ammonium molybdate solution from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and store in a polythene bottle. Prepare the acid ammonium molybdate solution as required by adding 4.3 ml of 9 *N* sulphuric acid to each 100 ml of 2.5% ammonium molybdate solution, and adjusting the pH to 1.3.

Recommended procedure

Weigh a sample (0.2–0.5 g) into a 250-ml Teflon beaker, add 20 ml of water, 4.5 ml of nitric acid, 1.5 ml of hydrochloric acid, and 0.4 ml of 40% hydrofluoric acid. Dissolve the sample at 85°. Transfer the sample to a 100-ml polythene cylinder containing 30 ml of saturated boric acid, dilute to 100 ml and mix. After 15 min, pipette an aliquot containing 5–10 μg of silicon into a polythene beaker, add saturated boric acid to increase the total volume of boric acid to 7.5 ml, and dilute to 25 ml with water.

Adjust the pH to 1.2 using 9 *N* sulphuric acid or ammonia and mix well. Add 0.2 ml of 10% hydroxylamine hydrochloride solution, and 20 ml of acid ammonium molybdate solution with stirring. Let stand for 10 min. Add 10 ml of 20% tartaric acid and after 1 min add 6.5 ml of 9 *N* sulphuric acid. Transfer to a 100-ml separating funnel and adjust the volume to 70 ml with water. Add 10 ml of isoamyl alcohol, shake for 1 min and continue with the extraction, reduction and colour measurement as described in the previous paper¹. Make a standard addition of 5 μg of silicon.

Results and discussion

The recommended amount of acid is sufficient to dissolve 0.5 g of a sample, but when 1 g of sample is selected (*e.g.* copper sheet and bronze) an acid mixture containing 6.5 ml nitric acid, 1.5 ml hydrochloric acid, and 0.4 ml of 40% hydrofluoric acid must be used.

The previous paper¹ showed that hydrofluoric acid must be added at the beginning of the dissolution to prevent any losses of silicon (as for pure iron), and that 1.2 is the minimum pH for the development of the yellow silicomolybdate complex in the presence of 0.1 ml of 40% hydrofluoric acid and 7.5 ml of saturated boric acid. This is decreased to 1.1 when the sample aliquots contain large amounts of nitrates.

The acid ammonium molybdate (pH 1.3) was introduced because the pH of the ammonium molybdate solution was too high, and reproducible results could not be obtained when sample aliquots containing large amounts of copper were taken.

TABLE I
SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN COPPER ALLOYS

<i>Sample</i>	<i>Certificated Si (%)</i>	<i>Si found (%)</i>	<i>Recovery on standard addition (%)</i>
Cupro-nickel "A"	0.12	0.111	99
BCS 180	(Range 0.10-0.14)	0.109 ^a	
Copper sheet	—	< 0.0002	90
Copper-beryllium alloy	—	0.0770	99
Manganese brass	—	0.0236	98
BCS 179			
Bronze "A" BCS 183	—	0.0018	90
Phosphorus-bronze (0.25% P)	—	< 0.0003	90

^a Reported previously¹.

Phosphorus interferes badly and therefore the weight of phosphorus in a sample aliquot must be less than 300 μg , which gives an error equivalent to 0.15 μg of silicon.

Several copper alloys containing trace amounts were selected for analysis, and the determined silicon results are shown in Table I.

The author wishes to acknowledge the assistance of Mrs. B. McALLISTER with the experimental work.

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The determination of bromine in the presence of fluorine and positron emitters using fast neutron activation analysis

The obvious choice for the determination of bromine with 14-MeV neutron activation analysis is the isotope ^{78}Br which is a positron emitter with a half-life of 6.4 min. The detection limit for this isotope has been given by CUYPERS AND CUYPERS¹ as 0.05 mg. Unfortunately, fast neutron activation can produce over 50 positron emitters and if it is assumed that serious interference is encountered by emitters with half lives varying between half and twice that of ^{78}Br , such interference will be caused by ^{140}Pr (3.4 min), $^{89\text{m}}\text{Zr}$ (4.18 min), ^{38}K (7.7 min), ^{143}Sm (9.0 min), ^{53}Fe (9.0 min), ^{136}La (9.5 min), ^{62}Cu (9.8 min), ^{13}N (10.0 min) and $^{162\text{m}}\text{Ho}$ (11.8 min). Further, the presence of other positron emitters may necessitate prolonged decay curve analysis.

If rapid analysis is required, and rapidity is one of the main reasons for using 14-MeV neutron activation analysis, then bromine cannot be determined via the ^{78}Br isotope if positron emitters are also produced. The only possible alternative is to use the isotope $^{79\text{m}}\text{Br}$ ($t_{1/2}$ 5.0 sec)², the sensitivity of which is very much lower and has been given as 1.0 mg¹. The purpose of this investigation was to determine the limits of usage of the 0.207-MeV peak from this isotope for estimation under the worst possible interference conditions likely to be encountered from positron emitters. A value of approximately 10,000 counts/sec in the positron peak was taken as representative of the worst conditions under which such an analysis would be likely to be attempted. At the same time it seemed reasonable to investigate possible interferences from other halogens and of these the only significant interference can come from the reaction $^{19}\text{F}(n,p)^{19}\text{O}$. The half-life of ^{19}O is 29.4 sec and this isotope produces a γ -peak at 0.20 MeV. The detection limit for this isotope has been given¹ as 0.96 mg which is only marginally worse than that of ^{18}F , a positron emitter, given as 0.68 mg. The method was therefore used to estimate the fluorine as well as the bromine.

Experimental

The apparatus used consisted of a Kaman 1003 neutron generator with an automatic sample transfer mechanism which has been described elsewhere³. The neutron flux measurement system consisted of a BF_3 counter connected to a ratemeter and scaler. The ratemeter was, in turn, connected to a recorder having a chart speed of 1 cm/sec and a balancing time (95% of scale) of ca. 1 sec. With isotopes of short half-life, some workers^{4,5} have used a ratemeter time constant equal to the mean life ($1.44 t_{1/2}$) of the activation product. The flux recording is then self-correcting for the effects of any variation in the neutron flux and all activations may then be used. In the present experiments the value of the neutron flux was obtained from the scaler but any irradiations showing a variation of more than 3% on the recorder chart were rejected. A new target was used for the experiments and a check made on the homogeneity of the neutron emission across the target using nuclear film. The flux at the target centre was 9% higher and at the edge 4% lower than the mean value. Experience has shown that, with the present system, variations greater than this can be tolerated without a detectable variation in accuracy.

The samples were made up in polythene tubes using 1,4-dibromobenzene as the source of bromine. Copper powder was mixed with the sample when high positron

backgrounds were required and graphite dust was used as an inert diluent to maintain sample geometry when only small amounts of bromobenzene were required. Polytetrafluoroethylene was used to provide the fluorine interference as required.

Samples were irradiated for 10 sec and counting commenced 3 sec after the irradiation. The detection system consisted of a 3×3 " sodium iodide scintillator coupled, via a linear amplifier, to a 100-channel pulse-height analyser. The analyser was set to count for 5-sec live time and the real time was also determined. An increase in the counting time to, say, 10 sec would double the positron background contribution whilst the peak counts would only increase by about 50%. The peak count-to-background ratio would therefore worsen and it is clear that there would be little point in such an increase.

The analyser controls were set so that the γ -peak was obtained in channels 2-10 and all other counts were cut off using the upper threshold control. When interference from fluorine was present, in addition to the above counting procedure, the sample was allowed to cool for 40 sec after irradiation and the ^{19}O contribution then counted over a period of 30 sec.

Results and discussion

The γ -spectra were assessed by COVELL's method⁶ using 4 channels on either side of the peak. When short-lived isotopes of moderately high activity are counted, dead-time corrections cause difficulties. This has been accentuated in recent years by the use of multichannel analysers which tend to have relatively high dead-times of the order of 20 μsec . Most analysers have a live-time counting system which, under normal circumstances, is self-correcting for dead-time by appropriate extension of the counting period. However, in the case of a short-lived isotope being counted for a time interval of the order of a half-life or more, the count rate falls significantly during the interval and time lost at higher counting rates is made up at lower counting rates.

The following procedure was therefore used for the calculation. The count rate at the commencement of the counting interval was determined by dividing the total counts in the tip (COVELL portion) of the peak by 5 to obtain the average count rate. This is corrected for dead-time by the instrument although it is clear, as indicated above, that the correction is not exact. The time, T , at which this average count rate occurred was calculated from the equation

$$T = -\lambda^{-1} \log_e \left\{ (1 - e^{-\lambda t}) / \lambda t \right\}$$

where λ is the radioactive constant and t the real counting time. When this time, T , has been obtained, the count rate can then be corrected back to zero time. Clearly, the same calculation procedure must be used on both the sample and the standard so that the dead-time errors will be, to some extent, self-correcting.

It is an inherent requirement of the COVELL method that the background should not vary abruptly across the peak. When fluorine interference is present this condition will not hold, since, for example, the analyser settings in the present investigation resulted in the peak tips of ^{19}O and $^{79\text{m}}\text{Br}$ being 1 channel apart. This potential error was eliminated by assessing the total ^{19}O count in channels 2-10 after 40-sec cooling (when the $^{79\text{m}}\text{Br}$ had virtually disappeared) and then correcting for decay in a similar manner to that used for the bromine. The integral contribution

was then calculated from this instantaneous count rate and the real counting time used in the bromine estimation.

When the COVELL method is used, the sum of the ^{19}O counts in channels 2 and 10 must be known. This was found experimentally to be $(6.83 \pm 0.35)\%$ of the total counts in the tip of the ^{19}O peak and hence could readily be obtained. Once this correction for fluorine has been obtained the bromine content may be calculated as before.

An assessment of the error involved in this procedure for making the fluorine correction was made with samples consisting of polytetrafluoroethylene only. These were irradiated for 10 sec, cooled for 3 sec, counted for 5 sec, cooled for 40 sec and counted for 30 sec. The experimental count for the 5 sec period was compared with that calculated from the 30-sec count. Errors varied between 7.75% for counts of 600/5 sec and 3.3% for counts of 20,000/5 sec.

When copper was used to produce the high positron background a correction was made for the slight shielding effect produced. The amount of copper added was always enough to give 10,000 counts/sec in the positron peak.

All results were calculated on an I.C.T. 1900 computer using Fortran IV language. Table I shows the results for the bromine and fluorine standards. Results throughout are the mean of 6 determinations with no results rejected apart from those in which the neutron flux varied markedly during irradiation; both experimental

TABLE I
ANALYSIS OF STANDARDS

<i>Wt. of halogen (mg)</i>	<i>Counts/time unit/mg/10^9 Neutron flux</i>	<i>% s.d.</i>	<i>Theor. % s.d.</i>	<i>Counts in "Covell" peak</i>
<i>Bromine</i>	<i>time unit: sec</i>			<i>per 5 sec</i>
5.57	46.95	6.3	6.7	820
21.86	46.71	3.6	4.2	3200
45.51	45.76	3.5	3.4	6150
100.71	45.59	2.8	2.9	15800
Mean	46.25			
<i>Fluorine</i>	<i>time unit: min</i>			<i>per 30 sec</i>
4.40	471.2	5.6	6.3	800
23.30	480.4	3.9	3.0	4100
53.21	482.2	2.3	2.4	9350
103.00	478.8	2.1	2.2	18200
Mean	478.2			

TABLE II
BROMINE IN HIGH POSITRON BACKGROUND

<i>Bromine taken (mg)</i>	<i>Bromine found (mg)</i>	<i>% s.d.</i>	<i>Theor. % s.d.</i>	<i>% Error</i>
6.60	6.86	6.6	8.7	+3.9
13.28	13.81	5.1	5.3	+4.0
27.70	28.25	5.7	4.8	+2.0
52.41	53.98	4.3	3.7	+3.0

TABLE III

DETERMINATION OF BROMINE AND FLUORINE WITH HIGH POSITRON BACKGROUND

<i>Br: F</i> <i>ratio</i>	<i>Bromine</i> <i>taken (mg)</i>	<i>Bromine found</i> <i>(mg)</i>	<i>% s.d.</i>	<i>Theor. % s.d.</i>	<i>% Error</i>
<i>Bromine in presence of fluorine</i>					
2:1	24.68	24.99	4.0	4.6	+1.3
1:1	9.88	9.56	8.3	7.7	-3.2
1:2	11.46	10.76	9.7	12.6	-6.1
1:5	9.86	9.11	19.8	16.4	-7.6
<i>In presence of fluorine + high positron background</i>					
2:1	21.33	20.74	6.3	6.7	-2.8
1:1	10.62	10.02	10.3	10.0	-5.7
1:3	9.76	8.03	15.0	17.4	-17.7
<i>Br: F</i> <i>ratio</i>	<i>Fluorine</i> <i>taken (mg)</i>	<i>Fluorine found</i> <i>(mg)</i>	<i>% s.d.</i>	<i>Theor. % s.d.</i>	<i>% Error</i>
<i>Fluorine in presence of bromine</i>					
2:1	11.92	11.68	2.7	4.4	-2.0
1:1	11.25	11.03	3.6	4.2	-2.0
1:2	24.47	24.80	5.5	3.3	+1.3
1:5	47.27	46.50	4.1	2.8	+1.6
<i>In presence of bromine + high positron background</i>					
2:1	11.86	11.64	7.2	8.5	-1.9
1:1	12.84	13.51	6.4	8.0	+5.2
1:3	30.97	30.74	3.4	4.2	-0.7

and theoretical standard deviations are shown. Table II shows the effect of the high positron background and Table III shows the effect of fluorine interference with and without the high positron background.

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Analysis of very small samples of sulfide minerals

Sulfur in sulfide minerals may be determined by the method of HARDING¹ which involves the dissolution of the mineral in hydrobromic acid in the presence of tin. The sulfur in the hydrogen sulfide evolved during the reaction is oxidized to sulfate by hydrogen peroxide. The sulfate is then precipitated and determined as barium sulfate. In order to aid dissolution of minerals TREADWELL² uses hydrochloric acid and tin. LUKE³ in determining sulfur in nickel, accelerated the dissolution of the metal in hydrochloric acid using platinum chloride. MURTHY *et al.*⁴ describe an iodometric method for the determination of the sulfur content of 0.1–1 g samples. A method of speeding up this analysis for pyrite and chalcopyrite samples is given by MURTHY AND SHARADA⁵. None of these methods is readily applicable to small samples of, say, 100 μg to 1 mg.

For small quantities of sulfide, colorimetric determination with *p*-aminodimethylaniline sulfate and iron(III) chloride to form methylene blue is suitable. ALMY⁶ used this method to determine sulfide in foods. The hydrogen sulfide produced is swept into a 0.6% zinc acetate solution with carbon dioxide. Hydrogen sulfide in gases⁷ and traces of sulfide and reducible sulfur in alkalis⁸ have been determined similarly.

In the following study a tin–hydrochloric acid dissolution procedure together with the methylene blue colorimetric reaction are adapted to allow the determination of sulfur in microgram or milligram sulfide mineral samples. Atomic absorption is applied to the pot liquids from the sulfur determination to complete the scheme of sulfide analysis.

Apparatus and reagents

The all-glass reaction and absorption apparatus used was the same as that used by BUDD AND BEWICK⁸. A Beckman model B Spectrophotometer, a Sartorius Microbalance, and a Perkin Elmer 303 Atomic Absorption Spectrophotometer fitted with a Boling Burner Head were also used.

The following reagents were prepared as indicated by BUDD AND BEWICK⁸. Boiled distilled water, aluminum foil strips, zinc acetate stock solution, stock amine solution, dilute amine solution, iron(III) chloride solution, 0.1 *N* iodine solution, 0.1 *N* sodium thiosulfate solution, sodium sulfide solution and treated hydrochloric acid.

In addition the following reagents and special treatments were required.

Analysed reagent-grade reagents were used for atomic absorption standards; standard stock solutions were prepared in dilute acid with concentrations of about 1000 p.p.m. Lead-free reagent-grade tin foil (1/2000" thick) was cut into 1-cm squares.

A few drops of acetic acid were added to 100 ml of the stock zinc acetate solution and the solution was diluted to 1 l with distilled water. A stream of nitrogen gas was passed through this solution for 30 min before use.

The nitrogen gas (analytical grade; Canadian Oxygen Co.) required deoxygenation by scrubbing with an acidic solution of vanadium(II) chloride over heavily amalgamated zinc. The nitrogen was then bubbled through water to remove any acid or vanadium carried over in the gas stream⁹.

Procedure

Place 100 μg –1 mg of finely ground mineral, *ca.* 100 mesh, in a square piece of tin foil and weigh accurately. Wrap the mineral in the foil and drop in the reaction flask containing 15 ml of water. Add 35 ml of 2% zinc acetate solution and 2 ml of 4% sodium hydroxide solution to the absorption flask. Fill the stem of the funnel with water and assemble the apparatus⁸. Bubble nitrogen gas through the apparatus for 10 min at a rate sufficient to cause strong agitation of the solution in the absorption flask. Then place the absorption flask in a water bath and maintain at 23–25°. Add 15 ml of concentrated hydrochloric acid dropwise to the reaction flask and reduce the nitrogen flow to 3–5 bubbles/min. Heat the reaction solution to near boiling for *ca.* 30 min until all the mineral has dissolved. Remove the heat and bubble nitrogen through for another 10 min. Disconnect the absorption flask, quickly add 2.00 ml of the dilute amine solution and mix the solution until any residue is dissolved. Add 5 drops of iron(III) chloride solution, allow to stand for 15 min and then transfer to a 50-ml volumetric flask. Dilute to the mark with water, transfer a 10-ml aliquot to a 100-ml volumetric flask, dilute to the mark with water and read the absorbance of the solution in a 10-mm cell at 670 nm. Run a blank determination under exactly the same conditions but without the sample.

Calibration curve

Immediately after the preparation and the standardization of a 0.001 *N* sodium sulfide solution, transfer 3-, 4-, 5-, 6-, and 7-ml aliquots to 50-ml graduated cylinders each containing 20 ml of the 2% zinc acetate solution. Dilute to 35 ml with 2% zinc acetate solution and then add 2 ml of 4% sodium hydroxide. Stir well with a glass rod, add 2.00 ml of the amine solution, mix again and add 5 drops of iron(III) chloride solution. After 15 min transfer the solution to a 50-ml volumetric flask, dilute to the mark with water, transfer 10 ml to a 100-ml volumetric flask, dilute to the mark and measure the absorbance as described above. Prepare a blank under the same conditions omitting the sulfide solution.

Atomic absorption analysis for metals

Evaporate the pot solution from the above procedure to dryness on a steam bath, take up the residue with a few drops of concentrated hydrochloric acid, transfer with water to a 25-ml volumetric flask, and dilute with water to volume. Prepare working solutions for the standard curve from the stock solutions so that they contain the concentrations of metal ion shown in Table I together with the approximate amount of the other solution constituents. Aspirate the working and sample solutions under the conditions listed in Table I.

Results and discussion

In preliminary tests, it was shown, by taking aliquots of fresh 0.001 *N* sulfide solution through the colorimetric procedure and through the entire procedure, that the recovery of sulfide in the evolution process is quantitative. With aliquots containing 91.4–145.0 μg S, the maximum error was under 0.2%.

However, in the initial development of the method, low recoveries of sulfide by the evolution method were obtained; this was found to be due to contamination of the absorption flask with traces of hydrochloric acid, and to traces of oxygen in the

TABLE I

CONDITIONS USED FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

	<i>Pb</i>	<i>Bi</i>	<i>Cu</i>	<i>Fe</i>
Wavelength (nm)	217	223	325	250
Slit width	4	3	4	3
Lamp current (mA)	10	30	35	15
Flame	air-acetylene (oxidizing)	air-acetylene (oxidizing)	air-acetylene (oxidizing)	air-acetylene (oxidizing)
Working solution concentration	5-10-15-20	5-10-15-20	5-10-15-20	5-10-15-20

TABLE II

SULFUR RECOVERY FROM VARIOUS MINERALS

<i>Mineral</i>	<i>Weight of sample (μg)</i>	<i>Sulfur found (%)</i>	<i>Mean value (%)</i>	<i>Range of S values quoted in standard texts (%)</i>	<i>Theor. sulfur value (%)</i>
Pyrite	447	52.90	52.9	52.45-53.53	53.45
	414	52.92			
	513	52.95			
Bornite	552	24.82	24.8	25.17-25.65	25.56
	436	24.77			
	522	24.86			
Chalcopyrite	561	35.16	35.1	33.97-36.50	34.94
	432	35.06			
	497	35.08			
Cosalite	681	16.04	16.0	15.76-17.20	16.15
	724	16.02			
	574	15.95			
Enargite	460	32.45	32.5	31.44-33.23	32.57
	502	32.51			
	512	32.55			
Sphalerite	538	32.54	32.5	32.23-33.57	—
	492	32.52			
	511	32.44			
Galena	484	13.37	13.4	—	13.40
	821	13.39			
	853	13.40			
Bournonite	559	18.87	18.9	19.17-20.40	19.68
	622	18.78			
	435	18.96			

nitrogen. Addition of sodium hydroxide to the receiver prevented the difficulties caused by carry-over of hydrogen chloride (which could cause errors up to 40%), and scrubbing the nitrogen properly eliminated the oxygen (which could cause errors of 5%).

Occasionally, high recoveries (*ca.* 1%) of sulfide were obtained by the evolution procedure, compared with direct colorimetry; bubbling nitrogen through the zinc acetate solution for 30 min before use in the direct colorimetric procedure prevented this error.

In order to obtain reproducible results, the methylene blue reaction should be allowed to proceed for at least 15 min before the absorbance is read, otherwise the error may reach 1%. If the side-arm inlet tube is used to introduce liquid samples, an error of 10% may result, because of oxidation of sulfide by trapped atmospheric oxygen; this can be avoided by introducing such samples from the top funnel.

Atomic absorption interferences

Serious interference was found with the determination of bismuth. As a precaution, all the expected metallic ingredients were added (the match need be no better than 20% of amount present) to the standards.

TABLE III

RESULTS OF METAL ION DETERMINATION BY ATOMIC ABSORPTION (%)

	<i>Pb</i>	<i>Cu</i>	<i>Fe</i>	<i>Bi</i>
Galena	85.9 (86.0)*	—	—	—
Chalcopyrite	—	37.7 (36.6)	27.6 (28.4)	—
Bournite	—	61.6 (63.3)	11.4 (11.1)	—
Cosalite	44.1 (43.8)	—	—	39.8 (40.1)
Pyrite	—	—	46.3 (46.6)	—
Bournonite	42.8 (42.4)	12.6 (13.0)	—	—
Enargite	—	43.0	—	—
		43.2 (48.4)		
		43.0		

* Values in brackets are theoretical values.

Applications

Several different sulfide minerals were analyzed as described above. The results shown in Table II indicate that excellent recoveries were obtained.

Pot liquids containing Fe, Cu, Bi and Pb were analyzed by atomic absorption spectrophotometry (Table III). The results agree quite well with the theoretical values except in the case of enargite. Three results obtained for copper in enargite are shown in order to illustrate the precision obtained; it was supposed that in this case the metallic constituents varied from the accepted values.

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Gravimetric determination of bismuth with N-benzoyl-N-phenylhydroxylamine

Very few organic reagents have been found useful for the gravimetric determination of bismuth. Cupferron has been used¹ but, as with other metals, the precipitate requires ignition to the oxide before weighing. 8-Hydroxyquinoline², 8-hydroxyquinoline-5-sulphonic acid³, α -naphthoquinoline⁴, salicylaldoxime⁵, benzenearsonic acid⁶, thionalide⁷, etc. have been employed with variable success.

In the present investigation N-benzoyl-N-phenylhydroxylamine (BPHA) was found to be a satisfactory reagent for bismuth. The metal was precipitated quantitatively from a solution containing tartrate ions at pH 6.0-6.8 with BPHA and weighed directly after drying at 110-115°. The bismuth complex is creamy white, granular, and insoluble in water up to 80°. The complex is freely soluble in chloroform but only sparingly in ether, acetone, benzene, carbon tetrachloride, ethanol, glacial acetic acid and ethyl acetate. It is decomposed when treated with moderately concentrated mineral acids and melts with decomposition at $172 \pm 1^\circ$. The analytical results indicate the composition of the complex as $\text{Bi}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_3$.

Chemicals

Metal solutions: Pure bismuth subnitrate was dissolved in nitric acid and diluted so that there was no turbidity in the final stock solution. The solution was standardized by the oxine method.

Weighed amounts of sulphate, chloride or nitrate of various metals and requisite amounts of sodium, potassium or ammonium salts of molybdenum, tungsten, arsenic, vanadium and other anions were separately dissolved in water. Acids were added, wherever necessary, to prevent hydrolysis of the ions.

Reagent solution: A solution of BPHA in 95% ethanol was prepared for the precipitation of metal ions; for 0.2 g of the reagent 10-15 ml of alcohol was used.

All the chemicals used were of A.R. quality.

Determination of bismuth

Take an aliquot of bismuth solution, add 2.0-2.5 g of sodium potassium tartrate and dilute with distilled water to 200 ml. Heat the solution to 50-55° and add dropwise a solution of 0.2-0.4 g BPHA in 10-15 ml of alcohol. Raise the pH of

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the solution to 6.0–6.8 by adding dilute ammonia solution dropwise with constant stirring and digest the precipitate on a hot water bath for about 30–45 min. In order to avoid any decomposition of the complex, the precipitation and digestion should not be carried out above 65°. When the supernatant solution becomes transparent, filter the precipitate on a No. 3 sintered glass crucible and dry at 110–115° to constant weight. Calculate the metal content on the basis that the complex contains 24.71% of bismuth. Typical results are shown in Table I.

Optimum conditions for precipitation of bismuth

With other conditions the same, bismuth was precipitated with different amounts of BPHA. The precipitation of the metal complex was complete when the supernatant solution contained about 0.05% (w/v) of the reagent in excess at pH 6.0–6.5. The precipitation commenced at pH 5.0 and was quantitative in the range of pH 6.0–7.6. Below this range the precipitate did not coagulate readily and above pH 7.6 both the reagent and the precipitate tended to decompose.

TABLE I
DETERMINATION OF BISMUTH WITH BPHA

<i>Bi taken</i> (mg)	<i>Wt. of ppt.</i> (mg)	<i>Bi found</i> (mg)	<i>Error</i> (mg)
6.47	25.6	6.32	-0.15
6.47	26.4	6.52	+0.05
12.94	52.4	12.94	0.00
12.94	52.7	13.02	+0.08
19.41	78.4	19.36	-0.05
19.41	78.6	19.42	+0.01

TABLE II
SEPARATION OF BISMUTH FROM DIVERSE METALS WITH MASKING AGENTS

<i>Bi taken</i> (mg)	<i>Foreign ions added</i> (mg)	<i>Masking agent</i>	<i>Bi found</i> (mg)	<i>Error</i> (mg)
6.47	Be ²⁺ 16.5	Tartrate + citrate	6.62	+0.15
6.47	Pb ²⁺ 14.5	Tartrate + citrate	6.57	+0.10
6.47	Sb ³⁺ 24.0	Tartrate + citrate	6.32	-0.15
12.94	La ³⁺ 25.8	Tartrate + citrate	12.94	0.00
6.47	Th ⁴⁺ 11.6	Tartrate + citrate	6.37	-0.10
6.47	As ⁵⁺ 26.8	Tartrate + citrate	6.37	-0.10
6.47	U ⁶⁺ 25.2	Tartrate + citrate	6.42	-0.05
12.94	Co ²⁺ 16.0	Tartrate + cyanide	13.04	+0.10
6.47	Ni ²⁺ 13.5	Tartrate + cyanide	6.62	+0.15
6.47	Cu ²⁺ 6.0	Tartrate + cyanide	6.52	+0.05
12.94	Zn ²⁺ 17.5	Tartrate + cyanide	13.04	+0.10
12.94	Cd ²⁺ 12.0	Tartrate + cyanide	13.04	+0.10
6.47	Hg ²⁺ 16.8	Tartrate + cyanide	6.62	+0.15
12.94	Pd ²⁺ 8.8	Tartrate + cyanide	12.94	0.00
6.47	Mn ²⁺ 18.5	Tartrate + cyanide	6.62	+0.15
12.94	Sn ⁴⁺ 11.5	Tartrate + oxalate	12.84	-0.10
6.47	Al ³⁺ 27.0	Tartrate + oxalate	6.57	+0.05

Separation of bismuth from foreign ions

By pH adjustment. A mixture containing known amounts of bismuth (6.47 mg) and molybdenum(VI) (13.5 mg), tungsten(VI) (21.0 mg), vanadium(V) (14.0 mg), titanium(IV) (12.0 mg) or iron(III) (15.0 mg) was taken and the foreign ion was precipitated with BPHA at a pH less than 4.5 in presence of tartrate. The precipitate was filtered and washed with a solution containing tartrate ions at pH 4.0. The filtrate and washings were collected, concentrated to 200 ml and bismuth was precipitated from the solution with further amounts of BPHA after the pH had been increased to 6.0–6.4. It was dried and weighed as before. Accurate results were obtained in the presence of molybdenum(VI). In the presence of the other ions, the results obtained were only very slightly low (error: -0.12 till -0.17 mg).

By masking agents. Bismuth was precipitated with BPHA from a hot solution containing lead, arsenic(V), antimony(III), thorium, uranium, lanthanum or beryllium ions at pH 5.8–6.0 in presence of tartrates and citrates. It was washed first with a solution of tartrate-citrate at pH 6.0 and then with hot water before drying and weighing.

In order to separate bismuth from cobalt, nickel, copper, zinc, cadmium, mercury, palladium or manganese, sodium potassium tartrate and potassium cyanide were added to the solution before its pH was adjusted to 6.0–6.4. Bismuth was subsequently precipitated from the solution with BPHA.

Oxalates were added as the masking agent in the separation of bismuth from tin(IV) and aluminium.

Typical results are shown in Table II.

Effect of various anions

Cyanides, fluorides, phosphates, tartrates, oxalates, citrates and ascorbic acid did not interfere with the determination. EDTA masked the bismuth ions; on adding excess of calcium ions, the metal could, however, be precipitated with the reagent in the presence of EDTA. Thioglycollic acid was found to mask bismuth totally.

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The determination of trace amounts of total nitrogen in petroleum distillates

The analysis of trace amounts of nitrogen in petroleum distillates has been widely studied. Since MILNER¹ discussed available methods in 1963, other useful procedures have been described²⁻⁵. Many of the more recent methods call for combustion of small amounts of nitrogenous material followed by detection of nitrogen as $N_2^{2,3}$, as NO_2^4 and by coulometric titration of NH_3^5 .

The method of GOUVERNEUR⁶ proved to be suitable for the analysis of nitrogen ranging from 0 to 500 p.p.m. in a wide variety of petroleum products submitted to this laboratory. This method is advantageous in that it can be carried out with ordinary Kjeldahl apparatus when more sophisticated combustion apparatus is either unavailable or in use for more important research. To obviate the large sample requirement for distillates that contain less than 10 p.p.m. of nitrogen, the method was modified so that smaller samples could be analyzed more quickly with suitable accuracy. The general approach consisted of reduction by a factor of ten of all quantities recommended in the GOUVERNEUR method. Digestion of the column contents followed by steam distillation furnished a solution that could yield enough ammonia for conversion to indophenol blue⁷. A 1:1 mixture of iron(III) chloride and zinc chloride⁸ was added to the percolation column along with sulfuric acid supported on pumice to improve the extraction of nitrogen.

Reagents and apparatus

The percolation column was made from an 11-cm length of 10-mm borosilicate glass tubing connected to a 125-ml separatory funnel by a 14/35 ST outerjoint. An Aminco micro Kjeldahl digestion and steam distillation system was used. Preparation of the reagents has been previously described^{6,7}.

Procedure

Percolation. Insert a 1-cm plug of glass wool into the column about 0.5 cm from the bottom of the opening. Add 2 g of the sulfuric acid-pumice mixture. Add a layer of dry pumice just sufficient to cover the acid-pumice mixture followed by 1 g of 1:1 zinc chloride-iron(III) chloride mixture. Connect the column to a 125-ml suction flask by a rubber stopper and insert the separatory funnel that contains enough sample to yield at least 50 μ g of nitrogen. Adjust the percolation rate to about 60 drops per min using suction if necessary. After the contents of the separatory funnel have passed through the column, rinse the separatory funnel with 2 ml of isoctane, and allow it to drain through the column. Determine a reagent blank with each set of samples.

Digestion. Transfer the contents of the column to a tared 100-ml Kjeldahl flask that contains 25 mg of catalyst mixture. Use 8 ml of sulfuric acid to aid the transfer. Digest the contents according to the method of GOUVERNEUR⁶. Using the weight of the flask contents, W , estimate the amount, A , of potassium sulfate to be added by: $A(g) = (W - 3) 0.72$.

Steam distillation. Assemble the Kjeldahl flask to the steam distillation apparatus. Add 25 ml of 50% sodium hydroxide and distill the ammonia, collecting the distillate to the mark of a 50-ml volumetric flask containing 10 ml of concentrated

boric acid solution.

Color development. After all the samples have been distilled, pipet a 10-ml aliquot of each distillate into 25-ml calibrated test tubes. Add 7 ml of saturated boric acid solution, 2.5 ml of chlorine water and 2.5 ml of 8% aqueous phenol solution. An electric test tube shaker aids mixing after the addition of each reagent. Place the test tubes in boiling water for 3 min. Cool in ice water, add 2.5 ml of 3 *M* sodium hydroxide and dilute to the mark. Measure the absorbance in a 1-cm cell at 625 nm against distilled water. Prepare a calibration curve ranging from 10 to 50 μg of nitrogen per 25 ml by converting suitable quantities of ammonium chloride to indophenol blue.

Results

Successful use of this analysis requires the attainment of low and reproducible blank values. Six reagent blanks determined simultaneously yielded a mean absorbance value of 0.073 with a standard deviation of 0.0087. To determine the effect of

TABLE I

ANALYSIS OF TOTAL NITROGEN IN TRANSFORMER OIL AT VARIOUS CONCENTRATIONS

<i>p.p.m. N added</i>	<i>Sample (g)</i>	<i>Number of determinations</i>	<i>p.p.m. N found</i>	<i>Standard deviation</i>
2.5 ^a	40	12	2.0	0.26
7.9	10	13	7.9	1.04
18.3 ^b	5	12	18.1	1.41
11.0	5	10	10.5	1.34

^a Nitrogen added as equivalent amounts of carbazole, 2,3-dimethylquinoxaline, and pyridine to transformer oil that contained 0.32 p.p.m. N by the GOUVERNEUR method.

^b Nitrogen added as equivalent quantities of 2,3-dimethylquinoxaline, pyridine, and 8-hydroxyquinoline.

TABLE II

APPLICATION OF PROPOSED METHOD TO ROUTINE SAMPLES; COMPARISON WITH THE METHOD OF GOUVERNEUR

<i>Sample</i>	<i>p.p.m. Nitrogen</i>	
	<i>Proposed method</i>	<i>Gouverneur method</i>
Gas Oil	44.7	44.0
Gas Oil	18.6	15.2
Gas Oil	36.6	38.4
Kerosine	5.7	5.8
Gasoline	9.5	9.2
Gasoline	51.0	46.2
Gasoline	87.0	82.8

nitrogen originating from various reagents, a number of analyses were made with the purified reagents suggested by MILNER *et al.*⁹ Nitrogen impurities in the pumice caused the greatest irregularity of the blank. Heating the pumice to 900° eliminated this source of error. Table I presents typical results obtained by this procedure. Although the ideal sample should contain 100 μg of nitrogen, analyses of sufficient accuracy can be obtained from samples containing as little as 50 μg . Since analyses of

distillates by the Technicon phenol-hypochlorite method¹⁰ agree well with those performed by the present colorimetric method, most of the error is probably attributable to the percolation and digestion steps.

Application of the phenol-hypochlorite reaction to total Kjeldahl digests described by MANN¹¹ has been considered. A sample preparation system to which this method can be applied is being developed.

The proposed method yields essentially the same results as the GOUVERNEUR method (Table II). The use of smaller samples enables the completion of 8 analyses a day, permits the use of micro Kjeldahl digestion and eliminates the hazard of handling large quantities of acid and base.

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Gas-liquid chromatographic determination of pyridine bases without tailing effects

Gas-liquid chromatographic analysis of pyridine bases is hindered by tailing. This tailing obscures small peaks and makes quantitative examination inaccurate or impossible. The tailing effects are caused by adsorption phenomena on the solid support¹ and decrease with increasing polarity of the stationary phase. However, with a common polar stationary phase such as polyethylene glycol the asymmetrical peaks do not disappear sufficiently for an exact analysis. Moreover, a restriction on the choice of liquid substrates may be undesirable for other reasons.

A rather satisfactory solution has been found in an alkali treatment of the solid support²⁻⁵, but there was still appreciable tailing when nonpolar or slightly polar stationary phases were used⁶. The free alkali on the support can also bring about breakdown reactions of the injected substances⁷ and stimulate the alteration of the liquid phases^{3,4}. DECORA AND DINNEEN⁸ prepared a solid support from a commercial detergent containing alkylaryl sulfonate by heating it and then extracting

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it with petroleum ether. The porous residue was used as a liquid substrate carrier and showed symmetrical peaks when nonpolar stationary phases were applied. The same authors also obtained good results after alkali treatment of the porous residue⁹. By adding ethylenediamine to the carrier gas a distinct improvement was achieved¹ with application of stationary phases of divergent polarity. A drawback of this method is the fact that a special apparatus has to be installed for a constant flow of gaseous ethylenediamine.

The proposed solution of the problem consists of adding a relatively non-volatile amine to the liquid phase before coating the solid support. As non-volatile amines were especially used triethanolamine (TEA) and Armeen SD (mixture of aliphatic primary amines). TEA was found to be preferable to Armeen SD because of its better thermal stability.

Apparatus

The experiments were carried out in a Becker gas chromatograph (Delft, The Netherlands) equipped with a 2.5 mV Honeywell recorder. The column consisted of a stainless steel U-tube with a length of 2 m (internal diameter, 4 mm). The temperature was maintained at about 70°. The carrier gas nitrogen had a flow rate of about 70 ml/min. The pressure at the outlet was atmospheric and the pressure drop over the column 0.7 atm. A hydrogen flame ionization detector was used with a hydrogen flow rate of about 30 ml/min and an air flow rate of about 300 ml/min. The sample volume was 0.2 μ l.

Preparation of packings

Celite (60–72 mesh; acid-washed) (J.J.'s Ltd., King's Lynn, Norfolk, England) and Kieselguhr 200–250 i.e. 60–72 mesh) (Chemie-Erzeugnisse und Absorptionstechnik A.G., Muttenz, Switzerland) acid- and base-washed were used as the support for the liquid phases. The stationary phases were composed of polyethylene glycol 1000 (PG 1000), dioctyl sebacate (DOS) or silicone oil DC 550 as liquid substrate and triethanolamine (TEA) or Armeen SD as the non-volatile amine. Armeen SD is a mixture of aliphatic primary amines manufactured by Armour Chemical Co.

The desired mixture of liquid substrate and non-volatile amine was dissolved in a volatile solvent (methanol for PG 1000 and acetone for silicone oil and DOS). The solid support was added to this solution and the solvent was evaporated by gently heating, with stirring.

When not in use, the column should be closed to prevent neutralization of the amine by carbon dioxide.

Pyridine bases

The materials studied were of natural origin and had been recovered from coal tar by fractionation and isolation. They consisted of a mixture of pyridine and its homologues such as picolines, lutidines and collidines, and of aromatic amines such as aniline and toluidines.

Results and discussion

In general, columns with stationary phases composed of liquid substrates of divergent polarity and a relatively non-volatile amine produce symmetrical peaks,

although the composition is not totally free. It appears that with decreasing polarity of the stationary phase a thicker film of the liquid phase on the solid support must be present for the same good results to be achieved. Excellent chromatograms were obtained when the solid support was coated with 9% PG 1000 and 1% TEA (Fig. 1) or 20% DOS and 1% TEA. Very slight and negligible tailing occurred after coating with 30% silicone oil and 1% TEA (Fig. 2). On the other hand, much tailing was found when only 20% DOS or 30% silicone oil was used as the coating. Slight tailing was found with a coating of 3.5% silicone oil and 0.5% TEA.

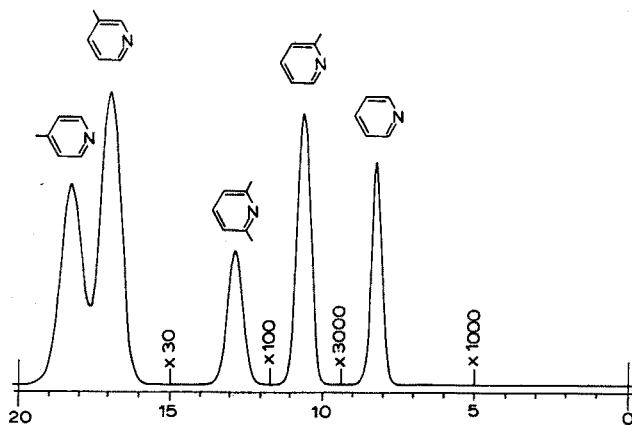


Fig. 1. Chromatogram of some components from pyridine bases. Support was coated with 9% PG 1000 and 1% TEA.

The use of these columns, in which the solid support is coated with DOS or silicone oil, has the advantage that together with the determination of pyridine and its homologues, aromatic amines such as aniline and toluidines can be carried through the column at velocities suitable for practical purposes. The high affinity of aromatic amines for polyethylene glycol results in an excessive retention time in relation to that of the pyridines.

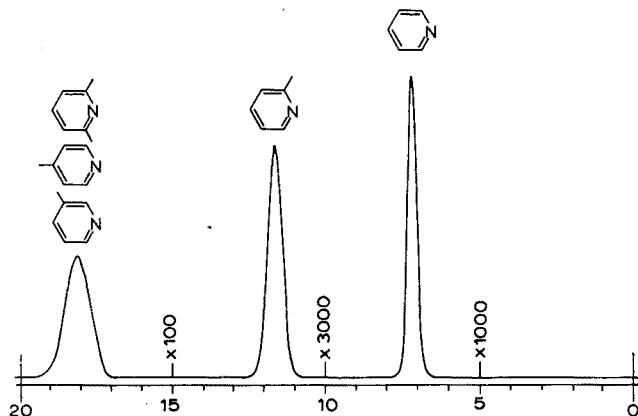


Fig. 2. Chromatogram of some components from pyridine bases. Support was coated with 30% silicone oil and 1% TEA.

Another advantage of using TEA is that there is more selectivity in determining the components of mixtures of pyridine bases. When the solid support was coated with 9% PG 1000 and 1% TEA, it was possible to separate 2,5-lutidine from the other lutidines and make a quantitative determination of this component.

Both Armeen SD and TEA gave good results but TEA has a better thermal stability. There was no difference in behaviour between Celite and Kieselguhr.

When non-volatile amines are used in the composition of column packings, there are three factors of great importance for reducing tailing: (a) the neutralization of the acid positions of the solid support by the non-volatile amine, (b) the polarity of the stationary phase, and (c) the film thickness of the stationary phase. The neutralization of any acidic groups on the solid support prevents the adsorption of the pyridine bases. Only columns without TEA produced imperfect chromatograms. Differences in detail between the results obtained by columns with TEA can be explained by the two remaining factors.

When the results with and without TEA in the stationary phase are compared, it can be seen that, as expected, the polarity of the stationary phase increases when the TEA is present and so reduces the tailing. However, the degree of polarity is not the only factor that controls tailing. As was mentioned above, a support coated with 3.5% silicone oil and 0.5% TEA gave more tailing than one with 30% silicone oil and 1% TEA, although the former is more polar. In this case, the film thickness of the stationary phase becomes significant; with too thin a film, the pyridine bases tend to be adsorbed on the solid support, while the effect disappears for practical purposes with sufficient thicknesses.

To summarize, it can be concluded that the neutralizing effect of a non-volatile amine on the stationary phase prevents tailing. The polarity and the film thickness of the liquid phase also contribute to the prevention of tailing; decreased polarity can be corrected for by increasing the film thickness.

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The determination of calcium and magnesium in acetylene flames

A detailed investigation was reported recently on the determination of calcium and magnesium by atomic absorption spectroscopy using an oxy-hydrogen flame¹. The results indicated that in the absence of releasing or masking agents the procedure is subject to interference from several extraneous ions and compounds. This communication presents the results of our investigations with air-acetylene and nitrous oxide-acetylene flames for these determinations. Few interferences were found in these flames, and methods are proposed for overcoming those interferences that were found.

Apparatus

All absorption measurements were made with a Perkin-Elmer (Model 303) atomic absorption spectrometer. For studies with nitrous oxide-acetylene flames, the standard burner head on the Perkin-Elmer burner mount was replaced by a nitrous oxide-acetylene burner head with a slot length of 3 in and a width of 0.015 in. Calcium and magnesium hollow-cathode lamps (Ransley Glass Instruments, Melbourne, Australia) were used as radiation sources.

Reagents

Stock solutions containing 1 mg/ml of calcium and magnesium were prepared by dissolving oven-dried calcium carbonate and pure magnesium turnings in dilute hydrochloric acid and diluting to volume with distilled water. EDTA (disodium salt) and strontium chloride were used as aqueous 4% and 5% solutions respectively. All other solutions used in interference studies were made from reagent-grade chemicals.

Procedure

Table I lists the optimum operating conditions established by atomizing solutions containing 4 p.p.m. and 0.4 p.p.m. of calcium and magnesium respectively. With a nitrous oxide-acetylene flame, absorption measurements were made at the rose red inner cone of the flame, about 1 cm from the burner head. The zero of the instrument was set while water was aspirated into the flame. The sample feed rate under the conditions established was about 4 ml/min.

TABLE I
OPERATING CONDITIONS AND SENSITIVITY

	Type of flame	Lamp current (mA)	Slit width (Å)	Oxidant (P.S.I.)		Acetylene (l/min)	Sensitivity (p.p.m. for 1% absorption)
				Atomizer	Auxiliary		
Calcium 4227Å	NO-C ₂ H ₂	20	2	30	10	5	0.1
	Air-C ₂ H ₂	20	13	25	10	1.2	0.1
Magnesium 2852Å	NO-C ₂ H ₂	6	2	30	10	5	0.03
	Air-C ₂ H ₂	6	2	25	10	1.2	0.02

Interference studies

The effect of the presence of a number of ions and compounds listed in Table II on the absorption of calcium and magnesium were investigated with both air-acetylene

and nitrous oxide-acetylene flames. The concentration of calcium and magnesium in these investigations was 4 p.p.m. and 0.4 p.p.m. respectively, and that of interferent 200 p.p.m. The effect of acids was examined by adding 5 ml of the appropriate concentrated acids before diluting to 100 ml water. Separate analyses were made for each interferent using each flame under the conditions described in Table I.

TABLE II

INTERFERENCE STUDIES

Group I.	Li ⁺ , Na ⁺ , K ⁺ , Cu ²⁺ , Ag ⁺
Group II.	Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Zn ²⁺ , Cd ²⁺ , Hg ₂ ²⁺ , Hg ²⁺
Group III.	B ₄ O ₇ ²⁻ , Al ³⁺ , Ce ⁴⁺
Group IV.	HCO ₃ ⁻ , SiO ₃ ²⁻ , Ti ⁴⁺ , Zr ⁴⁺ , Sn ²⁺ , Sn ⁴⁺ , Pb ²⁺
Group V.	NH ₄ ⁺ , NO ₃ ⁻ , HPO ₄ ²⁻ , VO ₃ ⁻ , HAsO ₄ ²⁻ , Sb ⁵⁺ , Bi ³⁺
Group VI.	SO ₃ ²⁻ , SO ₄ ²⁻ , Cr ³⁺ , SeO ₃ ²⁻ , MoO ₄ ²⁻ , TeO ₃ ²⁻ , WO ₄ ²⁻ , UO ₄ ²⁻
Group VII.	F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ , Mn ²⁺
Group VIII.	Fe ³⁺ , Co ²⁺ , Ni ²⁺ , Pd ²⁺
Miscellaneous substances.	Citrate, tartrate, oxalate, detergents (Dreft*), hydrochloric acid, sulfuric acid, nitric acid, perchloric acid, and acetic acid.

* Dreft, trade name of an alkylbenzene sulfonate detergent.

TABLE III

INTERFERENCE FROM VARIOUS SUBSTANCES IN THE DETERMINATION OF CALCIUM AND MAGNESIUM WITH AIR-ACETYLENE FLAME

Interferent (200 p.p.m.)	% Absorption		Interferent (200 p.p.m.)	% Absorption	
	Calcium (4 p.p.m.)	Magnesium (0.4 p.p.m.)		Calcium (4 p.p.m.)	Magnesium (0.4 p.p.m.)
None	32.6	21.6	Na ⁺	35.8	22.0
F ⁻	15.6	21.6	K ⁺	34.6	21.8
SO ₄ ²⁻	22.4	21.0	Li ⁺	34.1	24.2
SO ₃ ²⁻	24.6	21.4	Be ²⁺	12.2	21.6
PO ₄ ²⁻	20.7	21.8	La ³⁺	35.6	21.9
SeO ₃ ²⁻	19.4	18.6	Ti ⁴⁺	0.0	18.2
TeO ₃ ²⁻	21.4	22.0	Zr ⁴⁺	5.7	19.6
WO ₄ ²⁻	25.0	18.6	Cr ³⁺	22.7	21.6
SiO ₃ ²⁻	9.0	12.4	Pd ²⁺	18.4	21.0
CO ₃ ²⁻	13.9	18.0	Al ³⁺	9.0	16.4
HCO ₃ ²⁻	20.1	21.4	UO ₂ ⁴⁺	19.7	21.6
HAsO ₄ ²⁻	22.4	21.5			

Air-acetylene flame. Results obtained for calcium and magnesium indicated that only a few ions interfere (Table III). In the case of calcium, with the exception of SiO₃²⁻, CO₃²⁻, HCO₃⁻, F⁻ and Ti⁴⁺, all other interferences were eliminated by the presence of 0.5% strontium chloride. The interference of carbonate and bicarbonate was overcome by the presence of 0.4% EDTA (or the alkalinity can be neutralized) and that of fluoride by the addition of 1 mg/l of sodium borate. EDTA or strontium chloride eliminated the interference of silicate and titanium when the concentration of each was less than 50 p.p.m. The alkali metals interfered by enhancing the absorption by calcium. This effect may be corrected by adding excess alkali to both standards and samples. Alternatively, the determination can be done in the presence of EDTA or SrCl₂, the

addition of which is essential to overcome certain interferences as indicated above.

Acetic acid enhanced the absorption due to both calcium and magnesium by about 12 and 20% respectively. If its presence is suspected, it should be overcome by preparing comparable standard solutions in acetic acid. The recovery of calcium in the presence of hydrochloric, nitric and sulfuric acids was reduced by about 8%, although no such effect was noticed in the case of magnesium.

Very few ions interfered in the determination of magnesium (Table III). However, the determination may be made free from interference if the solution contains 0.5% strontium chloride.

Nitrous oxide-acetylene flame. Interference studies in nitrous oxide-acetylene flame indicated that alkali metals, strontium, "drecht", acetic acid and sulfuric acid interfered in the determination of calcium and magnesium. None of the other substances caused interferences. Sulfuric acid suppressed the absorption by both calcium and

TABLE IV

INTERFERENCES IN NITROUS OXIDE-ACETYLENE FLAME

(No interference from other interferents studied (see Table II))

<i>Interferent</i>	% Absorption	
	<i>Calcium</i> (4 p.p.m.)	<i>Magnesium</i> (0.4 p.p.m.)
None	35.3	11.6
Sodium (200 ppm)	43.1	13.2
Potassium (200 ppm)	42.8	13.4
Lithium (200 ppm)	42.9	13.8
Strontium (200 ppm)	43.0	13.4
Acetic acid (5%)	44.0	13.8
Sulfuric acid (5%)	28.8	9.0
Drecht(200 ppm)	46.2	12.0

magnesium by about 20%. The other compounds interfered by enhancing the original absorption signal of either calcium or magnesium (Table IV). The presence of 0.5% strontium chloride or 0.4% of the disodium salt of EDTA overcame the interferences by alkali metals. The enhancement by acetic acid may be similar to that of organic solvents and that of drecht due to decrease in the surface tension of the solutions.

Conclusions

This investigation indicates that the determination of Ca and Mg with air-acetylene or nitrous oxide-acetylene flames is more selective than with oxy-hydrogen flames. The decrease in chemical interference in nitrous oxide-acetylene flame is particularly noteworthy, but care must be exercised in the presence of alkali metals, which are associated with most samples analysed for Ca and Mg. Errors due to the presence of alkali metals can be overcome by preparing standards and samples to contain 0.5% SrCl₂ or 0.4% EDTA (disodium salt). The presence of EDTA and/or SrCl₂ also overcame all the interferences in calcium and magnesium determinations with air-acetylene flames.

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Spectrophotometric determination of copper

While syntheses of 2-pyridyl-substituted pyrazines and quinoxalines have been described, and their potential use as chelating agents mentioned¹⁻⁶, no analytical procedures using these compounds have yet appeared. The present work shows 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline (DMDPQ) to be a suitable colorimetric reagent for copper. This reagent is remarkably selective toward copper, and the analysis is subject to few interferences.

Reagents

DMDPQ. The reagent was obtained from Aldrich Chemical Company, and was used without purification. The reagent is insoluble in water, and only slightly soluble (1.221 g/100 ml) in ethanol. A saturated solution of DMDPQ in ethanol is used.

Procedure

Dissolve the sample containing 50-500 μg copper in any convenient acid. If hydrochloric or perchloric acid is used, add 5 ml of sulfuric acid after the sample is dissolved and distil off the lower boiling acid. Dilute with 100 ml of water, add 20 ml of aq. 10% hydroxylammonium chloride soln., 5 ml of 15% tartaric acid-15% NaClO_4 soln. and 2 ml DMPDQ soln. Adjust the pH to 4. The solutions are well buffered in this range, and 10 *M* sodium hydroxide can be used for this purpose. Transfer the solution to a separatory funnel and extract once with 15 ml of nitrobenzene. After the phases have separated, drain the nitrobenzene layer into a 50-ml volumetric flask and dilute with ethanol almost to the mark. There is a negative heat of mixing and the solution should be warmed to ambient temperature before making the final dilution. Measure the absorbance of the solution at 514 nm against a distilled water blank.

A calibration curve is constructed by dissolving 50-75 mg of copper wire in a few ml of nitric acid, diluting with distilled water to the mark in a 1-1 volumetric flask, and following the above procedure with 1-10 ml aliquots as samples.

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Reactions with metal ions

DMDPQ reacts with copper(II) to yield a green soluble product. With copper(I) a more intensely colored reddish-brown product is obtained which precipitates on standing. The copper(I) compound exhibits a broad absorption maximum at 514 nm in 3:7 nitrobenzene-ethanol mixtures, and conforms to Beer's law in concentrations up to $1.5 \cdot 10^{-4}$ M. The molar absorptivity at 514 nm is 4100. Color intensity does not vary with pH through the range pH 3.5-5, and is constant for at least 24 h. Using the method of continuous variation the ligand-to-metal ratio was found to be 2:1. DMDPQ does not form colored compounds with any of the other metals tested.

Influence of foreign ions

The influence of foreign ions was determined by adding 200 mg of the ion in question to 318 μ g of copper and following the recommended procedure. Interference of less than 2% was caused by iron, manganese(II), nickel, chromium(III), cobalt, calcium, zinc, tin(II), lead, acetate, bromide, chloride, fluoride, sulfate, nitrate, molybdate, and arsenate. Indicated amounts of the following ions could be tolerated without causing greater than 2% error: perchlorate, 67 mg; vanadate, 10 mg; phosphate, 50 mg; iodide, 30 mg; aluminum, 40 mg; cerium(IV), 20 mg.

TABLE I

ANALYSIS FOR COPPER IN NBS STANDARD SAMPLES

Sample	% Cu found	% Cu certified
82a (Fe)	0.072, 0.071, 0.070	0.076
73b (Fe-Cr)	0.125, 0.123	0.126
53d (Pb-Sb-Sn)	0.265, 0.267	0.268

Results

Three NBS samples were analyzed according to the recommended procedure. The results are shown in Table I. Samples of NBS 53d were dissolved in sulfuric acid. Samples of NBS 82a and 73b were dissolved in hydrochloric acid, which was then removed by fuming with sulfuric acid.

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Microgram determination of iodide by the use of isotopic exchange

It has been known for several years¹ that an interchange of iodine atoms takes place when alkyl iodides and alkali iodides are mixed in certain solvents. This exchange can be observed if one of the reactants is labelled with radioactive iodine. The purpose of this communication is to show that an exchange reaction of the type mentioned may be employed to determine microgram amounts of iodide. It appears not unlikely that the sensitivity might be extended to the nanogram level.

Principle of the method

The method may be outlined as follows. A known quantity of the alkyl iodide (n_1 moles) is mixed in a suitable solvent with the unknown amount (n_2 moles) of the inorganic iodide labelled with radioactive iodine. The radioactivity, A_0 , of the sample is measured. After exchange equilibrium has been reached, the organic iodide is separated off and the remaining activity, A_∞ , of the sample determined.

The unknown quantity is calculated from the expression,

$$n_2 = n_1 A_\infty / (A_0 - A_\infty) \quad (1)$$

which is derived on the assumption that the equilibrium constant of the exchange reaction is equal to unity (isotope effects may be neglected²).

Experimental

For practical reasons it is desirable that exchange equilibrium is reached as fast as possible. The exchange reaction between methyl iodide and iodide ions in acetone as a solvent medium was therefore selected. The choice of methyl iodide is due to the fact that this compound exchanges its iodine atom more easily than do alkyl iodides with more than one carbon atom^{1,3}. Acetone was used because reactions of the type concerned are comparatively rapid in aprotic solvents. The rates of the methyl iodide-iodide ion exchange reaction in water⁴, methanol⁵, ethanol⁶, and acetone⁶ respectively are in the ratios 1:7:22:17000.

Reagents. Methyl iodide (Merck, *purum* grade) was distilled in a column filled with copper turnings⁷ to remove traces of hydrogen iodide and iodine. It was stored over mercury in the dark.

Sodium iodide (*pro analysi* grade) was dried at 110° for 3 h and stored in a desiccator.

Acetone (*pro analysi* grade) was dried over anhydrous calcium sulphate⁸ and fractionally distilled. It should be noted that anhydrous acetone must be used because the presence of even small amounts of water strongly inhibits⁹ the exchange reaction.

Radioactive iodide ($^{131}\text{I}^-$) in a dilute sodium thiosulphate solution was evaporated to dryness and dissolved in dry acetone.

Solutions of methyl iodide and sodium iodide in acetone were prepared at 25° using volumetric flasks filled with dry nitrogen.

Procedure. A 0.100-ml portion of $8.27 \cdot 10^{-4} M$ methyl iodide in acetone was mixed in a narrow test tube (volume slightly exceeding 0.2 ml) with an equal volume of an $1.090 \cdot 10^{-4} M$ sodium iodide solution containing $0.2 \mu\text{C } ^{131}\text{I}^-$. The test tube was closed with a ground glass stopper and its γ -activity (A_0) measured in a well-type NaI(Tl) scintillation detector. The activity reading was corrected for dead time,

background, and isotope decay in the usual manner. In each case, sufficient counts were registered in order to maintain a standard deviation of less than 0.2%.

The sample was left for 1 h at 25° to allow exchange equilibrium to be established. From the second-order velocity coefficient⁶ for the methyl iodide-iodide ion exchange reaction in dry acetone, 8.2 l-mole⁻¹-sec⁻¹, it can be calculated that 40 min is sufficient at the concentrations of the iodides used to reach equilibrium to within 0.1%. The time necessary to reach equilibrium may of course be reduced by increasing the temperature. The solution was then carefully evaporated to dryness by directing a weak stream of nitrogen into the test tube. This procedure required 1 h. Before measuring the remaining radioactivity (A_{∞}), the solid residue was dissolved in 0.2 ml of acetone. Thus A_0 and A_{∞} could be measured under comparable geometrical conditions.

Results

Typical results are shown in Table I, where the amounts of iodide in the second last column, calculated using eqn. (1), should be compared with the figure in the second column.

TABLE I
DETERMINATION OF IODIDE BY PROPOSED METHOD

CH_3I (μg)	I^- taken (μg)	A_0 (counts/sec)	A_{∞} (counts/sec)	I^- found (eqn. (1)) (μg)	$\frac{I^- \text{ found}}{I^- \text{ taken}}$
11.74	1.383	2845	339.1	1.420	1.027
		2918	341.9	1.393	1.007
		2874	321.8	1.323	0.957
		Average = 1.379			

As can be seen, the calculated values deviate in all cases by less than 5% from the value in column 2 and the average deviates by less than 1%. It is concluded that the technique developed may be employed to determine microgram amounts of iodide with an uncertainty of only 1-2%.

The possibility of increasing the sensitivity by decreasing the methyl iodide concentration and the volume of the sample is under investigation.

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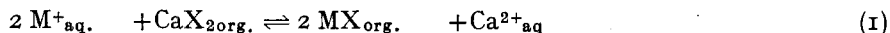
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Determination of calcium and oxalate with an ion-exchange electrode

A study of the calcium activity electrode, recently introduced by Orion Research Incorporated, Cambridge, Massachusetts, for the compleximetric determination of calcium and zinc ions is described in this communication; in a previous communication¹, the response of this electrode and its possible use in potentiometric titrations were discussed. THOMPSON AND ROSS² have used it for the determination of calcium in sea water. The electrode is fairly selective and sensitive for both calcium and zinc ions and detects them just as a conventional glass electrode detects hydrogen ions. The electrode develops a potential across the thin layer of water-immiscible liquid ion-exchanger held mechanically rigid by a thin porous inert membrane disc. The liquid exchanger contains a calcium salt of an ester of phosphoric acid of the general formula³ $\text{Ca}[(\text{RO})_2\text{POO}]_2$, where R represents hydrocarbon groups of sufficient chain length to confer a high solubility of the salt in a solvent of low dielectric constant and at the same time, render the salt essentially insoluble in aqueous phase. The solvent is principally a high-molecular-weight organic phosphonate of the type, $(\text{RO})_2\text{POR}$, which is virtually immiscible with water. The highly polar $\text{P}\rightarrow\text{O}$ group can solvate calcium(II), thereby reducing the energy required for its transfer from the aqueous to the organic phase via an ion-exchange process. The porous membrane simply maintains the liquid organic phase in the form of a thin layer between the aqueous sample and internal reference solutions; it is a cellulose acetate base material, specially treated so that the membrane is preferentially wetted by the organic phase, and any residual carboxylic acid groups which would interfere with the exchange of calcium ions, are removed. The selectivity of the electrode depends on the fact that the equilibrium at the interface in presence of an interfering ion, M^+ ,



lies far to the left. Over a wide range of aqueous solution composition, only the calcium ion can exist in large concentrations in the organic phase and is, therefore, the only species capable of transporting charge between the sample and internal solutions. The internal solution of calcium chloride contacts the internal membrane surface; these calcium ions provide a stable potential between the inside of the membrane and the filling solution so that changes in potential are entirely due to changes in the calcium activity of the sample solution. The electrode exhibits Nernstian behavior down to 10^{-4} moles/liter of calcium. For solutions containing a

mixture of two potential-determining ions, the Nernst equation must be modified by the introduction of the selectivity ratio, K ,

$$E = E^0 + (RT/nF) \ln (a_{Ca^{2+}} + K_{aM^+}) \quad (2)$$

where K is the exchange constant for the process represented by equilibrium (1).

Assembly of the electrode

Place the porous membrane exactly at the center of the membrane spacer assembly at the bottom of the electrode. Charge the electrode with the liquid ion exchanger. Check the correct wicking of the ion-exchanger. As the membrane takes up ion-exchanger from the reservoir, it becomes translucent. Charge the electrode with the internal filling solution of calcium chloride at the center. Connect the electrode to the input of a glass electrode in a conventional expanded-scale pH-meter. A commercial saturated calomel electrode can be used as the reference electrode.

General procedure

Adjust the solution to the appropriate pH with 7 M ammonia solution. Titrate, with constant magnetic stirring, measuring the potential 30–60 sec after each addition. Before the end-point measure the potentials at 0.5–1 ml increments of the titrant and near the end-point at 0.1–0.2 ml increments.

Titration of calcium with EDTA

Calcium(II) can be titrated with 0.01 M EDTA solution at pH 10. A typical titration curve is shown in Fig. 1; the mid-point of the inflection represents the end-point of the titration. For 2–10 mg of calcium(II) the relative error is between 0 and 3.2% with an average error of 2% over the whole range. The precision and accuracy, however, are improved remarkably in presence of alkali metal ions (Table I). In presence of Ba^{2+} , Mg^{2+} , and Zn^{2+} , a single inflection represents the combined

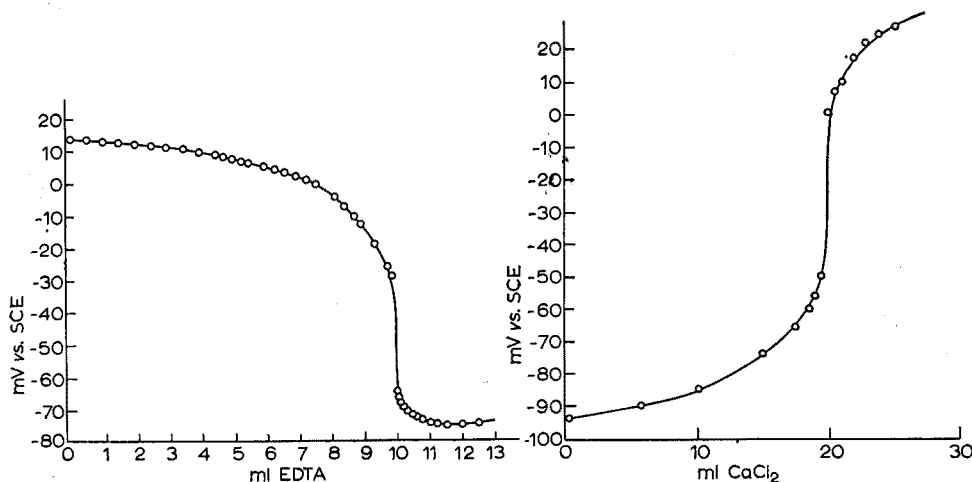


Fig. 1. 10 ml of 0.01 M $CaCl_2$ solution + 30 ml of water titrated with 0.0100 M EDTA.

Fig. 2. 20 ml of 0.0993 M $K_2C_2O_4$ titrated with 0.0977 M $CaCl_2$.

titration of calcium and these ions. In presence of strontium, the curve is drawn out and the end-point cannot be detected accurately. Ammonium ion causes no interference. Among the anions, Cl^- , Br^- , I^- , CN^- , NO_3^- , NO_2^- , SO_4^{2-} , CrO_4^{2-} , ClO_3^- , ClO_4^- , SCN^- , $\text{Fe}(\text{CN})_6^{4-}$, formate and arsenate do not interfere. Phosphate, fluoride, and oxalate interfere; carbonate interference can be eliminated by prior acidification before the pH adjustment.

Titration of oxalate with calcium

Oxalate ions can be titrated with standard 0.1 *M* calcium chloride solution at pH 7–11. A typical titration curve is shown in Fig. 2. Amounts of oxalate ranging from 8.3 to 33 mg were titrated, the relative error varying from 2.3% to 0.6% as the amount of oxalate increased.

TABLE I

DETERMINATION OF CALCIUM IN PRESENCE OF ALKALI METAL IONS

<i>Calcium present (mg)</i>	<i>Alkali metal ion (mg)</i>	<i>Calcium found (mg)</i>	<i>Error (%)</i>
15.00	230 Na^+	15.00	0.00
10.00	230 Na^+	10.00	0.00
5.00	195 Na^+	5.00	0.00
15.00	391 K^+	14.99	0.06
10.00	391 K^+	10.00	0.00
5.00	196 K^+	5.00	0.00
15.00	70 Li^+	15.00	0.00
10.00	70 Li^+	10.00	0.00
5.00	35 Li^+	5.00	0.00

Titration of zinc with EDTA

When *ca.* 40 ml of solution containing 10–40 mg of zinc solution is mixed with 2 drops of 7 *M* ammonia solution, a precipitate appears but this disappears as the titration with 0.01 *M* EDTA solution proceeds. The shape of the titration curve is very similar to that shown in Fig. 1 for the calcium titration. The accuracy and precision of the zinc titrations are not as good as for the calcium titrations; over the 10–40 mg range, the relative error varied from –3.0% to +1.9%.

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Anal. Chim. Acta, 40 (1968) 354–356

Measurement of flow rate and pressure of gases in flame spectrometry

It has been brought to our attention through communications with numerous workers using flame spectrometric methods, that a great deal of confusion exists regarding the matter of gas regulation for nebulizer-burners. In particular, there seems to be some question concerning the relative significance of monitoring gas pressures and flow rates. The various books and monographs on flame spectrometry have been rather vague or even void in their treatment of this topic. Perhaps the authors have assumed that a detailed treatment would be superfluous. The instrument manufacturers have further added to the uncertainty of the situation because they have not even agreed upon the requirements for proper gas control, as can be determined by the variety of gas control packages which they market or recommend. In this communication, an attempt is made to minimize this confusion by indicating some of the major objectives in designing and setting up a gas control system for nebulizer-burners.

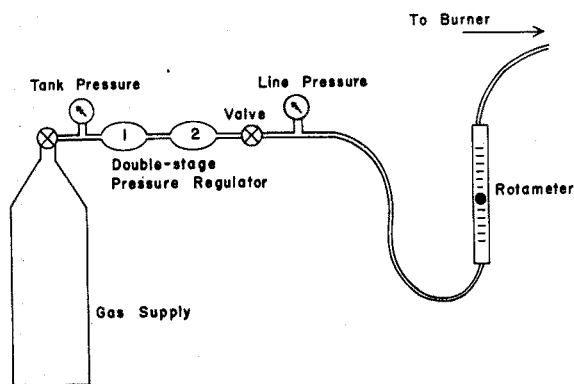


Fig. 1. Typical gas control system for nebulizer-burner.

The actual gas control system used for operating a nebulizer-burner is not particularly important as long as provision is made for measuring the pressure at the point in the line where the rate of flow is being measured. Such measurements are particularly important with regard to flame stoichiometry, consistency of flame conditions and solution aspiration rates, and reproducibility of recommended flame conditions. A typical gas flow scheme meeting this requirement is shown in Fig. 1. Two stages of pressure regulation may not be needed if a ballast is placed downstream from the single-stage regulator. It is important that there be nothing between the final pressure gauge and the rotameter which will cause a pressure drop, *e.g.*, a needle valve or an ultra-fine frit filter. Most flip-flop open-shut valves are adequate if a valve is desired in this position. For instance, when a tank-mounted double-stage regulator is used alone, the lower pressure gauge on this regulator reads the line pressure and may be used without accessory downstream gauges *if no* needle valve or other constriction causing a pressure drop is used between the regulator and the rotameter.

With regard to flame stoichiometry, most rotameters are calibrated for use with air at atmospheric pressure (one end open to the atmosphere), and the flow

rates obtained are meaningless without a knowledge of the gas type and its pressure. The pressure can be read on either side of the rotameter since the ones used in these applications have no appreciable pressure drop across them. Correction curves for converting gas (air) flow rates to atmospheric pressure are usually supplied by the rotameter manufacturers; and it is recommended that this be done since this is a convenient and preferred way to report such data. Thus the *two* calibration curves for rotameters should be used; one for converting the usual readings into flow rates and the other for further applying pressure corrections. For gases such as hydrogen or acetylene, the rotameters must be calibrated by the usual laboratory techniques described by manufacturers of rotameters, or with somewhat reduced accuracy, the specific gravity correction curves published by some manufacturers can be used.

The pressure-drop across most total-consumption burners is nearly zero for the gas not used to aspirate (usually the fuel). It is usually not necessary to apply pressure corrections to this flow rate, because it is already at atmospheric pressure. Each burner should be evaluated, however, because this may not be true with all types. Also, significant back pressures may develop when very high flow rates are used, *e.g.* with extremely fuel-rich flames.

A further necessary advantage of knowing the gas pressures and flow rates simultaneously is that any significant change in gas pressure required to maintain a certain rate of flow is a signal that the characteristics of the burner have been altered. This could mean that partial clogging has occurred, a leak between ducts has developed, or the capillary tip has become misaligned, etc. These are not uncommon occurrences with flame nebulizer-burners.

With regard to burner characteristics, it should be mentioned that a collection of identical nebulizer-burners (same make and model) will usually exhibit a rather wide range of pressure-flow rate properties. The pressure drop across the nebulizer tip of a burner and the flow rate at that pressure are related to one another by the particular geometry and dimensions of the burner assembly. We have observed that two new commercial burners of identical make and model may require such different back pressures as 10 and 20 psig for maintaining the same flow rate of oxygen. This is reason enough to discredit the frequently published procedures and flame condition data which list only gas pressures. It is unlikely that others can reproduce the flame

TABLE I
CORRECTED FLOW CALIBRATION DATA FOR BURNER #3

Rotameter reading* (cm)	Pressure (psig)	Correction factor*	Flow rate* at ambient pressure (l/min)	Corrected flow rate (1 atm) (l/min)
8.0	3.5	1.10	1.65	1.82
8.5	4.5	1.14	1.78	2.03
9.0	9.0	1.26	1.91	2.41
9.5	9.7	1.27	2.04	2.59
10.0	13.3	1.37	2.17	2.97
10.5	16.0	1.43	2.29	3.27
11.0	21.0	1.55	2.44	3.78

* For a size 4-15-2 rotameter, Ace Glass Inc., Vineland, New Jersey. Correction factors and flow rate values for various rotameter readings taken from Ace Supplement No. 1 to Ace Catalog 50.

conditions of such studies or even that the laboratory of origin can for that matter.

As long as a burner's characteristics remain constant, a corrected flow calibration curve can be improvised for that *one* burner by taking a series of simultaneous flow and pressure readings and applying corrections. In this manner, true flow rates (reduced to atmospheric pressure) can be read directly from a single calibration curve. Of course, the pressure-flow rate relation should be periodically checked to insure that the burner's characteristics have not changed. To demonstrate the importance of applying the pressure corrections, some data for a typical medium bore total-consumption Beckman nebulizer-burner are given in Table I (a corrected flow rate calibration curve would then be plotted using the corrected flow rate as the ordinate and the rotameter readings as the abscissa).

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BOOK REVIEWS

A. RINGBOM, *Les Complexes en Chimie Analytique*, Traduit par M. PÂRIS, Ed. Dunod, Paris, 1967, xiv + 369 pp., relié toile sous jaquette N.F. 68.—

Cet ouvrage, paru en anglais en 1962, a eu un grand succès. L'idée était donc heureuse d'en donner une traduction française. Le Professeur M. PÂRIS s'en est chargé; en tant que spécialiste des complexes, il l'a fait avec le plus grand soin. Il est pourtant regrettable que l'index des matières ait été quelque peu réduit, ce qui rend plus difficile la recherche de certaines constantes.

Actuellement, cet ouvrage est certainement le plus clair et le plus original de ceux qui traitent de l'application des complexes (dans le sens le plus général) en chimie analytique. Chaque chapitre est accompagné d'exemples pratiques, de problèmes avec leurs solutions. Cet ouvrage renferme en outre, sur plus de 80 pages, un nombre considérable de constantes.

C'est un instrument indispensable aux chimistes qui se trouvent devant des problèmes de plus en plus délicats. Ils apprendront comment on peut les résoudre et à quels critères il faut faire appel pour déterminer les conditions optimum de tel ou tel dosage.

D. MONNIER (Genève)

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The Chemistry of the Carbonyl Group, Edited by S. PATAI, Interscience-J. Wiley and Sons, Inc., New York, 1966, xii + 1027 pp., price 220 s.

This book forms part of the series, *The Chemistry of Functional Groups*, and consists of 17 chapters written by specialists in particular aspects of carbonyl chemistry. The volume "attempts to encompass all facets of the functional group and to give up-to-date descriptions of the nature of the carbonyl group... and of its main modes of reaction". The scope of the volume is so wide that one reviewer cannot be qualified to discuss all its aspects critically.

Most of the chapters cover the literature up to 1962 or 1963 with occasional references to 1964. Some important contributions to the chemistry of azomethine bonds and aldol condensations published in 1964 and 1965 are omitted and no reference is made to the exhaustive review by E. M. ARNETT on quantitative comparison of weak organic bases (*Progr. Phys. Org. Chem.*, 1 (1963) 223) in the chapter on the basicity of carbonyl compounds. In the section on *Electrochemical Reduction of Carbonyl Compounds* (O. H. WHEELER) it is surprising to find a discussion of electrochemical reductions with no distinction between controlled potential and controlled current procedures. The possibility of electropreparation of stereoisomers of pinacols (reported by H. LUND) is not mentioned. The subsection on polarography is based on the literature only up to 1952 and is thus obsolete.

The chapter on methods of analysis (J. G. HANNA) opens with a fair general discussion of the merits of various methods. The section on qualitative chemical methods is orientated towards the identification of individual compounds. The discussion of optical and titrimetric methods seems adequate, but the statement in the rather obsolete section on polarography that "the direct polarographic determination of carbonyl compounds is limited, in general, to aliphatic aldehydes" is wrong; polarography has been successfully applied to many different types of aromatic and heterocyclic ketones and aldehydes. There are other surprising omissions in other parts of the book, considering the extensive data available on the polarographic properties of the carbonyl group.

Nevertheless, although the reviewer was less than impressed by the sections in the area of his own special interests, the total wealth of information collected in this volume is impressive. The book should serve as a first source of information for initial study. For example, analytical chemists will find little new information on analytical methods, but the information on chemical reactions and physical properties could be valuable in the interpretation of existing methods or in the development of new procedures.

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P. J. PROSZT, V. CIELESZKY AND K. GYÖRNBÍRÓ, *Polarographie mit besonderer Berücksichtigung der klassischen Methoden*, Akademiai Kiado, Budapest, 1967, 587 pp., price 140 s.

A textbook of moderate size has been needed in polarography and has now been prepared by these Hungarian authors. This German version is a translation of

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the Hungarian edition published in 1964. In the first 90 pages the most important polarographic techniques are described and then diffusion currents, currents governed by the rate of a chemical reaction, adsorption effects and maxima are discussed. The last part of Section I is devoted to techniques related to polarography; the principles of controlled potential electrolysis and amperometric titrations are discussed in some detail and oscillographic polarography, single-sweep and rectangular voltage polarization techniques, anodic stripping, polarocoulometry, chromatopolarography, etc. are briefly mentioned. Section II is devoted to inorganic systems; the behaviour of metallic and non-metallic species is described and selected examples of analysis of alloys are given. In Section III, organic systems are discussed according to the electroactive group involved; the behaviour of each class of compound is outlined briefly with some information on the course of the electrode process. Only references are given for analytical applications. There are some inaccuracies in the general introduction to the organic section.

The great advantage of this book is its simple, clear presentation which is entirely suitable for the beginner. On the other hand, most of the references date from the mid-fifties so that the interpretation is sometimes obsolete. The translation is good and there are few printing errors; the price is high. If it is borne in mind that some of the statements should be checked against the later literature, then this book is a useful source of information; it can be recommended as an introductory text.

P. ZUMAN (Prague)

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B. CAPON, M. J. PERKINS AND C. W. REES, *Organic Reaction Mechanisms*. 1966, Interscience Publishers—J. Wiley and Sons, London, 1967, viii + 480 pp. Price 84 s.

The second volume of this series gives a survey of organic reaction studies published in 1966. The material is classified as (1) reactions of classical and non-classical carbonium ions; (2) nucleophilic aliphatic substitutions; (3) electrophilic aliphatic substitutions; (4) elimination reactions; (5) addition reactions; (6) nucleophilic aromatic substitutions; (7) radical and electrophilic aromatic substitutions; (8) molecular rearrangements; (9) radical reactions; and reactions of (10) carbenes and nitrenes, (11) aldehydes and ketones, (12) acids and their derivatives; (13) photochemical reactions; and (14) oxidations and reductions.

Some areas are discussed in detail whereas for others the material is simply listed. The coverage of the literature is uneven; the leading Anglo-Saxon journals predominate and there are few references to Russian work (the journal *Organic Reactivity* is not reviewed) and almost none to Eastern European work. The concept of reaction mechanism is very wide and includes not only kinetic studies but also calculated guesses made on the basis of product isolation. However, this is a useful reference source and is a distinct aid to those with "current awareness" problems in organic reactions.

P. ZUMAN (Prague)

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W. T. ELWELL AND I. R. SCHOLLES, *Analysis of Copper and its Alloys*, Pergamon Press, Oxford, 179 pp., price 42 s.

This book, written by the Chief Analyst and a Technical Officer of Imperial Metal Industries, Ltd., will be received with great interest since it is a first-hand report by analysts of wide industrial experience on the up-to-date procedures developed and confirmed in the company's Research Department. Previous books dealing with this subject are either obsolescent or written from second-hand information.

In this book, the determinations of the common elements, some less-common elements and gases are dealt with in detail, but for some reason, elements such as calcium, gold, lithium and magnesium have been omitted. For each element, there is a short introductory section and then the practical procedures for different types of alloy are given. Absorptiometric (for 18 elements) and volumetric (for 12 elements) methods predominate, but the share of time-consuming gravimetric methods is surprisingly large (for 10 elements) and precipitation methods are often used for separations. Polarographic methods are used and are especially successful for traces of lead and bismuth. The use of EDTA titrations is restricted to the determinations of aluminium, nickel and zinc. A rapid procedure is given for aluminium, but for zinc an initial electrolytic separation of copper and precipitation of zinc with hydrogen sulphide are necessary and the authors have had to resort to an indirect final determination. EDTA titrations of lead, tin and zirconium are not used.

The most interesting chapters are those dealing with the determinations of non-metals and gases in which low-pressure, vacuum-fusion, combustion and evolution procedures are described.

The newest technique of analytical chemistry—atomic absorption spectrophotometry—is represented by the determinations of cobalt, lead, silver and zinc; information on the determination of other important elements such as Al, Fe, Cd, Cr, Mn and Ni would have been of general interest here.

The electrolytic determination of copper is discussed very thoroughly; interferences and different means of overcoming these are described. With regard to sampling, the authors give only some general comments without going into detail; for example, segregation of tin bronzes and methods of avoiding this are not mentioned.

Clearly, every analytical chemist will find something useful to this own practice in this book with its selected list of references. The book itself is essential reading for metallurgical analysts.

JORMA KINNUNEN (Pori)

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Review of J. W. ROBINSON, *Atomic Absorption Spectroscopy*, Marcel Dekker, Inc., New York, 1966, 216 pp., price \$9.75.

The author has briefly surveyed the basic relationships, the instrumentation, the analytical parameters, and the analytical applications in atomic absorption spectroscopy. This book is not intended for the atomic spectroscopist but rather for the analyst who wants to know generally what atomic absorption spectroscopy is and "if" and "how" this method is applicable to his problem. The theoretician or experi-

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mentalist in spectroscopy will be disappointed because of the lack of depth, particularly with regard to such theoretical considerations as the profile of atomic absorption lines, the equilibrium in the flame gases influencing the degree of atomization of the salt introduced, and the influence of spectral, flame gas compositional and instrumental parameters on the absorption signal and the absorption signal to-noise ratio. The analyst, on the other hand, will find the first four chapters of the book quite useful; the author has fulfilled his stated objectives *i.e.*, to use a broad approach which will be useful to the graduate student, the research chemist who wishes to know the applicability of the method, and the analytical chemist responsible for providing rapid, accurate analyses.

In Chapter 1 the advantages and disadvantages of atomic absorption spectroscopy are discussed; the treatment is rather concise and the discussion could beneficially have been transferred to the end of the book. In Chapter 2, the pertinent factors concerning the various instrumental components in an atomic absorption spectrometer are covered. In Chapter 3, analytical parameters influencing the atomic absorption signal are considered; except for lack of depth, this chapter is of some value to the analyst. Chapter 4 is a truly outstanding chapter in the book. This chapter is concise yet quite comprehensive. The author gives recommended procedures for the measurement of about 50 elements. He clearly indicates sensitivities obtained for each element, experimental conditions, possible interferences, and types of applications. Adequate references (up to early 1965) are given for procedures for a variety of practical materials. This chapter alone warrants the purchase of the book. In Chapter 5, the author discusses the measurement of oscillator strengths, the use of the vacuum ultraviolet for absorption measurements and atomic fluorescence flame spectrometry. This is the poorest written chapter in the book and certainly of the least use to the analyst. Measuring oscillator strengths by the procedure outlined would be difficult. The section concerning atomic absorption spectroscopy in the vacuum ultraviolet is interesting, as is the section on atomic fluorescence flame spectrometry but the latter was premature at the time of writing.

However, this book is of value to the analyst and beginning researchers and should be a part of their personal libraries.

JAMES D. WINEFORDNER (Gainesville, Fla.)

Anal. Chim. Acta, 40 (1968) 362-363

G. D. RIECK, *Tungsten and its Compounds*, Pergamon Press, Oxford, 1967, x + 135 pp., price 45 s.

This monograph is aimed at a readership of chemists, physicists and metallurgists. Most of the book is concerned with the element, its physical properties and its metallurgy, and the remainder with its compounds. There are only two pages on analytical aspects. The section on tungsten compounds contains many recent references and tabulated data, and the whole forms a useful review of tungsten chemistry.

A. J. EDWARDS (Birmingham)

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PUBLICATIONS RECEIVED

KIRK-OTHMER, *Encyclopedia of Chemical Technology*, 2nd Edn., Executive Editor, A. STANDEN, Vol. II, *Hexanes to Ion Exchange*, Interscience-Wiley, New York, 1967, xiv + 899 pp. price 375 s. (single copy) or 300 s. (subscription price).

L. N. MULAY, *Magnetic Susceptibility*, Interscience-Wiley, New York, 1967, 132 pp., price 23 s.

This is a soft-bound reprint of a section from *Treatise on Analytical Chemistry*, Part I, Vol. 4, published in 1963.

Méthodes d'Analyse CÉTAMA—1966, Recueil No. 3, Méthodes 151 à 200, Commissariat à l'Energie Atomique, Presses Universitaires de France, Paris, 1967.

J. ROSIN, *Reagent Chemicals and Standards*, 5th Edn., D. van Nostrand Co., Inc., Princeton, N. J., 1967, ix + 641 pp., price 132 s.

This new edition incorporates about 30 new reagents. Many new assay tests have also been added and others have been revised or brought up to date.

R. THEISEN UND D. VOLLATH, *Tabellen der Massenschwächungskoeffizienten von Röntgenstrahlen*, Verlag Stahleisen mbH., Düsseldorf, 1967, 40 S., DM 22,—.

Progress in Nuclear Energy, Series IX, Vol. VIII, Part I, Edited by H. A. ELION AND D. C. STEWART, Pergamon Press, Oxford, 1967, 139 pp., price 45 s (soft bound).

This contains reviews on the Analytical Chemistry of Protactinium (D. BROWN AND A. G. MADDOCK), Extraction Photometry with Oxine and 2-Methyloxine (K. MOTOJIMA), and Analytical Chemistry of Actinium (H. W. KIRBY).

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ANNOUNCEMENT

THIRD POLISH ANALYTICAL CONFERENCE

The Third Polish Analytical Conference organized by the Commission of Analytical Chemistry of the Polish Academy of Sciences, under the auspices of the International Union of Pure and Applied Chemistry, will be held in Warsaw, Poland, September 10-15, 1968.

The main subjects to be dealt with are as follows:

1. Basic problems of analytical chemistry (new reagents, new reactions, ionic equilibria, accuracy and precision, etc.);
2. Analytical methods in inorganic industry;
3. Analytical methods in organic industry;
4. Techniques of analytical chemistry (new apparatus, automation, standards, sampling etc.).

The final date for sending abstracts of paper to be read on the conference is January 15, 1968.

Further information may be obtained from The Secretary of the Organizing Committee, Dr. ADAM HULANICKI, Warszawa 22, ul. Pasteura 1, Poland.

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